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Photorefraction in BaTiO$_3$

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PHOTOREFRACTION IN \text{BaTiO}_3

by

Stephen Ducharme

A Dissertation Presented to the
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Abstract

This thesis summarizes the results of experimental investigations of the photorefractive properties of melt-grown BaTiO₃ single crystals. Three basic photorefractive material properties are studied: 1) the effective density of photorefractive charges, 2) the photoconductivity of the photorefractive charges, and 3) the relative contributions of electron and hole photoconduction. Volume holographic measurement techniques are used: two-beam energy coupling, four-wave mixing, and erasure of volume holograms. The photorefractive properties were altered experimentally by chemically reducing or oxidizing a BaTiO₃ crystal. I have extended the "hopping conduction" model of photorefractive transport to include simultaneous electron and hole photoconduction. The extension of the hopping conduction model also describes all ranges of photorefractive site occupancy as observed in photorefractive crystals. The photorefractive speed, and hence the photoconductivity, is shown experimentally to be sublinear in the optical intensity in contrast to the predictions of existing models of photorefractive transport. A model of the photorefractive sites is proposed to explain the observed changes in the photorefractive properties of BaTiO₃ when a crystal is oxidized or reduced. The model postulates that oxygen vacancies produced by reduction combine with iron impurities to form photorefractive donors, and that the remaining iron impurities are the photorefractive acceptors. The model of the photorefractive sites describes the experimental observation that the photorefractive sites switch from acceptor to donor and the photoconductivity from hole- to electron-dominated at the same density of oxygen vacancies as oxygen vacancies are introduced into a BaTiO₃ crystal.
The electrooptic and piezoelectric coefficients of $\text{BaTiO}_3$ were measured by interferometric techniques and compared to holographic measurements. In addition, A technique for electrical poling of multidomain single crystals of $\text{BaTiO}_3$ containing both $90^\circ$ and $180^\circ$ domain walls is described.
I INTRODUCTION

The Discovery of "Optical Damage"

The discovery of the photorefractive effect dates back to the "optical damage" of LiNbO$_3$ described by Ashkin [1966] and Chen [1967]. These workers observed that illumination of LiNbO$_3$, LiTaO$_3$, and KTN electrooptic crystals with visible light resulted in long-lived inhomogeneities in the refractive index of the crystals. The light-induced refractive index inhomogeneity could be induced in about a minute at illumination intensities of a few watts per square millimeter. The inhomogeneity was called "optical damage" because it caused light to diverge after passing through the crystal, thus degrading these materials and making their use as optical frequency conversion devices, electrooptic, acoustooptic modulators, or other optical devices, impractical.

A clear understanding of the cause of this inhomogeneity was sought in order to find a way to reduce or eliminate it and, perhaps, to exploit it. The fundamental mechanism by which illumination produced the refractive index inhomogeneity was first proposed by Chen [1969]. Chen [1969] attributed the cause of the "optical damage" to the drift and retrapping of photoionized charges out of illuminated regions and into dark regions, thus producing a spatial redistribution of the charges among the partially filled trapping sites. The space-charge electric field produced the refractive index inhomogeneity through the linear electrooptic effect. This model, generally called the band conduction model, remains the basis of the current understanding of optical damage.
The two key material-dependent characteristics of the photorefractive effect are: 1) the dynamics of the photorefractive transport and 2) the origin of the trapping "sites" among which the charges (electrons or holes) are distributed.

**Models of Photorefractive Transport**

Chen's [1969] qualitative band conduction model of the photorefractive effect was analyzed quantitatively by a number of workers including: Young [1974], Alphonse [1975], von der Linde [1975], and Kim [1976]. The dynamics of this model were determined by the photoconductive properties of the crystal. The photorefractive trapping sites, though unspecified, were thought to be foreign impurities or intrinsic defects in the crystal lattice. The band conduction model was applied with much success to volume holographic experiments in which the crystal was illuminated by two intersecting coherent optical beams. The set of light and dark fringes in the crystal produced a corresponding variation in the refractive index, or volume hologram, by the photorefractive effect. This volume hologram could be read out by observing the coherent scattering of a third beam incident at the Bragg diffraction angle of the hologram. It was clear, then, that there were numerous possible applications of the photorefractive effect in holographic optical information storage (for example, see Chen's [1968] paper on holographic storage in LiNbO₃). The quantitative analyses of the band conduction model of photorefractive transport provided the basis for implementing applications.

The quantitative analyses of the band conduction model mentioned in the previous paragraph assumed that the incident light wave was not altered by the refractive index inhomogeneities it produced, but the refractive index
inhomogeneity refracts the incident wave which created it, thus distorting the wave which in turn causes the electrons to be further redistributed. This feedback from the optical wave to the space-charge distribution back to the optical wave was included in the quantitative analyses by [Staebler 1972, Ninomiya 1973, Vahey 1975]. The dynamic interaction of two or more optical beams was actually a form of real-time holography in which the feedback between the incident beams and the refractive index hologram was an important property; one beam could be used to alter another.

The culmination of the photorefractive band conduction models is attributed to Kukhtarev [1979], who set down the transport equations for photoionization, drift, diffusion, and recombination of the charges trapped in the deep impurity levels as well as the nonlinear feedback between the optical wave and the trapped charge distribution. Orlowski [1978] showed that both electron and hole contributions to the photoconductivity were important and the striking fact that the magnitude of the refractive index holograms was proportional to the difference in the electron and hole photoconductivities. Klein [1985], and Strohkendl [1986], made further refinements in the equations of the band conduction model which better describe photorefractive experiments. The band conduction model in its most recent form describes a wide range of photorefractive phenomena observed experimentally: the creation of volume holograms, the interaction of two or more optical beams bearing images, the complicated temporal behavior of space-charge build-up and relaxation, and many other phenomena.

An alternate model of photorefractive transport, the "hopping conduction" model, was proposed by Feinberg [1980a], with further refinements by Mullen [1985] and Ducharme [1986a]. The hopping model is
similar in most respects to the band conduction model except that the photoionization, drift and diffusion, then recombination mechanism by which a photorefractive charge moves from one trapping site to another in the band conduction model is replaced by an unspecified "hop" of the charge between sites. The hopping model is more restrictive than the band conduction model in one respect and more general in another. The hopping model does not explicitly account for the presence of electrons (holes) in the conduction (valence) band and thus is more restrictive than the band conduction model which does. But the hopping model admits the possibility of statistical correlations among the hopping charges, an important characteristic of many systems with low carrier mobility, while the band conduction model only with average rates and does not allow for statistical correlations. These two differences aside, the predictions of the band and hopping conduction models in their present forms are usually experimentally indistinguishable.

Identifying the Photorefractive Trapping Sites

Identifying the photorefractive trapping "sites" has proved a difficult problem to solve because the photorefractive materials are generally undoped and it is difficult to determine the relationship between the trace impurities and defects and the photorefractive trapping sites. Photorefractive experiments determine that the site density is generally ten to one hundred parts per million, the same range shared by many common impurities and intrinsic defects in photorefractive crystals. Early oxidation and reduction experiments by Peterson [1971] showed that iron impurities were the primary source of the photorefractive sites in LiNbO₃. Peterson [1971] showed that the photorefractive sensitivity increases as the ratio of the density of Fe²⁺ impurities to the density of Fe³⁺ impurities increases. The oxygen vacancies
produced by chemical reduction of the crystals were assumed inert as far as the photorefractive effect was concerned, and merely provided charge compensation to convert the iron from Fe$^{3+}$ to Fe$^{2+}$. Crystals with excess oxygen vacancies, though they had higher photorefractive sensitivities, also had high dark conductivities and large optical absorption, both deleterious to the photorefractive effect. Phillips [1974] showed that the photorefractive properties correlated well with the average density of the Fe$^{2+}$ impurities and that relatively mild chemical reduction (introduction of relatively few oxygen vacancies without significantly increasing the dark conductivity or optical absorption) was required to convert over 90% of the Fe$^{3+}$ to Fe$^{2+}$. Orlowski [1978] also found that the relative contributions of electron and hole photoconduction to the photorefractive sensitivity correlated well with the Fe$^{2+}$ to Fe$^{3+}$ density ratio. The photorefractive trapping sites in LiNbO$_3$ were assumed to be iron impurities which were considered occupied by an electron when in the Fe$^{2+}$ valence and unoccupied by an electron when in the Fe$^{3+}$ valence. The electrons could then be redistributed among the iron sites by the incident light.

The identity of the trapping sites in photorefractive BaTiO$_3$ was approached in a similar manner. Valley [1983] had proposed reducing BaTiO$_3$ crystals in the same way that LiNbO$_3$ crystals were reduced to increase the photorefractive sensitivity. Klein [1986] observed the correlation between the photorefractive properties and the Fe$^{2+}$ and Fe$^{3+}$ densities in several different undoped crystals of BaTiO$_3$. The general results were similar to those in LiNbO$_3$: 1) the photorefractive sites appeared to be iron atoms which were filled with (empty of) an electron when in the Fe$^{2+}$ (Fe$^{3+}$) valance and 2) the oxygen vacancies were again assumed inert.
Organization of the Thesis

The mechanism of the photorefractive effect is described in detail in Chapter II. The space-charge field resulting from nonuniform illumination of the crystal is derived using the hopping conduction model of Feinberg [1980a] with two important generalizations: both the electron and hole photoconductivities are included, and the applicable range of the theory is extended to include all ranges of occupancy of the photorefractive sites (from completely empty to completely full). Two distinct types of trapping sites are assumed to exist, one type acting as electron donors and the other type acting as electron acceptors, but only the type of site (donor or acceptor) with the greatest number density is photorefractively active. The last part of the chapter contains a derivation of the coupled wave equations for two coherent optical beams interacting by the refractive index variation produced by the photorefractive space-charge field. Figure I–1 shows a typical volume holographic experiment.

In Chapter III I report the results of measurements the strength of two-beam energy coupling (the interaction of beams 1 and 2 in Figure I–1) in photorefractive BaTiO₃ and compare the measurements to the theoretical relations developed in Chapter II. The photorefractive properties which are determined in the beam-coupling experiment are: the effective density of photorefractive charges, the relative contribution of electron and hole photoconductivities, and the electron and the hole "hopping" lengths.

The relative electron and hole photoconductivities were determined by measuring the magnitude of the two-beam coupling strengths in BaTiO₃ crystals. The effective densities of photorefractive charges and the
The two optical writing beams 1 and 2 create a refractive-index grating and exchange energy in a crystal of BaTiO$_3$. The crystal is aligned with its c-axis perpendicular to the grating planes as shown. The optical reading beam 3 is Bragg deflected by the grating and produces the signal beam 4, which propagates back along the writing beam 2 and is separated by a beamsplitter (not shown). The optical erasing beam 5 is incident from the top of the crystal and is uniform in intensity. Different combinations of these beams are used in volume holographic measurements of the photorefractive properties of crystals.
characteristic transport, or "hopping," lengths for both electrons and holes were determined from the dependence of the two-beam coupling strength on the spacing of the interference fringes of the two interfering beams. The results of Chapter III are in good agreement with the predictions of the extended hopping model calculation of Chapter II.

The principal contribution of this thesis to the understanding of photorefractive transport is the detailed characterization of the sublinear dependence of the photoconductivity on optical intensity in BaTiO$_3$ described in Chapter IV. The photoconductivity is proportional to the photorefractive speed which was measured by monitoring the decay of photorefractive holograms under uniform illumination. The photorefractive speed, and hence the photoconductivity, follows a simple sublinear power law in the intensity over at least four decades of intensity. It was previously thought that the sublinear behavior was due to saturation of the photoconductivity, however the data contained here are inconsistent with any reasonable saturation phenomenon. Now, two years after publishing this data [Ducharme 1984a], there is still no satisfactory explanation for the sublinear photoconductivity.

Another result of the erasure experiments reported in Chapter IV is the temperature dependence of the dark or thermal erasure of photorefractive gratings. The dark erasure data yield a clear activation dependence, with a characteristic energy of one electron volt.

The results of chemical oxidation and reduction treatments which vary the density of oxygen vacancies in a crystal of BaTiO$_3$ are discussed in Chapter V; the oxidation and reduction treatments change the photorefractive properties of a crystal of BaTiO$_3$ and show that the density of the
photorefractive donors in BaTiO$_3$ is controlled by the density of oxygen vacancies. The effective density of photorefractive charges and the electron and hole contributions to the photoconductivity, measured by techniques described in Chapter III, changed after each treatment in a manner consistent with the assignment of two distinct types of photorefractive sites discussed in Chapter II. In the model proposed in Chapter II, the photorefractive sites in nominally "pure" crystals are either lone iron impurity atoms (acceptors), or iron impurity atoms with associated oxygen vacancies (donors). The key evidence contained in the results of the oxidation and reduction experiments for this assignment of separate donor and acceptor sites in the crystal is the switch from a hole-dominated to an electron-dominated photorefractive coupling when there is complete compensation of the crystal, that is, when the donor and acceptor densities are equal.

The assignment in Chapter V of both donor and acceptor sites to the iron impurities, depending on whether or not there is an oxygen vacancy in close proximity to the iron atom, is an extension of the assignment presently attributed to photorefraction in LiNbO$_3$ [Staebler 1974, Phillips 1974, and Orlowski 1978] but including the role of the oxygen vacancies. These authors assumed that there is only one type of site, an iron impurity atom, which has valence Fe$^{2+}$ when filled by an electron and Fe$^{3+}$ when empty. Similarly, Klein [1986] established the connection between the iron impurities and the photorefractive sites in BaTiO$_3$ and assumed the same site identity as in LiNbO$_3$. I propose that the iron atoms acting as donors, though they have the 3+ valence when ionized, have oxygen vacancies in close proximity and thus are chemically and energetically distinct from the acceptors, which do not have a nearby oxygen vacancy. The assignment of the two types of iron
atoms, one with and one without an associated oxygen vacancy, is unique to the model proposed in this thesis.

The principal contribution of this thesis to the identification of the photorefractive sites in BaTiO$_3$ is the assignment of lone iron impurities to the photorefractive acceptors and iron impurities which are in combination with oxygen vacancies to the photorefractive donors, consistent with the results of the oxidation and reduction experiments described in Chapter V. This is the distinction between the assignment given in this thesis and the previous assignments of the photorefractive sites in BaTiO$_3$ [Klein 1986] and LiNbO$_3$ [Staebler 1974, Phillips 1974, and Orlowski 1978] which assumed that there was only a donor level, the Fe$^{2+}$ ion, which, when ionized, is converted to the Fe$^{3+}$ ion.

New measurements of the electrooptic coefficients $r_{13}$ and $r_{33}$ of melt-grown crystals of BaTiO$_3$, SBN, and LiNbO$_3$ are reported in Chapter VI. The piezoelectric coefficient $d_{13}$ was also measured in order to determine the correct electrooptic coefficients. The values of the electrooptic coefficients are important in the quantitative interpretation of photorefractive measurements. Previous measurements of the electrooptic coefficients of BaTiO$_3$ found in the literature were determined for flux-grown crystals, and are not applicable to the high quality melt-grown crystals used in the study of the photorefractive effect. The measured values of the electrooptic coefficients are compared to photorefractive measurements of the same coefficients.

Principles of ferroelectricity in BaTiO$_3$ are summarized in Appendix A in order to provide a ready reference for readers of this thesis who are not
familiar with ferroelectricity. Techniques developed in our laboratory for electrical poling of BaTiO$_3$ crystals are described in Appendix B for the guidance of prospective BaTiO$_3$ crystal users. These poling techniques were used to pole each of the crystals studied in conjunction with this work (ROCKY, the crystal studied in Chapter V, was poled after each oxidation and each reduction treatment).

Standard SI or MKS units are used throughout with the exception that most numerical values are given in centimeters instead of meters.
REFERENCES: CHAPTER I


II THE PHOTOREFRACTIVE EFFECT

This chapter begins with a brief description of the physics of the photorefractive effect, its place in nonlinear optics, and some of its important applications. The exchange of energy between two coherent optical beams in a photorefractive material is then derived. The derivation has three parts: 1) The model of the photorefractive material as a compensated semiconductor which contains both donor and acceptor sites, each playing a role in photorefractive phenomena, 2) the calculation of the photorefractive space-charge field using the hopping model [Feinberg 1980a], and 3) the solution of the coupled wave equations for the two optical beams.

The photorefractive effect was first observed as "optical damage", a semipermanent change in the refractive index of electrooptic crystals, after the crystals were illuminated with an optical beam [Ashkin 1966, Chen 1967]. The physical picture proposed by Chen [1969] remains the accepted explanation for the refractive index inhomogeneities observed in almost all electrooptic crystals. The mechanism of the photorefractive effect can be broken into three steps: 1) a crystal is illuminated in one or more finite regions and trapped charge is driven from the illuminated regions into the dark regions, 2) the displaced charge produces an electric field, and 3) the electric field changes the index of refraction by the linear electrooptic, or Pockels, effect.

Applications of the Photorefractive Effect

The photorefractive effect first appeared as "optical damage" in electrooptic crystals. But soon workers in nonlinear optics were finding uses for the photorefractive effect as a new nonlinear optical effect. It was
recognized that the photorefractive index change might be used to record an erasable volume hologram [Chen 1968]. Volume holograms could be recorded in electrooptic crystals by interfering coherent optical beams and the holograms subsequently erased by uniform illumination. This was all possible without intermediate development steps, as required for hologram recording in photographic emulsions. Indeed, volume holograms have been recorded and subsequently read out in just a few nanoseconds—hence the term "real time holography".


There are a number of photorefractive materials, including BaTiO$_3$. Generally, any insulating material which has a linear electrooptic (Pockels) effect will also be photorefractive. Photorefractive materials include: barium titanate BaTiO$_3$ [Feinberg 1980]; lithium niobate LiNbO$_3$ and LiTaO$_3$ [Ashkin 1966]; potassium tantalate niobate KTN [Chen 1967]; potassium niobate KNbO$_3$, bismuth silicate BSO, and bismuth germanate BGO [Gunter 1982]; strontium barium niobate SBN [Fischer 1982]; and indium phosphide InP and gallium arsenide GaAs [Glass 1984].
The Photorefractive Effect as a Nonlinear Optical Effect

Most nonlinear optical effects share these properties: 1) The strength of the effect increases with the optical intensity, 2) nonlinear optical effects are generally spatially local, and 3) the speed is independent of intensity. A good overview of nonlinear optical effects can be found in Shen's [1984] text. These "standard" nonlinear optical effects are described by field dependent terms in the expansion of the electromagnetic susceptibility in the electric field. For example, frequency doubling occurs in materials with a large second order (in electric field) nonlinear coefficient; four-wave mixing uses the third order coefficient, and so on through the menu of standard nonlinear optical effects.

The photorefractive effect differs fundamentally from the "standard" nonlinear effects in all three of these aspects: the spatial, temporal, and intensity dependence of the effect.

First, the strength of the photorefractive interaction is essentially independent of the optical intensity; strong photorefractive optical nonlinearities have been demonstrated using optical intensities of a few microwatts per square centimeter [Feinberg 1980c]. This is a significant advantage over scattering using a nonlinear medium such as ruby which requires much higher intensities. One does not need high-power pulsed lasers to achieve high diffraction efficiencies; a simple helium-neon laser works just as well (at the sacrifice of longer time constants)!

Second, the photorefractive effect is inherently nonlocal in space. The change in the index of refraction at a point in space depends not only on the intensity at that point, but on the intensity distribution throughout the
material, even to distances of several millimeters in practical situations. This is because the local change in index depends on the electric field resulting from the entire charge distribution throughout the crystal. It is the inherent nonlocal connection between charge and electric field in Poisson's equation that makes the photorefractive effect nonlocal. The nonlocal character makes calculation of the nonlinear coupling of coherent optical beams more difficult as the combination of spatial and temporal nonlocality result in hysteretic behavior. Indeed, we may describe the entire photorefractive interaction as a pure third-order nonlinear susceptibility which is described by both temporal and spatial frequency spectra. The problem could then be solved by generalizing the theory of nonlinear interaction by third-order susceptibilities developed in [Hellwarth 1977] to include spatially nonlocal interactions as spatial frequency spectra. Though this may be useful in weak, steady state degenerate four-wave mixing of plane waves, where only one temporal frequency and one spatial frequency are present, other problems should become intractable rapidly in Hellwarth's formulation as any of these restrictions are relaxed.

Third, the speed of the photorefractive interaction depends strongly on the optical intensity. Photorefractive theory predicts that the speed increases linearly with intensity while experiments described in this thesis show that the dependence is actual sublinear. To operate a photorefractive device with BaTiO$_3$ crystals presently available requires about one hundred fifty megawatts per square centimeter to achieve nanosecond response times. However, the speed can be improved dramatically by doping the crystals, chemically reducing them, raising their operating temperature, or all three.
Further Reading

An clear and concise presentation of the physics of the photorefractive effect is found in Feinberg's contribution to is Optical Phase Conjugation, edited by R. Fisher [1983], and the references cited therein. Gunter [1982] reviews photorefraction thoroughly and covers a lot of experimental work by many researchers. A more recent review is found in Hall [1985]. The work published since 1982 is hefty and a comprehensive review is promised in two volumes to be issued in mid-1987 by Springer-Verlag and edited by Peter Gunter. Recent work can be found in the "Special Issue on Materials for Optical Processing" in the February 1986 issue of the Journal of the Optical Society of America B: Optical Physics. An excellent source for phase conjugation in general is Optical Phase Conjugation, edited by Fisher [1983] and the references cited therein. The theory of phase conjugation by four-wave mixing begins with Hellwarth [1977] and the analogy with volume holography discussed by Yariv [1978]. For more recent developments (there are many!) I suggest consulting recent issues of Optics Letters and JOSA.

The Photorefractive Trapping Sites: The Compensated Semiconductor

Here I propose a model of the photorefractive material as a compensated semiconductor. The model correctly describes the results of the oxidation and reduction treatments in BaTiO$_3$ reported in Chapter V. Klein's [1986] measurements of the photorefractive properties of BaTiO$_3$ crystals with varying iron impurity content can also be described by this model. The model differs from models proposed by Peterson [1971], Phillips [1974], and Orlowski [1978] for photorefractive LiNbO$_3$ and of Klein [1986] for
donors or acceptors depending on the densities of both the donors and acceptors.

Consider mobile charges (either electrons or holes) occupying trapping sites distributed throughout the crystal. The trapping sites might be impurity atoms or point defects (such as oxygen vacancies). A trapping site can be occupied by either an electron or a hole. Figure II–1 shows how the movable charges will be redistributed among the trapping sites by diffusion when illuminated nonuniformly. If electrons diffuse away from the illumination, then the resulting electrostatic field will be directed away from the light and towards the dark regions, as shown in Figure II–1a. If holes diffuse away from the illumination, then the space-charge field will be directed toward the light regions, as in Figure II–1b. In general both holes and electrons are movable, and their space-charge fields will oppose each other.

A steady-state charge distribution is obtained when the diffusive force on the charges due to nonuniform illumination is balanced by the electrostatic field produced by the displaced charges themselves. In a crystal lacking inversion symmetry this space-charge field causes a first-order change in the crystal’s refractive index by the linear electrooptic (Pockels) effect. This refractive-index change can be monitored with an optical beam.

If the material has only one kind of trapping site (e.g. an impurity atom or a point defect) and if the density of free electrons (holes) in the conduction (valence) band can be neglected, all of these sites are full; the charges cannot be redistributed and there is no photorefractive effect. However, if one adds another set of trapping sites that partially compensates the first set, then a redistribution is possible, and a photorefractive effect is possible. Figure II–2a shows an example in which the acceptor sites, with number
Figure II–1  Photorefractive Space-Charge

Rearrangement of charges by light in a photorefractive material. In (a) electrons have diffused away from the illuminated region, and in (b) holes have diffused away from the illuminated region. In general both processes may occur simultaneously producing opposing space-charge fields as shown.
FIGURE II-1
density $N_A$, are partially filled by electrons transferred from the donor sites, which have number density $N_D$. In this example the acceptor sites are more numerous ($N_A > N_D$). The remaining $N_A - N_D$ holes may then be redistributed by light among the acceptor sites. If, as in Figure II–2a, the density of acceptors exceeds the density of donors, $N_A > N_D$, then the average probability that the site is occupied by an electron is $W_0 = N_D/N_A$, and the total number of sites will be $N = N_A$.

Figure II–2b shows the opposite case, in which the donor sites are more numerous ($N_D > N_A$) and the acceptor sites are full. The remaining $N_D - N_A$ electrons may then be redistributed by light among the donor sites. If, as in Figure II–2b, the density of electron donors exceeds that of acceptors $N_D > N_A$, then the average probability that a site is occupied by an electron will be $W_0 = 1 - N_A/N_D$, and the total number of sites will be $N = N_D$.

Note that charge transport is possible by both electron and hole conduction in either of figures II–2a or b. The electron and hole contributions to ordinary photoconductivity add. In contrast, the electron and hole contributions to the photorefractive space-charge electric field compete (see Figure II–1).

**Photorefractive Transport: The Hopping Conduction Model**

There are currently two models describing photorefractive charge transport. The "band conduction model" [Kukhtarev 1979] is a three-step process shown for electron transport in Figure II–3a. The three steps are:
Schematic of donor and acceptor trapping sites in a photorefractive semiconductor. In (a) the density of acceptors exceeds the density of donors, and holes can be redistributed by light among the acceptor sites. In (b) the density of donors exceeds the density of acceptors, and electrons can be redistributed by light among the donor sites.
FIGURE II-2
FIGURE 11-3 Band and Hopping Conduction

Two mechanisms of photoconduction. Band conduction (a) is a three-step process: 1) photo-ionization, 2) drift and diffusion within the band, and 3) recombination at an empty trapping site. Hopping (b) is a one-step process. These examples show electron conduction; hole conduction is also possible.
FIGURE II-3
1) photoionization of a carrier bound at a trapping site, 2) drift and diffusion of the carrier through the conduction band, and 3) recombination at a trapping site. The "hopping conduction model" [Feinberg 1980a] considers single hops between sites, as shown in Figure II–3b. The two models predict the same results as long as the electron (or hole) recombination time, i.e. the duration of step 2 in Figure II–3a, is short compared to any optical transients. The hopping conduction model does not explicitly describe the mechanism by which electrons and holes move from one site to another, whether band conduction, tunnelling, small polaron hopping, or some other transport mechanism. The experiments reported in this thesis do not distinguish between the two models.

Here I generalize the hopping equations of Feinberg [1980a] to include both electron and hole photoconduction, and also to allow site occupation probabilities $W_n$ that are not necessarily small [Ducharme 1986]. The derivation of Feinberg [1980a] contains a number of assumptions and simplifications which are not valid in the experiments reported in this thesis and which I will relax in the following derivation. These assumptions are:

1) The fractional occupancy of the photorefractive sites $W_n \ll 1$.
2) Only one charge conduction process occurs (e.g. hole conduction).
3) Only short-range hopping occurs (Mullen [1985] included long-range hopping for a single carrier in the hopping model).
4) Beam depletion is neglected.
5) The reflection of the pump beam off of the back face of the crystal is neglected.
In this derivation I assume that there is no applied or photovoltaic electric field, consistent with the conditions of the experiments reported in this thesis. In this derivation, as well as in Feinberg [1980a], it is assumed that:

1) There is negligible population of the conduction band by electrons or of the valence band by holes. This assumption is valid as long as the photoionization rates of electrons or holes is smaller than their rate of recombination with deep traps (i.e. donors and acceptors). Experiments with high power pulsed lasers indicate that the band populations are indeed negligible up to optical intensities of ~100 MW/cm² [Lam 1981].

2) The sites are evenly spaced and have hopping rate coefficients $D_{nm}$ which depend only on the site separation $n-m$. This assumption eliminates the effects of statistical correlations which are found in percolating systems. Statistical correlations are also eliminated by this assumption. Since the average site occupation probability $W_0 \sim 1$ in many photorefractive crystals, there are bound to be strong statistical correlations.

3) The hopping rate coefficients $D_{nm}$ are symmetrical in $x$. This eliminates the bulk photovoltaic effect (~10 V/cm at 1W/cm²) which has been measured in BaTiO₃ [Gower 1986]. Introducing asymmetrical hopping probabilities $D_{nm} < D_{mn}$ would suffice to model the bulk photovoltaic effect with the hopping model.

4) Plane-wave interference pattern. Gaussian beams with diameters much less than a millimeter result in nonexponential erasure. Hall [1985] found that gratings erased with narrow Gaussian beams exhibit an inverse time dependence of the grating amplitude during erasure.
5) Small modulation of the optical intensity so that gratings with higher spatial frequencies may be neglected.

6) The electrostatic potential difference between sites is small compared to $k_B T$. With site densities of $\sim 10^{18}/\text{cm}^3$ the fields necessary to violate this assumption would be $\sim 25,000 \, \text{V/cm}$, much larger than any fields attainable with the photorefractive effect ($\sim 1000 \, \text{V/cm}$).

The probability that the $n$th site is occupied by an electron $W_n$ (the probability that a site is occupied by a hole is $1 - W_n$) changes with time according to:

$$
\frac{dW_n}{dt} = \sum_{m \neq n} D_{nm}^h (1 - W_n) W_m I_n \exp(\beta \phi_{nm}/2) - (1 - W_m) W_n I_m \exp(\beta \phi_{mn}/2) \\
- \sum_{m \neq n} D_{nm}^e W_n (1 - W_m) I_n \exp(-\beta \phi_{nm}/2) - W_m (1 - W_n) I_m \exp(-\beta \phi_{mn}/2). \quad (II-1)
$$

The first line in Equation II-1 accounts for holes hopping, and the second line for electrons hopping. Here,

- $n$ is the site located at position $x_n$,
- $W_n$ is the probability that an electron occupies site $n$,
- $1 - W_n$ is the probability that a hole occupies site $n$,
- $D_{nm}^e$ is the electron hopping rate coefficient between sites $n$ and $m$. 
$D_{nm}^h$ is the hole hopping rate coefficient between sites $n$ and $m$,

$\phi_{nm} = \phi_n - \phi_m$, where $\phi_n$ is the electrostatic potential at site $n$,

$I_n$ is the optical intensity at site $n$,

$\beta = e/k_B T$ (Note: $e > 0$ is the magnitude of the charge on the electron)

$k_B$ is Boltzmann's constant, and

$T$ is the lattice temperature.

Figure II–4 shows two typical hopping events and their contribution to the hopping rate (Equation II–1) for each event.

When two optical waves intersect at an angle $2\theta$ in the crystal then the grating wavevector is $k = k_1 - k_2$ where $k_1$ and $k_2$ are the wavevectors of the two optical plane waves (see Figure II–5). There will be an interference pattern of the form:

$$I_n = I_0 \{1 + \text{Re}[m_0 \exp(ik \cdot x_n)]\}. \quad (II–2a)$$

The grating spatial frequency is $k = (2n\omega/c)\sin \theta$ and $m_0 = 2E_1^*E_2^*/(|E_1|^2 + |E_2|^2)$ is the complex intensity modulation. The space-charge distribution and the resulting electric potential will have the form:

$$W_n = W_0 \{1 + \text{Re}[w \exp(ik \cdot x_n)]\}, \quad (II–2b)$$

$$\phi_n = \text{Re}[\phi \exp(ik \cdot x_n)], \quad (II–2c)$$
Typical hopping events between equally spaced sites in one dimension. (a) The short-range hop of an electron from filled site \( n \) to empty site \( n-1 \) contributes a term \( D_{n,n-1}^e I_n W_n (1-W_{n-1}) \exp(\beta \phi_{n,n-1}/2) \) in Equation II–1. (b) The long-range hop of a hole from site \( n-4 \) to site \( n+2 \) contributes a term \( D_{n-4,n+2}^h I_{n-4} (1-W_{n-4}) W_{n+2} \exp(\beta \phi_{n-4,n+2}/2) \) in Equation II–1.
FIGURE II–5  Coupling Two Optical Beams

Beam geometry for two-beam energy coupling experiments. The optical wavevectors of the beams in the crystal are \( \mathbf{k}_1 \) and \( \mathbf{k}_2 \). The \( +c \) crystal axis is oriented parallel to the grating wavevector \( \mathbf{k} = \mathbf{k}_1 - \mathbf{k}_2 \). If hole photoconduction is dominant, beam 1 experiences gain and beam 2 experiences loss as the two beams propagate through the crystal, as indicated schematically on the figure by the width of the beams. The intersection angle in the crystal is \( 20^\circ \).
where \(|m_0|\) and hence \(|w|\) and \(|\beta|\) are assumed small compared to unity.

Equation II–2c assumes there is no applied or intrinsic spatially uniform electric field and that we can neglect the higher grating harmonics for small modulation \(m_0 \ll 1\). For large modulation \(|m_0| \sim 1\) the harmonics will have significant amplitude and the fundamental will be reduced in amplitude.

Poisson's equation yields

\[
\phi = \frac{[W_0wNe]}{[\varepsilon \varepsilon_0 k^2]} \tag{II–3a}
\]

\[
E_{sc} = -\nabla(\phi_n) = -\text{Re}[ik(W_0wNe/\varepsilon \varepsilon_0 k^2)\exp(ikz_n)], \tag{II–3b}
\]

where \(N\) is the average density of sites, \(\varepsilon\) is the (dimensionless) dielectric constant, and \(\varepsilon_0\) is the permittivity of free space.

Keeping only those terms in Equation II–1 that are first order in the small quantities \(m_0\) and \(w\), Equation II–1 reduces to:

\[
dw/dt = -I_0\{w (D^e + D^h)(1 + k_0^2/k^2) + m_0(D^h - D^e)(1 - W_0)\} \tag{II–4a}
\]

\[
D^e = \sum_{m \neq 0} D_{nm}^e [1 - \exp(ik \cdot x_m)], \tag{II–4b}
\]

\[
k_0^2 = N_{pr} \varepsilon^2/(\varepsilon \varepsilon_0 k_B T), \tag{II–4c}
\]

\[
N_{pr} = N_A(1 - N_A/N_D) \quad N_A < N_D \tag{II–4d}
\]

\[
= N_D(1 - N_D/N_A), \quad N_D < N_A
\]
The effective density of photorefractive charges is \( N_{pr} \). The hopping rate coefficients \( D^e \) and \( D^h \) depend on the explicit form of the hopping probabilities, \( D^e_{nm} \) and \( D^h_{nm} \). Two different calculations of the hopping rate coefficients follow: for both short- and long-range hopping.

For **nearest-neighbor hopping** (see Figure II–4) between equally spaced sites separated by a distance \( u = N^{-1/3} \), the hopping rate coefficient \( D^e_{nm} = \delta_{n \pm 1, m} D^e_0 \), and the summation over \( m \) gives

\[
D^e = 2D^e_0 [1 - \cos(ku)] \approx D^e_0 (ku)^2 \quad \text{(for } ku \ll 1 \text{)} \quad (II-5a)
\]

with a similar term for holes. The site separation \( u \) applies to both electron and hole hopping rate coefficients as they hop between the same sites (see Figure II–2). (The more realistic situation is to assume nearest-neighbor hopping with randomly distributed sites. This is a difficult problem in three dimensions and a one dimensional approximation is probably not appropriate. The three dimensional problem is properly relegated to localization and percolation theory as discussed in [Shklovskii 1984].)

Another possibility is **long-range hopping** (see Figure II–4), extending over many sites, with an exponentially decreasing probability and with an average hopping distance \( 1/\kappa_e \approx u \) [Mullen 1985]. For this case \( D^e_{nm} = D^e_0 (1/\kappa_e |x_m - x_n|) \exp(-\kappa_e |x_m - x_n|) \) for electrons. The exact form of the rate coefficient is somewhat arbitrary, depending on the details of the hopping mechanism. The exponential fall off with increasing hopping distance is to be expected in almost all situations but the inverse dependence on the hopping
distance is chosen so that the results reproduce the predictions of the band conduction models. An inverse square dependence, for instance, is not much different and the resulting predictions are difficult to distinguish from the present choice [Mullen 1985]. Approximating the sum over m by a three dimensional integral:

\[ D^e = D_0^e (4\pi N/\kappa_e^3)/[1 + (\kappa_e/k)^2] \]  

(II–5b)

with a similar result for holes. Here, unlike in Equation II–5a, electrons and holes will have different long-range hopping lengths \( 1/\kappa_e \) and \( 1/\kappa_h \). These lengths are determined by the details of the hopping mechanism and can differ substantially for electrons and holes.

In steady state, \( dw/dt = 0 \), and equations II–3b, II–4 give:

\[ E_{sc} = -kRe[i (kBT/e)Rm_0]/[1 + (k/k_0)^2] \]  

(II–6a)

\[ R = \frac{(D^h - D^e)}{(D^h + D^e)} = \frac{(\sigma_+ - \sigma_-)}{\sigma_+ + \sigma_- + \sigma_d} \]  

(II–6b)

The parameter \( R \) weighs the photorefractive contributions of the hole photoconductivity \( D^h \sim \sigma_+ \) and the electron photoconductivity \( D^e \sim \sigma_- \) which depend on the spatial frequency and the inverse hopping lengths as in Equation II–5b).

The space-charge field \( E_{sc} \) (Equation II–3b) is plotted against the grating spatial frequency \( k \) in Figure II–6 for short-range hopping and two
cases of long-range hopping. At small grating spatial frequency \( k \) both
long- and short-range hopping (equations II–5a and b) yield the same result,
\( E_{SC} \propto k \), because the grating spacing \( 2\pi/k \) is much larger than the hopping
lengths. The curves differ substantially as \( k \) increases, and the grating
spacing becomes comparable to the electron or hole hopping lengths.

For the case of uniform illumination \( (m_0 = 0) \) and \( |w|>0 \), the grating will
decay exponentially with a rate \( \Gamma \):

\[
E_{SC} \sim \exp(-\Gamma t)
\]

(II–7a)

where the grating erasure rate is:

\[
\Gamma = [ I_0 (D^e + D^h) + \Gamma_d ] [1 + (k_0/k)^2 ].
\]

(II–7b)

The effective density of photorefractive charge carriers \( N_{pr} \) and the
relative contribution of electron and hole photoconductivities \( R \) can be
determined by two-beam energy coupling experiments. The hopping lengths
\( 1/\kappa_{e,h} \) can be determined through a combination of coupling and erasure
measurements [Strohendl 1986].
The spatial frequency dependence of the space-charge field for the cases of short and long-range hopping according to Equation II–7. \( k_0 = 0.8 \) \( n\omega/c \) for all curves. 

a) \( \kappa_h = \kappa_e \gg 2 \, n\omega/c \).  
b) \( \kappa_h = 0.9 \, n\omega/c \) and \( \kappa_e = 1.0 \, n\omega/c \).  
c) \( \kappa_h = 0.9 \, n\omega/c \) and \( \kappa_e = 1.2 \, n\omega/c \).
Optical Scattering: The Coupled Wave Equations

Two optical beams can exchange energy through the creation of the photorefractive space-charge field derived in Equation 11-6a. In this section I will derive the coupled wave equations for the interaction of the two beams and solve the equations for simple experimental situations. The intensities of the two optical beams change as they propagate through the photorefractive medium; one beam increases in intensity and the other beam decreases in intensity as shown in Figure 11-5. Therefore the magnitude of the space-charge field will also change as the beams propagate through the crystal.

The photorefractive index pattern generated by the space-charge field acts as a volume diffraction grating and partially Bragg-deflects each beam. One deflected beam adds constructively and the other deflected beam adds destructively to the transmitted beams, causing a net transfer in energy from one beam to the other as shown in Figure 11-5. Figure II–7 shows explicitly how the two diffracted beams combine with the transmitted beams. The transmitted beams, 1 and 2, have amplitudes $E_1$ and $E_2$ and phases $\phi_1$ and $\phi_2$, respectively, which are unchanged by the presence of the index grating. The diffracted beams, 1' and 2', have amplitudes $\eta E_1$ and $\eta E_2$ and phases $\phi_2 + 2\phi_g$ and $\phi_1 - 2\phi_g$, respectively. But $\phi_g = \phi_1 - \phi_2 + \pi/2$ in the absence of an applied electric field and there is constructive interference between transmitted beam 1 and diffracted beam 2' and destructive interference between transmitted beam 2 and diffracted beam 1'.
Schematic separation of two-beam coupling into the diffraction and subsequent coherent addition of the two beams. Beam $E_1$ diffracts with amplitude $\eta E_1$ and phase $\phi_1 - 2\phi_g$ where $\phi_g$ is the grating phase shift. If $\phi_g = \pi/2$, this diffracted beam interferes constructively with the transmitted part of beam 2. In the same way, the diffracted part of beam 2 adds destructively to the transmitted part of beam 1.
Let the two plane-wave coherent optical beams have intensities $I_1 \propto I_2$ and wavevectors $k_1$ and $k_2$, respectively, in the crystal. The resulting intensity modulation in the crystal is of the form of Equation II–2a with $k = k_1 - k_2$ and $m_0 = 2E_1^*E_2^*/(|E_1|^2 + |E_2|^2)$. Maxwell's equations yield [Shen 1984, Feinberg 1980a]:

\[
\nabla \times \nabla \times E_\omega - (\omega/c)^2(\varepsilon_\omega + i\varepsilon_{\omega i}) \cdot E_\omega = (\omega/c)^2 P_{NL}/\varepsilon_0, \quad (\text{II–8a})
\]

\[
P_{NL} = \chi \cdot E_\omega = \varepsilon_0 [\varepsilon_{\omega i} [r \cdot E_{sc}] \cdot \varepsilon_\omega] \cdot E_\omega, \quad (\text{II–8b})
\]

\[
E_\omega = E_1(r) \exp(i k_1 \cdot x - i\omega t) + E_2(r) \exp(i k_2 \cdot x - i\omega t). \quad (\text{II–8c})
\]

Here $E_{sc} = i(kB/2e)R[m_0 \exp(ik \cdot x) - m_0^* \exp(-ik \cdot x)]/[1 + (k/k_0)^2]$ as given by Equation (II–6b), $\varepsilon_\omega = n^2$ is the dispersive (real) part of the second rank optical dielectric tensor and $\varepsilon_{\omega i}$ is the absorption (imaginary) part of the dielectric tensor. The nonlinear polarization $P_{NL}$ is due to the second order optical susceptibility $\chi_\omega$ (the linear electrooptic, or Pockels, effect). The third rank tensor $r$ contains the electrooptic coefficients $r_{klj} = r_{ij}$ with $i = 1$ to 6 in contracted notation [Yariv 1975]. Equations II–10 are consistent with the Slowly Varying Envelope Approximation (SVEA) described in Jackson [1975] or in Shen [1984]; we assume that the transverse amplitudes $E_1(r)$ and $E_2(r)$ vary slowly within one optical wavelength. Since $\varepsilon_\omega$ and $\varepsilon_{\omega i} = \alpha \cdot \varepsilon_\omega$ are diagonal the optical waves are transverse waves and $\nabla \times \nabla \times E_\omega = -\nabla^2 E_\omega$.

Equations II–8 become:
Neglecting terms $\nabla^2 E_1$ and $\nabla^2 E_2$ in the SVEA we obtain

\[
\begin{align*}
2(k_1 \cdot \nabla)E_1 + (\omega/c)\alpha \cdot \nabla \varepsilon_{\omega} \cdot E_1 - \gamma E_2 \exp(ik \cdot x/2) \\
+ 2(k_2 \cdot \nabla)E_2 + (\omega/c)\alpha \cdot \nabla \varepsilon_{\omega} \cdot E_2 + (\omega/c)\gamma^* E_1 \exp(-ik \cdot x/2) \\
+ (\gamma^* E_2 \exp(-3ik \cdot x/2) - \gamma E_1 \exp(3ik \cdot x/2)) \frac{\omega}{c} & = 0
\end{align*}
\] (II–10)

The last term in Equation II–10 does not contribute to two-beam coupling because neither of the incident waves is Bragg-matched to the grating's higher spatial frequencies. Indeed, in calculating the steady state space-charge field in Equation II–3b I have neglected harmonics of the grating and thus there would be other terms in Equation II–10 with higher spatial frequencies. Equating the terms with like spatial frequencies in Equation II–10, the resulting coupled equations are then:

\[
\begin{align*}
2(c/\omega)(k_1 \cdot \nabla)E_1 & = + \gamma E_2 - \alpha \cdot \nabla \varepsilon_{\omega} \cdot E_1 \\
2(c/\omega)(k_2 \cdot \nabla)E_2 & = - \gamma^* E_1 - (\omega/c)\alpha \cdot \nabla \varepsilon_{\omega} \cdot E_2,
\end{align*}
\] (II–11a)

\[
\gamma = \frac{k_B T \omega/c}{[1 + (k/k_0)^2] [\varepsilon_{\omega} \cdot (r \cdot k) \cdot \varepsilon_{\omega}]} \frac{E_1 \cdot E_2^*}{\varepsilon_{\omega} \cdot (r \cdot k) \cdot \varepsilon_{\omega}}. \tag{II–11b}
\]

These equations are subject to the assumptions made in the derivation of the photorefractive space-charge field in equation II–6a as well as the SVEA.
Consider the situation with grating wavevector \( \mathbf{k} \) along the \( z \) axis (c-axis) and \( \mathbf{E}_1 \parallel \mathbf{E}_2 \). Then the vector relations reduce to 1-dimensional coupled wave equations:

\[
\frac{dI_1}{dx} = \left[ +\frac{gI_2}{(I_2 + I_1) - \alpha} I_1 \right]/\cos \theta,
\]

\[
\frac{dI_2}{dx} = \left[ -\frac{gI_1}{(I_2 + I_1) - \alpha} I_2 \right]/\cos \theta,
\]

(II-12)

If \( \theta \leq 90^\circ \) (e.g. the two beams enter the same face of the crystal as in Figure III-1) then the solution is:

\[
\frac{I_1(z_1)}{I_1(0)} = \frac{(1 + \beta) \exp[(g - \alpha)x_1]}{1 + \beta \exp(gx_1)},
\]

(II-13a)

\[
\frac{I_2(z_2)}{I_2(0)} = \frac{(1 + \beta) \exp[-(g + \alpha)x_1]}{1 + \beta \exp(-gx_1)},
\]

(II-13b)

where \( x_1 = x/\cos \theta \) is the coordinate along beam 1. The boundary conditions are \( E_{1,2}(0) = \sqrt{I_{1,2}(0)} \) so that \( \beta = I_1(0)/I_2(0) \). The exponential power gain coefficient \( g \) per unit length is:

\[
g = \frac{R(k) \delta k}{(n \omega/c)[1 + (k/k_0)^2]} [\mathbf{e}_1 \cdot \mathbf{e}_2^*],
\]

(II-13c)

where \( \mathbf{e}_1 \) and \( \mathbf{e}_2 \) are the unit polarization vectors of beams 1 and 2, respectively. If beams 1 and 2 are both polarized perpendicular to the \( z \)-axis (o-rays) then \( \mathbf{e}_1 \cdot \mathbf{e}_2^* = 1 \). If the beams are polarized in the \( x-z \) plane (e-rays) then \( \mathbf{e}_1 \cdot \mathbf{e}_2^* = \cos(2\theta) \).
The intrinsic photorefractive coupling gain \( \delta = n_i^4(\omega/c)^2(r_{ij3}k_B T/e) \) has units of inverse length and depends only on properties of the crystal lattice such as the Pockels coefficient, the index of refraction, and the temperature, but not on the density or transport properties of the photorefractive charges nor on the spatial frequency \( k \). The parameter \( k_0 \) is defined in Equation II–4c.

In the two-wave mixing experiments, we measure the intensity of beam 1 after it exits the crystal both with and without beam 2 present. For two beams entering the same face of the crystal

\[
\frac{I_1(\text{with beam 2})}{I_1(\text{without beam 2})} = \frac{(1 + \beta) \exp(g L_1)}{1 + \beta \exp(g L_1)},
\]

(II–14a)

where \( L_1 = L/\cos\theta \) is the interaction length along beam 1 and \( L \) is the thickness of the crystal along the bisector of the beams. The absorption and losses due to surface reflections do not appear in the final result (Equation II–14a) which make measurement of the coupling gain simpler and more accurate than relying on Equation 13.

If \( \theta \geq 90^\circ \) the pump beam is propagating in roughly the opposite direction to the probe, and now the solution depends weakly on the absorption (if \( \alpha L < 1 \)):

\[
\frac{I_1(\text{with coupling})}{I_1(\text{without coupling})} = \frac{[\sinh(\alpha L_1)/\alpha L + \beta L \exp(-\alpha L)]\exp(g L_1)}{[\sinh(\alpha L_1)/\alpha L + \beta L \exp(-\alpha L)\exp(g L_1)]}
\]

(II–14b)

where \( \beta L = I_1(0)/I_2(L) \) is the ratio of the input intensities.
By measuring the variation of the two-beam coupling gain $g$ with grating wavevector $k$, both $R(k)$ and $k_0^2$ can be determined. The factor $R(k)$ (Equations II–5 and 6) measures the competition between holes and electrons in forming the space-charge field. The parameter $k_0^2$ is proportional to the effective density of photorefractive charges (Equation II–4). In the following chapter we describe two-beam energy coupling experiments to measure these quantities.

Conclusions

The space-charge field produced by a sinusoidal optical intensity distribution is readily calculated in the limit of small modulation from the hopping conduction model of the photorefractive effect [Feinberg 1980a]. The assumptions inherent in Equation II–6 for the resulting photorefractive space-charge field can be separated into three categories:

1) Assumptions inherent in Equation II–1;

-There is negligible population of the conduction band by electrons or of the valence band by holes. This assumption is valid as long as the photoionization rates of electrons or holes is smaller than their recombination rates with deep traps (i.e. donors and acceptors). Experiments with high power pulsed lasers indicate that the band populations are indeed negligible up to optical intensities of $\sim 100 \text{ MW/cm}^2$ [Lam 1981].
2) Simplifying assumptions in the derivation leading to Equation II–6;

- The sites are evenly spaced and have hopping rate coefficients $D_{nm}$ which depend only on the site separation $n-m$. This assumption eliminates the effects of statistical correlations which are found in percolating systems. Statistical correlations are also eliminated by this assumption. Since the average site occupation probability $W_0 \sim 1$ in many photorefractive crystals, there are bound to be strong statistical correlations.

- The $D_{nm}$ are symmetrical in $x$. This eliminates the bulk photovoltaic effect ($\sim 10$ V/cm at 1W/cm$^2$) which has been measured in BaTiO$_3$ [Gower 1986]. Simply introducing asymmetrical hopping probabilities $D_{nm} < D_{mn}$ would allow the derivation of the bulk photovoltaic effect with the hopping model.

- Plane-wave interference pattern. Gaussian beams with diameters much less than a millimeter result in nonexponential erasure. Hall [1985] found that gratings erased with gaussian beams exhibit an inverse time dependence of the grating amplitude during erasure.

- Small modulation of the optical intensity so that gratings with higher spatial harmonics may be neglected. This assumption is good for modulation ratios less than 0.2, as determined experimentally.

- The electrostatic potential difference between sites is small compared to $k_BT$. With site densities of $\sim 10^{18}$/cm$^3$ the fields necessary to violate this assumption would be $\sim 25,000$ V/cm, much larger than any fields attainable with the photorefractive effect ($\sim 1000$ V/cm).

- There is no applied or photovoltaic electric field.
3) In deriving the two-beam coupling gain I have neglected second spatial derivatives in Equation II–8, commonly referred to as the Slowly Varying Envelope Approximation (SVEA), to the above assumptions. The SVEA is a proper assumption in all present photorefractive phenomena because the index changes are small ($\sim 10^{-3}$) and hence the phase and amplitude changes of the propagating waves are small within the distance of one wavelength.

Several assumptions of Feinberg [1980a] were removed in the above derivation. They are:

1) The photorefractive sites may have any fractional occupancy in the range $0 \leq W_0 \leq 1$.
2) Both electron and hole hopping events are included.
3) Long-range hopping is included (Mullen [1985] included long-range hopping for a single carrier in the hopping model).
4) Beam depletion is accounted for in two-beam energy coupling.
5) The reflection of the pump beam off of the back face of the crystal is included in two-beam energy coupling.
References: Chapter II


III TWO BEAM ENERGY COUPLING

When two coherent optical beams intersect in a photorefractive crystal they simultaneously create a photorefractive grating and are diffracted by it. The beams exchange energy as they propagate through the crystal because of the remarkable 90° phase shift of the photorefractive grating with respect to the phase of the optical interference fringes of the two beams which was discussed in Chapter II (especially regarding Figure II-7). This exchange of energy is a simple and direct measure of the space-charge electric field produced by the intersecting beams.

In this chapter I report measurements of the exchange of energy between two optical beams which intersect in a BaTiO₃ crystal and compare the results of these experiments to the theoretical predictions given in Chapter II. There are two objectives of these two-beam energy coupling experiments. The first objective is to determine the accuracy and validity of photorefractive theory. The second objective is to measure several photorefractive properties which vary from crystal to crystal because of variations in impurity and defect densities. The photorefractive properties determined from the two-beam coupling experiments reported in this chapter are the effective density of photorefractive charges, the relative contribution of electron and hole photoconductivities, and the electron and hole transport or "hopping" lengths.

Energy Coupling Experiments

The two-beam energy coupling experiments were performed with an argon-ion laser operating in a single longitudinal and Gaussian TEM₀₀ mode.
at a wavelength of 514.5 nm (unless otherwise noted). Two coherent beams with intensities $I_1 \sim 10^{-4}$ W/cm$^2$ and $I_2 \sim 10^{-1}$ W/cm$^2$ and diameters of 3mm were aligned so that the direction of the grating wave vector $\mathbf{k}$ was parallel to the c-axis of the BaTiO$_3$ crystal (see Figure 11–5). The beams were polarized perpendicular to the plane containing the two beams and the c-axis, and so were ordinary rays in the crystal. (Extraordinary rays cause experimental problems: they have a much larger coupling strength, which can cause significant depletion of the stronger beam. Also, the effective Pockels coefficient $r_{\text{eff}}$ depends more sensitively on the alignment of the crystal with respect to the optical beams for extraordinary rays [MacDonald 1984].)

The coupling of two beams oriented as described in the previous paragraph (see also Figure 11–5) was calculated in Chapter II with the approximation that the beams are plane waves in the crystal. But there are two properties of the Gaussian beams actually used which may introduce deviations in the experimental results from the plane-wave calculation: 1) the TEM$_{00}$ Gaussian beam divergence of 0.03° in air and 2) the finite beam width. To examine the effect of the finite beam divergence, we measured the energy coupling gain at crystal angles down to $\theta_x = 0.1°$ and saw no deviation from the prediction of equation II–13c that the coupling gain is linear in the grating spatial frequency at small spatial frequency as shown in Figure III–1. Another possible source of error is the finite beam width. Figure III–2 shows the decrease in the effective interaction length $L$ of two beams of finite size; as the crossing angle in the crystal $2\theta_x$ increases, the effective interaction length decreases. The largest internal crossing angle used was $\theta_x = 22°$
Two-Beam Energy Coupling Gain at Small Spatial Frequencies

The measure two-beam energy coupling gain coefficient in the DOYLE BaTiO$_3$ crystal at small spatial frequencies. The crossing angle $\theta_X$ in the crystal ranges from $0.01^\circ$ to $4^\circ$. 
FIGURE III–2 Effects of Finite Beam Width

The geometric constraints on the effective gain region for beams of finite width. Equation III–6 assumes that the beams overlap for all of the shaded regions (a) and (b) but the actual overlap of the beams is the region (a) which comprises a fraction $1 - (L \sin \theta)/2d$. 
(θ_{air} = 70°). Since L > H (Table III–1) and \( l_2 \gg l_1 \) (m<1) in all of our measurements, then the minimum effective interaction region (shaded dark) was about 70% (m = 1) and exceeds 95% when m < 0.4 as was the case for all measurements. Therefore, the measured two-beam energy coupling gain in all of the data presented was not measurably affected by the Gaussian beam divergence or finite width.

The coupling of two beams in a real crystal is further complicated by the reflection of the beams inside the crystal. The \(~18\%\) reflection of the strong pump beam 2 from the right-hand crystal face in Figure II–5 is much stronger than the probe beam and alters its intensity in two additional ways:

First, the reflected beam partially erases the grating created by beams 1 and 2, thus decreasing the overall coupling gain by a factor of \( 1 + r \) (\( r = \) the intensity reflectivity of the right-hand face \( \sim 18\% \) in BaTiO₃). Second, the reflected beam couples with the probe beam with positive gain. The effective gain actually measured in the forward two-beam coupling experiments is:

\[
geff = \frac{g(k) + [1/2][\sin \theta_x][(Ar)^2/(1 + Ar)][g(k=2n\omega/c)]}{1 + Ar}, \quad \text{(III–1a)}
\]

\[
A = \exp(-\alpha L) \sinh(\alpha L)/\alpha L. \quad \text{(III–1b)}
\]

For forward two-beam coupling \( g_{eff} = [g(k) + .01(\sin \theta_x)g(k=2n\omega/c)]/(1.17) \) for \( \alpha L = 1 \). For counterpropagating beams \( k = 2n\omega/c \) and:

\[
geff \approx g(k=2n\omega/c)/(1 + Ar). \quad \text{(III–2)}
\]
The above expressions for the effective gain were used to determine the correct coupling gain in the two-beam energy coupling experiments reported in this chapter and in Chapter V.

Another practical problem is the tendency of BaTiO$_3$ to set up internally self pumped phase conjugating loops in the crystal [Feinberg 1982, MacDonald 1983]. This did not occur when the beams were polarized perpendicular to the crystal c-axis and care was taken to avoid self-pumping when the beams were polarized parallel to the c-axis.

To determine the coupling gain coefficient, the increase in the transmitted intensity of the weak beam $I_1$ due to the presence of the strong beam $I_2$ was measured, and the small-signal gain coefficient $g$ was determined from Equation III–1 or III–2. The magnitude of the grating wave vector $k = \vert k_1-k_2 \vert = (2n_0\omega/c)\sin \theta$ was varied by changing the crossing angle $2\theta$ of the beams. A plot of the measured gain coefficient $g$ vs. grating spatial frequency $k$ in a BaTiO$_3$ crystal is shown in Figure III–3, along with a theoretical fit using Equation II–13c and the following constants: $r_{eff} = r_{13} = 33 \times 10^{-12}$ m/Volt (the unclamped Pockels coefficient for ordinary rays [Ducharme 1986b]), $n_0 = 2.48$ [Wemple 1968], $\varepsilon = 150$ [Camlibel 1971], $T = 23$ °C, $\lambda = 514.5$ nm, $L_1 = L/\cos \theta$. The dimensions of all crystals studied in conjunction with this work are listed in Table III–1.
Two-beam energy coupling gain coefficient $g$ vs. the grating spatial frequency (in units of optical wavevector $n_0\omega/c$) in the DOYLE BaTiO$_3$ crystal. The solid line is a theoretical fit of the data to Equation II–13c.
**TABLE III–1: CRYSTAL DIMENSIONS**

<table>
<thead>
<tr>
<th>crystal</th>
<th>L(c-axis)</th>
<th>W</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWISS</td>
<td>0.46</td>
<td>0.42</td>
<td>0.48</td>
</tr>
<tr>
<td>CAT</td>
<td>0.54</td>
<td>0.435</td>
<td>0.56</td>
</tr>
<tr>
<td>DOYLE</td>
<td>0.445</td>
<td>0.235</td>
<td>0.565</td>
</tr>
<tr>
<td>FREE</td>
<td>0.73</td>
<td>0.54</td>
<td>0.53</td>
</tr>
<tr>
<td>ROCKY</td>
<td>0.37</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>SBN:60</td>
<td>0.70</td>
<td>0.55</td>
<td>0.54</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>0.80</td>
<td>0.54</td>
<td>0.65</td>
</tr>
</tbody>
</table>

(All dimensions are ±0.005 cm)
Spatial Frequency Dependence

The energy-coupling in Figure III–3 grows linearly with small $k$, reach a maximum at $k = k_0$ and then decreases for large $k$. The theoretical fit to Equation II–13c has 4 adjustable parameters: $k_0$, $\kappa_e$, $\kappa_h$ and $R(k=0)$. The value of $k_0^2$ is controlled by the effective density of photorefractive charges $N_{pr}$ (Equation II–4c). The parameter $R(0)$ is the relative contribution of electron and hole photoconductivities (Equation II–6b), and is proportional to the slope at small $k$ of each of the curves of Figure III–3. The sign of $R(0)$ determines the sign of the coupling coefficient $g$: $R$ is positive for hole-dominated photoconduction, and negative for electron-dominated photoconduction.

The parameter $k_0^2 \propto N_{pr}$ and the inverse squares of the hopping lengths ($\kappa_h^2$ and $\kappa_e^2$) affect the shape of the coupling gain curve (see Figure II–6) in a similar way and are consequently difficult to separate experimentally. The values of $k_0$, $\kappa_h$, and $\kappa_e$ in Table III–2 have a large uncertainty for this reason. The values of $k_0$ and $N_{pr}$ reported in Table III–2 differ from values reported in Ducharme [1986a] which were calculated from the same two-beam coupling data but without the added dependence on $\kappa_h$, and $\kappa_e$.

Table III–2 is a summary of the measured density of photorefractive charges $N_{pr}$, the relative contribution $R$ of holes and electrons to
**TABLE III-2: PHOTOREFRACTIVE PARAMETERS**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$k_0$</th>
<th>$\kappa_h$</th>
<th>$\kappa_e$</th>
<th>$N_{pr}$</th>
<th>$R$</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(units of optical wavevector, $n\omega/c$)</td>
<td>($10^{16}$ cm$^{-3}$)</td>
<td>(°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>aROCKY:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 atm*</td>
<td>0.49</td>
<td>0.48</td>
<td>0.64</td>
<td>4.2</td>
<td>+0.33</td>
<td>126.3</td>
</tr>
<tr>
<td>as grown</td>
<td>0.30</td>
<td>0.30</td>
<td>0.33</td>
<td>1.6</td>
<td>0.07</td>
<td>-----</td>
</tr>
<tr>
<td>0.2 atm*</td>
<td>0.32</td>
<td>0.66</td>
<td>0.57</td>
<td>1.7</td>
<td>-0.12</td>
<td>125.5</td>
</tr>
<tr>
<td>$10^{-6}$ atm*</td>
<td>0.52</td>
<td>0.62</td>
<td>0.51</td>
<td>4.7</td>
<td>-0.18</td>
<td>120.0</td>
</tr>
<tr>
<td><strong>eMMD:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as grown</td>
<td>&gt;0.17</td>
<td>-----------</td>
<td>&gt;0.6</td>
<td>0.11</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>120°C#</td>
<td>&gt;0.13</td>
<td>-----------</td>
<td>&gt;0.3</td>
<td>0.07</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>$10^{-3}$ atm**</td>
<td>&gt;0.25</td>
<td>-----------</td>
<td>&gt;1.1</td>
<td>+0.37</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td><strong>cCAT</strong></td>
<td>0.97</td>
<td>1.3</td>
<td>2.8</td>
<td>16.0</td>
<td>+0.20</td>
<td>127</td>
</tr>
<tr>
<td><strong>dSWISS</strong></td>
<td>&gt;0.56</td>
<td>-----------</td>
<td>&gt;4.7</td>
<td>+0.39</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td><strong>eDOYLE</strong></td>
<td>0.50</td>
<td>large</td>
<td>1.5</td>
<td>4.4</td>
<td>+0.41</td>
<td>-----</td>
</tr>
</tbody>
</table>

Experiments using these crystals are reported in:

a This study and [Ducharme 1984b], b [Feinberg 1980a] and [Lam 1981], c [Feinberg 1982], d [MacDonald 1984], e not previously reported

* Oxygen partial pressure during treatment at 650°C
** Oxygen partial pressure during treatment at 550°C
# Dow 200 Silohexane

**TITLE**

The photorefractive inverse Debye screening length $k_0$, the inverse hole and electron hopping lengths $\kappa_h$ and $\kappa_e$, the effective density of photorefractive charge carriers $N_{pr}$, the relative contribution of hole and electron photoconduction $R = (\sigma^+ - \sigma^-)/(\sigma^+ + \sigma^-)$, and the temperature of the ferroelectric-to-cubic phase transition $T_c$ for a variety of BaTiO$_3$ crystals.
photoconduction, and the inverse electron and hole hopping lengths for the ROCKY crystal in this work and a number of other BaTiO₃ crystals studied previously or in conjunction with this work. All crystals were melt-grown by Sanders Associates [Belrus 1971]. Note that the experimentally determined values of R fall between −1 and +1, as predicted by Equation II–6d. All of these crystals, as grown, exhibited hole-dominated photoconduction (R > 0). Electron photoconduction dominated when a crystal was heat treated in an oxygen deficient atmosphere (The ROCKY crystal: These treatments are: discussed in detail in Chapter V). To my knowledge, only one BaTiO₃ crystal has exhibited electron dominated photoconduction as grown (without and heat treatments) as reported by Klein [1985a]. Strohkendl [1986] showed that this crystal was almost perfectly compensated (Np ≈ Na, see Figure II–2 and Equation II–4d). Another key question raised by the data summarized in Table III–2 is why are the electron and hole photoconductivities always within a factor of four of each other (R ≤ 0.41) for so many different crystals? This may just be because they were all grown under similar conditions by the same crystal grower.

**Wavelength Dependence**

Figure III–4 shows the variation of the two-beam energy coupling gain with wavelength in the CAT and SWISS BaTiO₃ crytals. There is little variation except that in the CAT crystal the coupling gain decreases dramatically at longer wavelengths. The only other significant difference between these crystals which might explain the difference in the wavelength dependence of the coupling is the unusually short dark storage time (~1 second) for gratings in the CAT crystal compared to a storage time of several
FIGURE III–4

Two-Beam Energy Coupling Gain: Wavelength Dependence

Photorefractive coupling gain $g$ versus the wavelength $\lambda$ of the two coherent optical beams in the CAT and SWISS crystals.
Conclusions

Two-beam energy coupling experiments yield the effective density of photorefractive charges, the relative contributions of electron and hole photoconductivities, and the electron and hole hopping lengths. In practice, the measurements are complicated by the reflected pump beam and by the fact that the shape of the coupling gain curve depends in a similar manner on the hopping lengths and on $k_0$. 
References: Chapter III


IV ERASURE

The temporal behavior of the photorefractive effect is of theoretical and practical interest. The characteristic photorefractive speed, or rate of change of the refractive index, is an important consideration in device design. According to photorefractive theory, the speed is essentially proportional to the photoconductivity and is thus dependent on a number of photorefractive material properties such as the carrier mobilities and the impurity and defect content of the material. In this chapter I describe measurements of the speed of the photorefractive effect in a crystal of BaTiO$_3$ and examine the dependence on optical intensity, temperature, and grating spatial frequency.

The most important result of the experiments described in this chapter, from both theoretical and practical points of view, is the pronounced sublinear dependence of the photorefractive speed on intensity. The speed of many BaTiO$_3$ crystals is sublinear, proportional to the optical intensity raised to a power "x", where the exponent x ranges between 1/2 and 1 and varies from crystal to crystal, depending on the impurity and defect levels. At present I know of no theoretical explanation for the sublinear behavior. Both the band conduction (band conduction) [Kukhtarev 1979] and hopping conduction [Feinberg 1980a] models of transport predict linear photoconductivity; the speed should increase linearly with intensity. Prior to the first reports of the experiments contained in this chapter [Ducharme 1983, and Ducharme 1984a] the observed sublinear scaling of the speed was attributed to photoconductive saturation but the range of the data presented here covers four decades of intensity, thus eliminating saturation as an explanation. Saturating photoconductivity exhibits an apparently sublinear dependence on intensity only over one decade in intensity.
The speed of photorefractive devices is of great importance but presents the biggest challenge in material selection and preparation. The photorefractive materials with the highest coupling gain, such as BaTiO$_3$ and SBN are also notoriously slow. When illuminated with visible light intensities of a watt per square centimeter both of these materials have grating rise times of about one tenth of a second. The rise times increase with wavelength, making near infrared operation even slower. Faster photorefractive materials like BSO (~ microsecond at a watt per square centimeter in the visible [Mullen 1985]) and GaAs (~ 0.1 microsecond at a watt per square centimeter in the near infrared [Klein 1984b]) tend to have much smaller coupling strengths.

A Simple Picture of Erasure

The dynamics of erasure of photorefractive gratings can be demonstrated by an analogy. The photorefractive space-charge distribution created by the two writing beams can be thought of as a series of capacitors; two such capacitors with opposite charge make up one grating period. A "grating period capacitor" is pictured schematically in Figure IV-1. The capacitor will discharge through the internal resistance $R$ (from the bulk light-induced and dark conductivities) and the charge on the electrodes will decrease exponentially with the "RC" circuit time constant:

$$1/\Gamma = RC = (L/\sigma A)(Ae\varepsilon_0/L).$$  (IV-1)

Note that the RC decay time constant is independent of the geometrical parameters of the hypothetical "capacitor." The dielectric relaxation rate, $\Gamma = \sigma/\varepsilon_0$, is an intrinsic bulk property of space-charge relaxation in insulators.
"Simple Picture" of photorefractive grating decay as the discharge of a capacitor. The capacitor has capacitance C and resistance R, electrode area A, and separation L.
The simple picture, or capacitor analogy, of grating erasure is an accurate one as long as the grating spacing, the capacitor electrode separation, is large compared to the charge (Debye) screening length of the material. This is the same as saying that charge screening effectively smears out the influence of charge at distances larger than the screening length so that the discrete charge layers in the capacitor analogy appear smeared at large grating spacing. The derivation of the grating erasure rate in Chapter II, Equation II–7b shows the explicit deviation of the grating erasure rate from the dielectric relaxation rate as the grating spatial frequency \( k \) approaches the inverse charge screening length \( k_0 \).

**Grating Erasure Experiments**

The speed of light-induced refractive index changes in a photorefractive crystal of \( \text{BaTiO}_3 \) was measured under a variety of conditions. The experiments were performed by illuminating the \( \text{BaTiO}_3 \) crystal with two mutually coherent optical beams. These "writing" beams created and intensity interference pattern where they intersected in the crystal. The spatial frequency of the interference pattern was varied by changing the crossing angle between the two writing beams. According to the present models of the photorefractive effect [Feinberg 1980a and Kukhtarev 1979], charges (of unknown origin in \( \text{BaTiO}_3 \)) migrated the presence of the light pattern to create a spatially varying electrostatic field, which in turn altered the refractive index of the crystal by the linear electrooptic (Pockels) effect. The resulting refractive-index variation had a component with the same spatial frequency as the intensity interference pattern, and was monitored by another optical beam, the "reading" beam, incident at the Bragg angle of the refractive index.
If the writing beams were removed, the refractive-index grating persisted in the dark, although it was slowly erased both by the reading beam and by thermal charge transport. The grating could be rapidly erased by flooding the crystal with light from a uniform intensity erasing beam. By measuring the grating erasure rate as a function of the intensity of the erasing beam and of the temperature, both the dark and the light-induced erasure rates and their temperature dependences were determined.

The CAT BaTiO$_3$ sample, dimensions $4.3 \times 5.4 \times 5.6$ mm$^3$ (Table III–1), was mechanically and electrically poled into a single domain crystal with the c axis parallel to the 5.4 mm dimension. The crystal was contained in a quartz spectroscopic cuvette filled with silicon oil of refractive index $n = 1.4$. A thermistor temperature sensor and proportional feedback control was used to regulate the oil bath temperature to within $\pm 0.1$ °C of a set temperature.

The erasure experiments were performed in the following manner. Figure I–1 shows the arrangement of the crystal and the various optical beams. The writing beams 1 and 2 with optical wave vectors $k_1$ and $k_2$ respectively in the crystal, created an intensity interference pattern with grating wave vector $k = k_1 - k_2$. The magnitude of the grating wave vector was $k = (2\omega/c) \sin \theta_{\text{air}}$, where $2\theta_{\text{air}}$ is the full angle of intersection of the writing beams in air. The crystal was aligned so that the c-axis was parallel to the grating wave vector $k$. The reading beam 3 incident on the resulting photorefractive grating at the Bragg angle, was deflected by the grating to form the signal beam 4 which was monitored with a photomultiplier tube. All of these optical beams were polarized perpendicular to the plane of incidence so as to be ordinary rays in the crystal in order to minimize
two-beam energy coupling. An erasing beam 5 was incident from a direction perpendicular to the other four beams, so as to minimize scattering off of any refractive index grating formed by the other beams. The erasing beam was polarized parallel to the c axis of the crystal to minimize scattering into the signal beam 4 (although the photoconductivity [Kratzig 1980] and the optical absorption [Casella 1959 and Klein 1986] usually depend on the polarization, the erasure rate was unaffected by the choice of polarization of the erasing beam) and entered the top of the crystal after passing through the silicon oil meniscus which had been flattened by a thin plastic sheet with a hole for the beam.

To determine the light-induced erasure rate, a refractive index grating was first created by illuminating the BaTiO₃ crystal with the two writing beams and with the reading beam. After five seconds the writing beams were turned off and the erasing beam turned on by mechanical shutters and the signal decayed with time. The decay curve was digitized, the process repeated, and the average of typically five decay curves was fit by the method of least squares to a simple exponential decay. The decay or erasure rate is defined as the reciprocal of the exponential decay time constant. In all cases the observed decay curves were well fit by a single exponential decay. (No evidence was seen for nonexponential decay, although an initial fast decay shorter than 1 msec could not have been resolved due to the 1 msec closing time of the mechanical shutter).

All optical beams were derived from an argon ion laser operating at 514.5 nm on single longitudinal and transverse Gaussian modes. The spot size of beams 1, 2, and 3 was 200 µm (1/e²) in diameter for the light-induced erasure experiments. The erasing beam intensity was uniform over the
volume of the grating. The intensities of the various beams were: the writing beams $I_1 = I_2 = 4\text{W/cm}^2$, the reading beam $I_3 = 10^{-4}\text{W/cm}^2$, and the erasing beam varied over the range $I_5 = 10^{-4}$ to $10^2\text{W/cm}^2$. The observed erasure rate was independent of the relative intensities of the writing beams and therefore of the grating modulation depth. The intensity of the reading beam had no measurable effect on the grating erasure rate for erasing beam intensities exceeding $10^{-3}\text{W/cm}^2$. To measure the dark erasure rate no erasing beam was used; the writing and reading beams were increased in diameter to 3 mm ($1/e^2$) and the intensity of the reading beam was reduced to $I_3 = 2 \times 10^{-10}\text{W/cm}^2$, so as to have no measurable effect on the dark erasure rate. The diffraction efficiency $\zeta = I_4/I_3$ was deliberately made less than 20% so that $\sqrt{\zeta}$ was proportional to the light-induced refractive index change [Kogelnik 1969].

Light-Induced Erasure: Sublinear Photoconductivity

The results of light-induced erasure experiments at crystal temperatures of 16, 24, and 40 °C are summarized in Figure IV–2. The dark erasure rate is subtracted from the total erasure rate to obtain the light-induced erasure rate. (We assume that the dark and light-induced erasure rates are linearly additive. That this is a good assumption will become apparent below from the distinct temperature dependences of the dark and light-induced erasure rates.) A log-log plot of this light-induced erasure rate is linear over four decades of the erasing beam intensity, deviating only as the erasing beam intensity approaches the reading beam intensity of $10^{-4}\text{W/cm}^2$ where erasure caused by the read beam was comparable to that caused by the uniform erasure beam. At a crystal
Log-log plots of the light-induced decay rate $\Gamma_{\text{light}}$ vs. the intensity of the erasing beam for crystal temperatures of 16, 24, and 40 °C. This data was taken at a crossing angle of $2\theta_{\text{air}} = 30^\circ$. The dark decay rate $\Gamma_{\text{dark}}$ has been subtracted. The $T = 16$ °C plot is linear over four orders of magnitude, from 0.01 W/cm$^2$ to 100 W/cm$^2$, and shows a power law dependence of $I^{0.62}$. 
FIGURE IV-2

ERASING INTENSITY (watts/cm$^2$)

DECAY RATE (sec$^{-1}$)

- $T = 40^\circ C$
- $T = 24^\circ C$
- $T = 16^\circ C$
temperature of 16 °C the slope of the plot is $x = 0.62$ [see Equation IV–1], so that the grating erasure rate is proportional to $I^{0.62}$.

Observations of the sublinear dependence of the photorefractive speed on the intensity have usually been attributed to saturation of the photoconductivity. The data shown in Figure IV–2 clearly cannot be interpreted as due saturation because saturation would not result in a straight line on the log-log plot. Similar sublinear dependence of the erase rate on intensity was observed in a crystal of BaTiO$_3$ studied by Feinberg [1980a] though the sublinear dependence was attributed to saturation of the photoconductivity in that paper. Recent studies on the same crystal of BaTiO$_3$ studied in Feinberg [1980a] have confirmed a sublinear intensity dependence with exponent $x \sim 0.8$ [T. Y. Chang, private communication]. Kratzig [1980] measured the photoconductivity directly in several different BaTiO$_3$ crystals and found the same sublinear dependence on intensity with exponents ranging from $x = 0.6$ to $x = 0.9$, depending on the sample.

The important distinction between the sublinear intensity dependence of the photorefractive speed reported in this thesis and the interpretations reported by Feinberg [1980a], Townsend [1970], and others is the clear sublinear power law shown in figure IV–2. Present models [Feinberg 1980a], [Kukhtarev 1979] of the photorefractive effect do not account for the nonlinear dependence of speed on optical intensity seen here. [Townsend 1970] observed similar nonlinear dependence of the grating writing rate on optical intensity over a much smaller range of intensities, but the model they proposed (with the result speed $\sim I^{1/2}$) has since proved inadequate to explain other aspects of the photorefractive effect.
The photoconductivity exponent $x$ in crystals of $\text{BaTiO}_3$ can be changed. The photoconductivity exponent $x$ increases as the crystal temperature increases as shown in Figure IV–2 and Table IV–1. The photoconductivity exponent $x$ in a crystal of $\text{BaTiO}_3$ can also be altered by heating the crystal in different partial pressures of oxygen. A crystal which was chemically reduced by heating it in low partial pressures of oxygen had a photorefractive speed which was linear in intensity ($x = 1$), as discussed in Chapter V.

The light-induced erasure rate a crystal of photorefractive SBN:60 shown in Figure IV–3 for comparison. The grating erasure rate, and therefore the photoconductivity, is linear in the intensity, in contrast to the sublinear behavior in $\text{BaTiO}_3$. Otherwise, the photorefractive properties of the two materials are similar.

We have shown that the measured speed of erasure of a photorefractive grating increases less than linearly with the optical intensity $I$. This explains the results of Lam [1981] who observed a 20 nanosecond response time with a $\text{BaTiO}_3$ crystal illuminated by a pulsed laser with an optical intensity of 23 MW/cm$^2$. This response time was an order of magnitude slower than predicted by a linear extrapolation of the low intensity erasure rate. However their data is consistent with the sublinear optical intensity dependence with $x = 0.8$. Subsequent measurements at low optical intensity on the same $\text{BaTiO}_3$ crystal have since confirmed this intensity dependence [T. Y. Chang, private communication]. We have shown here that the sublinear intensity response can also vary with temperature; the power law exponent $x$ increases with increasing temperature.
**TABLE IV–1**

The Photoconductivity Exponent in the CAT \( \text{BaTiO}_3 \) Crystal

<table>
<thead>
<tr>
<th>Temperature</th>
<th>12 °C</th>
<th>16 °C</th>
<th>24 °C</th>
<th>40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoconductivity Exponent ( x )</td>
<td>0.62±0.02</td>
<td>0.62±0.01</td>
<td>0.68±0.02</td>
<td>0.71±0.02</td>
</tr>
</tbody>
</table>
The Light-Induced Erase Rate in the SBN Crystal

Log-log plots of the light-induced decay rate $\Gamma_{\text{light}}$ vs. the intensity of an erasing beam for in the SBN:60 crystal. This data was taken at a crossing angle of $2\theta_{\text{air}} = 30^\circ$ and at 23°C. The dark decay rate $\Gamma_{\text{dark}}$ has been subtracted. The slope of the plot is 1; the photorefractive speed increases linearly with intensity.
Dark Erasure: Thermal Activation

There was a dramatic fifty-fold increase in the measured dark erasure rate as the temperature of the BaTiO$_3$ crystal was increased from 12 to 40 °C as shown in Figure IV–4. The same data are plotted in Figure IV–5 to show the activated behavior of the dark conductivity. The data in Figure IV–5 can be fit by parallel straight lines over the limited temperature range used, giving a temperature dependence of $\exp(-T_0/T)$. The three different lines on Figure IV–5 correspond to three different values for the crossing angle between the two writing beams. From the slope of the lines the value of $T_0 = 11,800 \pm 400$ °K or $k_BT_0 = 1.0$ eV. This data used writing beams at 514.5 nm. Similar data using writing beams at 476.5 nm yielded the same value for the parameter $T_0$. A previous measurement [Townsend 1970] of the dark erasure rate in a similar crystal of BaTiO$_3$ showed the same temperature dependence, but with $T_0 = 8000$ °K or $k_BT_0 = 0.68$ eV.

Spatial Frequency Dependence

The variation of the dark grating erasure rate with grating spatial frequency can be used to measure the approximate photorefractive inverse screening length $k_0$ in Equation II–7b. By determining $k_0$ the number density of charges can be obtained. From Equation II–4c, $k_0$ can be found from a plot of the dark erasure rate shown in Figure IV–6. The ratio of the intercept to the slope yields $k_0 = 1.4 \omega/c = 1.7 \times 10^5$ cm$^{-1}$. Taking the low frequency dielectric constant to be $\varepsilon = 135$ [Camlibel 1971], assuming singly charged carriers.
Figure IV–4 The Dark Erasure Rate in the CAT Crystal

Measured dark erase rate vs. temperature. Note the fiftyfold increase over a small (~30 °C) temperature range near room temperature. The three curves correspond to data taken at three different crossing angles of the writing beams.
FIGURE IV-4

Dark Decay Rate (sec⁻¹)

- □ 2θ = 60°
- • 2θ = 30°
- ▲ 2θ = 10°

Temperature (°C)

10 20 30 40

7

6

5

4

3

2

1

0
FIGURE IV–5 The Dark Erasure Rate in the CAT Crystal

Natural log of the dark decay rate vs. reciprocal absolute temperature. Three different crossing angles yield straight line plots with the same slope, indicating the \( \exp(-T_\circ/T) \) dependence of Eq. (1), with \( T_\circ = 11,800\pm400 \) °K. The solid lines are least squares fits to the data.
FIGURE IV-5

[Graph showing dark decay rate vs. 1/T (10^3 °K⁻¹) with different symbols for 2θ = 60°, 30°, and 10°]
FIGURE IV–6 The Dark Erasure Rate: Spatial Frequency Dependence

The straight-line fit yields the value of $k_0$ from Equation II–7b.
FIGURE IV-6
e = 1.6 \times 10^{-19} \text{ C} \text{ and } T = 24 \, ^\circ\text{C}, \text{ Equation II–4c gives the effective density of photorefractive charges } N_{pr} = 6 \times 10^{16} \text{ cm}^{-3}. \text{ This value differs significantly from the value } N_{pr} = 16 \times 10^{16} \text{ cm}^{-3} \text{ obtained from two-beam energy coupling measurements in Chapter III (see Table III–2). The data in Figure IV–6 deviates from a straight line, bending over in a manner consistent with a dependence on electron and hole dark hopping lengths which may or may not be the same as those determined from the light-induced coupling experiments. The disagreement between the values of } N_{pr} \text{ determined by coupling and dark erasure experiments is therefore not contradictory as the two experiments are measuring different quantities.}

In the limit \( k \rightarrow 0 \), the dark erasure rate \( \Gamma_{\text{dark}} \) approaches the dielectric relaxation rate \( \Gamma_{\text{dark}} = \sigma/\varepsilon_0 \) as was discussed in the beginning of this chapter. From the intercept of Figure IV–6 we find \( \Gamma_{\text{dark}} = 0.56 \text{ sec}^{-1} \) (as \( k \rightarrow 0 \)) and hence the dark conductivity is \( \sigma_{\text{dark}} = 10^{-11} \text{ (} \Omega \text{ cm)}^{-1} \). The dark conductivity was measured directly using an electrometer and current source to obtain \( \sigma_{\text{dark}} \approx 6 \times 10^{-12} \text{ (} \Omega \text{ cm)}^{-1} \), which is in reasonable agreement with the above results. An attempt to measure the dc photoconductivity proved unsuccessful due to a photo-induced voltage that interfered with the measurement.

**Conclusions**

The experimental results given this chapter can be used to modify equation II–7b to read:
\[ \Gamma = I_{00}(D^e + D^h)(1 + k^2/k_0^2)(I/I_{00})^x + \Gamma_{do}(1 + k^2/k_0^2)\exp(-T/T_0), \] (IV–2)

where the factor \( \exp(-T_0/T) \) has been added to the second (dark erasure) term to show the explicit temperature dependence determined experimentally. The light-induced erasure (first) term in Equation IV–2 shows the experimentally determined dependence of the rate on intensity, which also differs from the prediction (Equation II–7b) of the band conduction and hopping conduction models. Here \( T \) is the crystal temperature and \( I \) is the erasure intensity. The parameters \( I_{00}, T_0, \) and \( x \) are determined by experiment. Both \( D^e \) and \( D^h \) depend weakly on temperature and also on the grating spatial frequency \( k \) through Equation II–5. \( \Gamma_{do} \) also depends on \( k \) producing the deviation from the straight line fit in Figure IV–6.

The ubiquitous sublinear scaling of the photorefractive speed with intensity in BaTiO\(_3\) is clearly a most important characteristic to consider in designing photorefractive devices. One would like to operate photorefractive devices at speeds of a nanosecond or faster but the power required in the CAT crystal at room temperature would be about \( 2 \times 10^{15} \) W/cm\(^2\) ! (At 40 °C the power required would be "only" \( 10^{14} \) W/cm\(^2\), an improvement of a factor of 20.) As we will see in the next chapter, it will be possible to make a photorefractive BaTiO\(_3\) crystal with linear photoconductivity, and could achieve room temperature nanosecond operation with an optical intensity of \( 5 \times 10^8 \) W/cm\(^2\).
References: Chapter IV


The photorefractive properties of a material can be altered by changing its impurity and defect content, by doping crystals with iron or heat treating them to introduce oxygen vacancies, as was demonstrated with LiNbO$_3$ by Peterson [1971] and others. Once the relationships between the photorefractive properties and the impurity and defect content of a material are known, the photorefractive properties can be tailored to optimize the material for a particular application. For example, doping LiNbO$_3$ with iron impurities increases the spatial resolution and sensitivity of that material for optical image processing applications.

From the results of the oxidation and reduction experiments reported in this chapter and a careful consideration of experiments reported in the literature I propose that the model of the photorefractive trapping sites developed in Chapter II applies to photorefractive BaTiO$_3$ and I further propose that the donors in that model are Fe$^{2+}$–$V_0$ complexes and that the acceptors are Fe$^{3+}$ ions. The model described in Chapter II assumes the photorefractive material behaves as a compensated semiconductor with both donor and acceptor trapping sites whose densities change when the density of oxygen vacancies changes. The results of the oxidation and reduction experiments described in this chapter were first reported in Ducharme [1984b] and Ducharme [1986a], but the conclusions of these two papers are refined here because the results of related experiments reported by Klein [1986a] provide additional information on the role of iron impurities in the photorefractive properties of BaTiO$_3$. In this chapter I describe experiments in which the photorefractive properties of the crystal of BaTiO$_3$ were altered by
heat treating the crystal to change the density of oxygen vacancies. The changes in the photorefractive material properties of a crystal of BaTiO$_3$ were monitored, using the measurement and analysis techniques described in Chapter III and IV, as oxygen vacancies were first introduced into the crystal and then later removed. The effective density photorefractive charges and the relative contributions of electron and hole photoconduction to photorefraction changed in a manner consistent with the predictions of the model developed in Chapter II.

**Crystal Treatment**

The ROCKY BaTiO$_3$ crystal was grown from a top-seeded melt by Sanders Associates and, as-grown, it was almost inactive photorefractively. We treated the crystal at elevated temperatures in several different oxygen atmospheres to create or eliminate oxygen vacancies. The partial pressure of oxygen during treatment determined the effective density of photorefractive charge carriers. The relative contributions of electron and hole photoconduction were also altered by the treatments; hole photoconduction dominated at high oxygen partial pressures (low oxygen vacancy densities) and electron photoconduction dominated at low oxygen partial pressures (high oxygen vacancy densities).

The crystal was first characterized by two-beam energy coupling, grating erasure, and bulk absorption measurements, and then repeatedly treated and recharacterized. Each treatment consisted of placing the crystal in a one-inch diameter fused-quartz process tube inside a tube furnace (see Figure V–1) and heating at 650 °C for 36 hours in an atmosphere containing a specific partial pressure of O$_2$. The temperature inside the process tube...
FIGURE V–1

Treatment Oven

Diagram of the oven and quartz gas process tube used to treat the ROCKY BaTiO$_3$ crystal.
followed the heating and cooling sequence shown in Figure V–2 with an accuracy of 0.5% and a stability of 0.2%. During heating and cooling the temperature was changed at rates not exceeding 33°C per hour and near the tetragonal-to-cubic phase transition (at about 130°C) the rate was decreased to 4 °C per hour to prevent stress fractures. A total of three treatments were performed with the following flowing atmospheres (in chronological order): 1) $2 \times 10^{-6}$ atmosphere of O$_2$ in ultra high purity (99.999%) argon at atmospheric pressure, 2) ordinary air (0.2 atmosphere O$_2$, including Los Angeles smog), 3) 2.0 atmospheres of medical grade (99.99%) oxygen.

Figure V–3 shows the temperature of the tetragonal-to-cubic phase transition after each crystal treatment. The measured transition temperature decreased as the oxygen pressure during treatment decreased. This decrease in the transition temperature was caused by the oxygen vacancies introduced into the crystal as the treatment oxygen pressure was reduced. The reduction of the transition temperature due to the presence of impurities and oxygen vacancies was previously demonstrated in experiments with polycrystalline [Seuter 1974], flux grown [Ikegami 1964], and melt grown [Hageman 1980] BaTiO$_3$ single crystals. The actual oxygen-vacancy density is not known, but the number of vacancies increase monotonically as the treatment oxygen pressure is reduced [Hageman 1980].

Figure V–4a shows the absorption spectrum of the crystal (at 23 °C) as grown and after each oxygen treatment, as measured with a Beckman DK2A spectrophotometer. Two features stand out: First, a broad absorption plateau extends throughout the visible spectrum from about 800 nm (1.6 eV) to the band edge at about 410 nm (3 eV). Note that this absorption plateau is smaller in the crystal as-grown, and also after the crystal had been treated in
FIGURE V–2 Treatment Temperature Cycle

Oven temperature versus time for a typical BaTiO₃ treatment cycle. Flow of the oxygen-containing gas was started at the point marked "a" and stopped at "b". The tetragonal-to-cubic phase transition of the crystal occurs at $T_c \approx 130^\circ$C in BaTiO₃.
TREAT at 650°C for 36 hrs

FIGURE V-2
FIGURE V–3  Transition Temperature

tetragonal-to-cubic phase transition temperature $T_C$ of the BaTiO$_3$ crystal versus the oxygen partial pressure of the most recent treatment.
FIGURE V-3
a) The bulk optical absorption coefficient for the ROCKY BaTiO$_3$ crystal as grown and after each treatment.

b) The bulk optical absorption coefficient and light-induced photorefractive grating decay rate at 5145Å after the oxidation and reduction treatments.
FIGURE V-4A
absorption at 5145 Å (cm⁻¹) vs. treatment oxygen pressure

FIGURE V-4b
0.2 atmosphere of O₂. Second, the band edge at approximately 410 nm shifted to longer wavelengths as the treatment oxygen pressure was reduced, indicating that the band gap was decreased or "softened" by the presence of oxygen defects. This agrees with the result reported by Ikegami [1964] and it also agrees with the decrease in the transition temperature in Figure V–3.

The absorption at 5145Å, on the plateau, is plotted in Figure V–4b along with the light-induced grating decay rate measured at the same wavelength to show how these two properties change as the oxygen treatment pressure changes. Both the absorption and the light-induced decay rate are minimum near the 0.2 atmosphere oxygen pressure treatment.

An additional narrow absorption line was observed at 2870 nm (0.43 eV) on an otherwise featureless background. Its width was ~12 nm and its height was: 0.35 cm⁻¹ for the crystal as grown; 0.11 cm⁻¹ after treating in 2 × 10⁻⁶ atmospheres of oxygen; and 0.15 cm⁻¹ after treating in 2.0 atmospheres. This absorption line is probably the O–H⁻ stretch vibration frequency, modified slightly by the crystal lattice potential, characteristic of many oxygen-containing materials.

**The Effective Density of Photorefractive Charges**

The effective density of photorefractive charges was altered by the oxidation and reduction treatments. The two-beam energy coupling gain measured in the crystal as-grown and after each treatment shown in Figure V–5 was fit to Equation II–13c and the effective density of photorefractive charges Nₚᵣ determined from this data is plotted in figure V–6a. Changing the treatment oxygen pressure drastically altered Nₚᵣ: especially near the
Two-beam energy coupling gain coefficient $g$ vs. grating spatial frequency (in units of optical wavevector $n_0\omega/c$) for the ROCKY BaTiO$_3$ crystal after treatment with various oxygen partial pressures. The solid lines are least-squares fits according to Equation III–5 with parameters $k_0$, $\kappa_0$, $\kappa_h$, and $R(0)$ listed in Table III–1.
FIGURE V-6 The Effective Density of Photorefractive Charges

a) The effective density of photorefractive charge carriers $N_{pr}$ vs. the oxygen partial pressure of the most recent treatment. The effective oxygen pressure for the crystal as grown is unknown, but is assumed to lie in the region indicated by the error bars, as discussed in the text. The solid line is a qualitative guide based on Equation II–4d.

b) The same data as in a) but with the oxygen pressures converted to approximate values of the oxygen vacancy density from the data reported in Hageman [1980] and $N_{pr}$ given a plus or minus sign depending on whether the dominant photorefractive sites are donors or acceptors, respectively.
FIGURE V-6a
FIGURE V-6b
oxygen treatment pressure of 1/2 atmosphere where the density $N_{pr}$ has an apparent minimum. The value of $N_{pr}$ for the crystal "as grown" is included and we assign an effective treatment oxygen pressure between the 0.2 atmosphere and 2.0 atmosphere data points (in the range indicated by the error bars in Figure V–6a).

The observed minimum in $N_{pr}$ at about a half atmosphere treatment pressure is a natural consequence of the model of the photorefractive material as a compensated semiconductor with both donor and acceptor sites (see Figure II–2). In the model, $N_{pr}$ is proportional to the difference in the donor and acceptor densities $N_D$ and $N_A$ and when the crystal is compensated the donor and acceptor densities are equal ($N_D = N_A$). According to Equation II–4d, $N_{pr}$ vanishes when $N_D = N_A$ because the donor sites are completely empty and the acceptors are completely full; no redistribution of the charges is possible. Above the 1/2 atmosphere treatment pressure $N_A > N_D$ as in Figure II–2a; below 1/2 atmosphere $N_D > N_A$ as in Figure II–2b. As the oxygen pressure during treatment is decreased, the photorefractive site switches from acceptor to donor. Therefore, according to the model, the decreasing oxygen pressure during treatment is either increasing the density of donors $N_D$, or decreasing the the density of acceptors $N_A$, or both.

The switch of the dominant sites from acceptors to donors is more clearly illustrated in Figure V–6b where the measured values of $N_{pr}$ are given a positive (negative) sign when the dominant photorefractive sites are the
acceptors (donors). The approximate oxygen vacancy density for a given oxygen treatment pressure was taken from Hageman [1980] to construct this graph. The absolute number of oxygen vacancies in the crystal studied by Hageman is not necessarily the same as in the ROCKY crystal studied in this work because the oxygen vacancy density depends on the density of iron impurities in each crystal; but the relative number of oxygen vacancies in the two crystals will be the same at each oxygen treatment pressures. Note also that the density of oxygen vacancies changed by only 20% even though the oxygen pressure during treatment ranges over six decades.

The absorption plateaus in the visible part of the spectrum (Figure V-4a) are also smallest after treatment near 1/2 atmosphere treatment pressure (see Figure V-4b). The absorption data in Figure V-4b and values of $N_{pr}$ in Figure V-6a have similar shapes, indicating that this absorption at 5145 Å is associated primarily with $N_{pr}$. The total photoconductivity (proportional to the light-induced grating decay rate in Figure V-4b) also has a minimum near the 1/2 atmosphere treatment pressure, the same treatment pressure as the minimum in the effective density of photorefractive charges. This additional agreement supports the hypothesis that the photorefractive sites are compensated ($N_A = N_D$) at the 1/2 atmosphere treatment pressure. At the compensation point there are no electrons in the donor sites and no holes in the acceptor sites so that: 1) there can be no redistribution of charge ($N_{pr} = 0$), 2) there is no absorption due to photoionization of the electrons (holes) in the donors (acceptors), and 3) both the electron and hole photoconductivities from the donor and acceptor sites, respectively, are zero.
Electron and Hole Photoconduction

It was pointed out in Chapter II, especially in Figure II–1, that electrons and holes diffuse in the same directions in the presence of a gradient in the intensity, thus producing opposing contributions to the photorefractive space-charge electric field. The space-charge electric field is therefore reduced from the "one carrier" maximum by the factor R, the relative contribution of the electron and hole photoconductivities (Equation II–6b).

The electron and hole contributions to the photoconductivity ($\sigma_+$ and $\sigma_-$) were found to vary with the density of oxygen vacancies introduced into the BaTiO$_3$ crystal. Figure V–7a is a plot of the relative contribution R for the ROCKY crystal, determined from the data in Figure V–5, versus the oxygen partial pressure during treatment. Electron photoconduction dominated ($R < 0$) after treatment with $2 \times 10^{-6}$ atmosphere or 0.2 atmosphere of oxygen and hole photoconduction dominated ($R > 0$) after treatment in 2.0 atmospheres of oxygen. The same data is plotted in Figure V–7b which shows the ratio of the hole photoconductivity to the electron photoconductivity. As the treatment oxygen pressure increases, the ratio of photoconductivities also increases, but the separate photoconductivities both tend toward a minimum (figure V–7c) near an oxygen treatment pressure of 1/2 atmosphere.

There is a clear correlation among the measured properties shown in figures V–4, 6, and 7. Near the oxygen treatment pressure of a half an atmosphere: 1) the effective density of photorefractive charges $N_{pr}$ is minimum, 2) the optical absorption is minimum, 3) the electron and hole photoconductivities ($\sigma_+$ and $\sigma_-$) are both minimum, and 4) the relative contribution of the electron and hole photoconductivities R switches sign from
FIGURE V–7  Relative Contributions of Electron and Hole Photoconduction

a) The relative contribution $R$ of hole and electron photoconduction versus oxygen pressure during treatment. The effective oxygen pressure for the crystal as grown is unknown but is assumed to lie in the region indicated by the error bars, as discussed in the text. Note that $R$ passes through zero at about 1/2 atmosphere of $O_2$. The solid line is a qualitative guide.

b) The ratio of hole to electron photoconductivities vs. treatment oxygen pressure calculated from the data in a).

c) The electron and hole photoconductivities at an intensity of 1 W/cm$^2$ from light-induced erasure data and the data in a).
\[ R = \frac{\sigma^+ - \sigma^-}{\sigma^+ + \sigma^-} \]

**FIGURE V-7a**

- Treatment oxygen pressure (atm)
- 'electrons'
- 'holes'

![Graph showing the relationship between treatment oxygen pressure and the ratio of \( \sigma^+ \) to \( \sigma^- \)]
FIGURE V–7b
FIGURE V-7c
hole-dominated to electron-dominated photoconduction. The correlation of all of these properties is a clear and direct consequence of the assignment of two separate types of photorefractive sites, donors and acceptors, in Chapter II (see Figure II–2). I will now summarize the connection between the four properties listed above and the predictions of the model of photorefractive BaTiO3 as a compensated semiconductor where the density of donors increases as the oxygen treatment pressure decreases.

1) The effective density of photorefractive charges \( N_{\text{pr}} \) (see Equation II–4d) decreases to zero from both sides of the compensation point, \( N_D = N_A \), as shown in Figure V–6a. Above the compensation point the acceptors are more numerous (Figure II–2a) and they are the partially filled photorefractive trapping sites among which the electrons and holes are redistributed. At the compensation point the donors are completely empty and the acceptors full and no redistribution of charge is possible; there is no photorefractive effect. Below the compensation point the donors are more numerous (Figure II–2b) and they are the partially filled photorefractive trapping sites.

2) The absorption due to the photoionization of the electrons or holes will be minimum at the compensation point because there are no electrons (holes) in the donor (acceptor) sites to be photoionized. Above (below) the compensation point the absorption due primarily to photoionization of the holes (electrons) appears. Some of the remaining photoconductivity at the compensation point is possibly due to the relatively weaker photoionization of holes (electrons) from the donor (acceptor) sites.
3) The electron and hole photoconductivities $\sigma_+$ and $\sigma_-$ are separately minimum at the compensation point, also because there are no electrons (holes) in the donor (acceptor) sites to be photoionized and produce photoconductivity. The remaining photoconductivity at the compensation point is possibly due to the relatively weaker photoionization of holes (electrons) from the donor (acceptor) sites.

4) The relative contribution of the electron and hole photoconductivities $R$ switches sign at the compensation point. Above the compensation point the photorefractive sites are the acceptors and thus holes are more readily photoionized than the electrons. Below the compensation point the photorefractive sites are the donors and electrons are more readily photoionized.

The model for the photorefractive trapping sites proposed in Chapter II is based on the results discussed so far in this chapter. The main deviation from the interpretation of similar oxidation and reduction experiments in LiNbO$_3$ [Peterson 1971, Phillips 1974, and Orlowski 1978] is the result that the dominant photorefractive trapping site actually changes when the treatment pressure is reduced. If indeed LiNbO$_3$ behaves the same way as BaTiO$_3$ does at the compensation point, Peterson [1971] and Phillips [1974] did not have the benefit of theoretical details of the behavior of the effective density of photorefractive charges or the relative contribution of the electron and hole photoconductivities with which to interpret their oxidation and reduction experiments. The first careful measurements of the relative contribution of the electron and hole photoconductivities by Orlowski [1978] should have helped but, again, there was no corroborating data on the
effective density of photorefractive charges or the absorption and photoconductivities and the possible switch of the photorefractive site at compensation went undetected.

**The Photorefractive Sites in BaTiO$_3$**

I now propose that the photorefractive charge acceptors are iron impurities Fe$^{3+}$ each entering substitutionally for Ti$^{4+}$ and that the photorefractive charge donors are complexes consisting of iron impurities with associated oxygen vacancies, denoted Fe$^{2+}$–$V_0$. The model is essential to understand how the presence of oxygen vacancies alters photorefractive properties BaTiO$_3$ and differs in two fundamental ways from the one proposed for LiNbO$_3$ by Peterson [1971] and Phillips [1974] and a similar model proposed for BaTiO$_3$ by Klein [1986]. The first difference is the identity of the donors as the complex Fe$^{2+}$–$V_0$. I propose that the oxygen vacancies are not merely providing charge compensation; they actually combine with iron impurities during high temperature treatment to produce a new species, the electron donor complex Fe$^{2+}$–$V_0$. The second difference is that either the donor or the acceptor levels can act as the photorefractive sites, depending on which is greater in number. In this section I describe the defect and impurity content of melt-grown single crystals to provide a basis for the proposed assignment of the donors and acceptors to the Fe$^{2+}$–$V_0$ complexes and the Fe$^{3+}$ ions, respectively.

The relative advantages of BaTiO$_3$ over LiNbO$_3$ in many potential applications led to a desire to identify the photorefractive trapping sites in BaTiO$_3$, as the sites were identified in LiNbO$_3$ in order to find out how to
improve the photorefractive properties, especially the speed, of BaTiO₃. Klein [1984 and 1986] set out to do just this by measuring photorefractive and other properties in several different crystals of BaTiO₃. The properties that were measured on these crystals included: the effective density of photorefractive charges, the optical absorption, the density of iron impurity atoms and, by electron spin resonance studies, the densities of the different valance states of the iron. The effective density of photorefractive charges showed a clear correlation with the iron impurity density. The additional evidence provided by the data reported in this chapter allow me to make the statements in the previous paragraph about the identity of the photorefractive sites.

In general, the donors and acceptors shown in Figure 11–2 can result from any type of impurity or crystal defect. There are two significant types of intrinsic defects which have been observed in melt-grown BaTiO₃ crystals. The first type is the neutral barium vacancy which occurs with densities of approximately 10¹⁷ cm⁻³ and has a thermal ionization energy for hole creation of 0.85 eV [Seuter 1974]. The second common defect is an oxygen vacancy. Oxygen vacancies in melt-grown crystals occur with densities approximately equal to the density of the iron impurities [Hageman 1980] which is also about 10¹⁷ cm⁻³. The actual oxygen vacancy density depends on how the boule is cooled during and after growth [Seuter 1974, Hageman 1980]. Since the oxygen atom exists as O²⁻ in the unit cell, the oxygen vacancies V₁⁻ left behind are double donors; they can give up both of the electrons left behind by the (now neutral) oxygen atom. There is strong evidence that the oxygen vacancies are always doubly ionized, denoted by V₁, at room temperature and would not be donors [Hageman 1980, Lewis 1986]. But if all the oxygen vacancies were ionized, one would expect the crystal to exhibit a significant dark conductivity. This is true in highly reduced crystals, but in mildly reduced
iron-doped crystals the oxygen vacancies can enter only in combination with
the iron impurities and thus give up one or both of the weakly bound electrons
to the iron impurities instead of to the conduction band. Hageman [1980]
observed that each oxygen vacancies entering the crystal changed the
valence (charge state) of the iron impurities by exactly $-2$ for the two electrons
the oxygen vacancy can donate. Berglund [1967b] observed absorption
peaks at 0.6 eV and 0.2 eV in highly reduced crystals and concluded that
these energies are the ionization energies of the two electrons on the $V_0^{2-}$. In
mildly reduced crystals the oxygen vacancy densities and the density of $Fe^{3+}$
obeys the charge conservation relations

$$2[V_0] = [Fe^{3+}] + 2[Fe^{2+}],$$
$$[Fe]_{\text{total}} = [Fe^{2+}] + [Fe^{3+}] + [Fe^{4+}],$$
$$[V_0]_{\text{total}} = [V_0].$$

density of oxygen vacancies is equal the iron impurity density. The
implication is that the oxygen vacancies can pair with iron impurities, creating
an impurity–defect complex. Whether an oxygen vacancy binds in the same
unit cell as an iron impurity is not clear from the results of Hageman [1980] but
the measured changes in the photorefractive donor and acceptor
concentrations, combined with the donor complex interpretation allow us to
infer that the photorefractive charge acceptors are iron impurities $Fe^{3+}$ and
the photorefractive charge donors are lone iron impurities with associated
oxygen vacancies ($Fe^{2+}$–$V_0$). In photorefractive LiNbO$_3$, though, the
photorefractive trapping sites are thought to be iron atoms only [Peterson 1971, Phillips 1974] and the oxygen is assumed inert.

Experiments performed on melt-grown iron-doped BaTiO$_3$ crystals [Ormancy 1983] may be used to improve our understanding of the nature of the donor and acceptor levels. The iron doped crystals exhibited broad optical absorption peaks at 2.1 eV and 2.6 eV due, possibly, to the Fe$^{3+}$ acceptor and the Fe$^{2+}$–V$_0$ donor respectively. It is possible that the oxygen vacancies were introduced into the crystal by applying a large electric field at room temperature.

The barium vacancies could also be the photorefractive acceptors because they occur in comparable numbers to the iron impurity and oxygen vacancy densities. Klein [1986] provided convincing evidence that the Fe$^{3+}$ density scaled with the effective density of photorefractive charges but this was a consequence of the changing oxygen vacancy density and does not guarantee that the Fe$^{3+}$ ions are the photorefractive acceptors. One way of determining whether the acceptors are barium vacancies or Fe$^{3+}$ ions would be to perform oxidation and reduction experiments using lower partial pressures of oxygen (10$^{-10}$ to 10$^{-6}$ atmosphere). The predictions of the two alternatives are shown in Figure V–8. The reduction treatment would increase the density of oxygen vacancies. If the acceptors are barium vacancies, only the donor density is changed and the effective density of photorefractive charges, determined directly from photorefractive measurements, would saturate to a constant value equal to the (constant) density of barium vacancies. If the acceptors are Fe$^{3+}$ ions, then the oxygen vacancies will combine with all the Fe$^{3+}$ ions and convert them to the Fe$^{2+}$–V$_0$ donor complex resulting in a complete depletion of the acceptor.
The density of photorefractive charge carriers $N_{pr}$ vs. the density of oxygen vacancies for the two assignments of donor and acceptor levels described in the text.
level density. In general we can expect that there may be some contribution from both the barium vacancies and the Fe\(^{3+}\) and, assuming they are not too far apart in energy, the acceptor density will be the sum of these two densities and Figure II–2 would still be appropriate. If the barium vacancy and the Fe\(^{3+}\) ion energy levels are far enough apart in energy, the correct model of the photorefractive sites should include two separate acceptor levels (i.e. in Figure II–2).

The O–H\(^{-}\) detected by the 2870 nm stretch-mode absorption could also be a trapping site which contributes to the photorefractive effect but the O–H\(^{-}\) density changes in a manner opposite to the measured photorefractive properties of the crystal. The O–H\(^{-}\) density is highest when the effective density of photorefractive charges is lowest and lowest when the effective density of photorefractive charges is highest.

**Other Changes in the Photorefractive Properties**

The oxidation and reduction treatments of the ROCKY BaTiO\(_3\) crystal caused a marked variation in the dependence of photorefractive speed on optical intensity. Figure V–9 is a plot of the light-induced erasure rate versus the erasing intensity for the electron-dominated and hole-dominated cases. Electron photoconduction dominated after the crystal was treated in \(2 \times 10^{-6}\) atmosphere of oxygen, and the speed increased linearly with optical intensity (speed \(\alpha I^1\)). After the crystal was treated at the higher oxygen pressures the speed increased sublinearly with optical intensity (speed \(\alpha I^x\)) whether electron or hole photoconduction dominated. The value of the exponent was \(x = 0.76\) after treatment at 0.2 atmosphere of oxygen (electrons), and \(x = 0.67\)
FIGURE V–9 Light-Induced Erasure Rate in the ROCKY Crystal

The log of the photorefractive grating erasure rate vs. the log of the light intensity, for various oxygen partial pressures during treatment: 2 atmospheres (open squares); 0.2 atmosphere (closed squares); 2 × 10^{-6} atmosphere (closed circles). The crystal temperature was held at T = 24 °C for these experiments, and the grating wavevector was k = 0.2(\eta_0\omega/c).
oxygen pressure during treatment

- □ 2.0 atm
- ■ 0.2 atm
- • $10^{-6}$ atm

**Figure V-9**

DECAY RATE $\Gamma$ (sec$^{-1}$)

ERASING INTENSITY, $I$ (W/cm$^2$)
after treatment with 2.0 atmospheres of oxygen (holes). This sublinear intensity dependence of the erasure rate in the present BaTiO$_3$ crystal and in two crystals previously studied [Ducharme 1984a, Lam 1981] has not yet been explained. (Both the band-conduction model and the hopping model predict a erasure rate that increases linearly with intensity.)

The fact that a BaTiO$_3$ sample reduced in $2 \times 10^{-6}$ atmosphere of oxygen responds linearly with optical intensity is of practical importance, for it implies that high-speed operation of a photorefractive device using this sample could be achieved with lower optical intensity than with oxidized samples, where the speed increases sublinearly with optical intensity. Figure V–9 shows that for the highly reduced sample, which has a linear photoconductivity, a constant erasure energy of 1J/cm$^2$ is required for a $1/e$ fold grating erasure, independent of intensity. This can be extrapolated to 1 nanosecond operation at an optical intensity of 1 gigawatt per cm$^2$. Sublinear extrapolation for the heavily oxidized BaTiO$_3$ sample (2.0 atmosphere treatment) predicts that an optical intensity 1000 times larger would be needed to obtain the same speed, but this high intensity would surely cause optical damage to the crystal.

The light-induced erasure rate showed a weak temperature dependence for both hole-dominated photoconduction (Figure V–10a) and electron-dominated photoconduction (Figure V–10b). Figure V–10 shows the measured light-induced and dark ($l_{\text{erase}}=0$) grating erasure rates in the ROCKY crystal as the temperature was varied over a 33 °C range near room temperature. The data shown in Figure V–10a was obtained after the crystal had been treated in 0.2 atmospheres of oxygen, which made electron
FIGURE V–10 Erasure Rate: Temperature Dependence

a) The logarithm of the grating erasure rate of the reduced BaTiO$_3$ crystal (oxygen pressure during treatment = 0.2 atmosphere; electron-dominated photoconduction) vs. inverse temperature of the crystal, for various light intensities: $I_{\text{erase}} = 1.35$ W/cm$^2$ (open triangles); $I_{\text{erase}} = 0.23$ W/cm$^2$ (open squares); $I_{\text{erase}} = 0.024$ W/cm$^2$ (open circles); dark erasure (closed circles).

b) The log of the light-induced grating erasure rate (the dark decay rate has been subtracted) of the heavily oxidized BaTiO$_3$ crystal ($O_2$ treatment pressure = 2.0 atmosphere, hole-dominated photoconduction) vs. inverse temperature of the crystal, for various light intensities: $I_{\text{erase}} = 0.23$ W/cm$^2$ (closed triangles); $I_{\text{erase}} = 0.023$ W/cm$^2$ (closed squares). The dark decay rate is also shown (open circles).
FIGURE V-10A

DEACY RATE $\Gamma$ (sec$^{-1}$)

Erasing Intensity
- $0.23$ W/cm$^2$
- $0.023$ W/cm$^2$
- Dark

2 atm (holes)

$10^1$ $10^0$ $10^{-1}$ $10^{-2}$

$3.1$ $3.2$ $3.3$ $3.4$ $3.5$ $3.6$

$1/T$ ($10^{-3}$ K$^{-1}$)
Figure V-10b

Decay rate $\Gamma$ (sec$^{-1}$)

- 0.2 atm (electrons)
- Erasing intensity
  - △ 1.35 W/cm$^2$
  - □ 0.23 W/cm$^2$
  - ○ 0.024 W/cm$^2$
  - ● Dark

$1/T$ (10$^{-3}$ K$^{-1}$)
transport dominant. Figure V–10b was obtained after the crystal had been treated in 2.0 atmospheres of oxygen, which made hole transport dominant.

The slope of the dark erasure rate data of Figure V–10b yields an "activation" energy of $T_0 = 11,400 \, ^\circ K = 1.0 \, eV$ for dark erasure. This dark erasure activation energy is the same as that measured in the CAT crystal of BaTiO$_3$ studied by Ducharme [1984a], and is possibly to be the thermal ionization enthalpy of the photorefractive acceptors. A summary of the dark erasure rates at $T=24 \, ^\circ C$ (after each treatment) is: $0.12 \, \text{sec}^{-1}$ ($2 \times 10^{-6}$ atmosphere); $\sim 3 \times 10^{-6} \, \text{sec}^{-1}$ (0.2 atmosphere); $\sim 1 \, \text{sec}^{-1}$ (as grown); $0.31 \, \text{sec}^{-1}$ (2.0 atmospheres).

Figure V–11 shows the dependence of the dark erasure rate on grating spatial frequency at $T=24 \, ^\circ C$ for the Rocky crystal after it had been treated in 2.0 atmospheres of oxygen. The spatial frequency dependence of the dark and light-induced erasure in Figure V–11 and V–12 followed the nonparabolic form of Equation II–7b when using the expressions in Equation II–5b for $D^e$ and $D^h$. The influence of the electron and hole hopping lengths is to reduce the overall speed at higher grating spatial frequencies. The values of the inverse electron and hole hopping lengths, $\kappa_e$ and $\kappa_h$, determined from two-beam energy coupling measurements in Chapter III are listed in Table III–2.

The response time of photorefractive materials is essentially the dielectric relaxation time $\varepsilon \varepsilon_0 / \sigma$ where $\sigma$ is the photoconductivity. The low mobilities ($\sim 0.001$ to $0.1 \, \text{cm}^2/\text{V-sec}$) of the carriers in BaTiO$_3$ are the primary
FIGURE V–11  Dark Erasure Rate: Spatial Frequency Dependence

Plot of the dark decay rate vs. spatial frequency squared \((k^2)\) of the refractive index grating at a crystal temperature of 24 °C in the ROCKY BaTiO\(_3\) crystal.
Figure V-11

\[ \text{DARK DECAY RATE (sec}^{-1} \text{)} \]

vs.

\[ \text{SPATIAL FREQUENCY } \left( \frac{k}{\left( \frac{n_0 \omega}{c} \right)} \right) = 2 \sin \theta \]
Light-Induced Erasure: Spatial Frequency Dependence

Plot of the light-induced decay rate vs. spatial frequency squared ($k^2$) of the refractive index grating at a crystal temperature of 24 °C in the ROCKY BaTiO$_3$ crystal.
reason for the small photoconductivity, hence long dielectric relaxation time. The adjustable material parameters are the donor and acceptor densities and the ratio of the photoionization rate to the recombination rate. One can change the densities by doping or, in an existing crystal, by chemical reduction [Ducharme 1986a]. The ratio of the photoionization rate to the recombination rate can be changed only by changing the identity of the donors and acceptors from iron, as found in the nominally pure "as grown" BaTiO₃ crystals [Klein 1986], to something like cerium [Hathcock 1985].

**Doping** BaTiO₃ crystals with iron or another impurity (such as cerium [Hathcock 1985]) holds much promise in improving the photorefractive speed and strength. Again there are useful limits; with heavier doping the optical absorption becomes too large and the crystal has a large dark conductivity, making it hard to pole [Marvin Klein, private communication] and operate with applied electric fields. The main improvement provided BaTiO₃-based photorefractive devices by heavier doping should be a linear increase in speed and strength while the absorption increases exponentially with dopant density. A more promising improvement may come from a different dopant which exhibits a higher "hopping" quantum efficiency, or fraction of charges moved per absorbed photon. This new "high efficiency" photorefractive material would benefit from increased speed and strength at moderate absorption and dark conductivity.

**Conclusions**

The oxidation and reduction treatments described in this chapter support the hypothesis that the photorefractive donors in nominally pure melt-grown crystals of BaTiO₃ are iron impurities each with a nearby oxygen
vacancy. The acceptors are probably lone iron impurities although the possibility that the acceptors are barium vacancies, or both barium vacancies and iron impurities, is also consistent with the data. The oxidation and reduction treatments altered the oxygen vacancy density as indicated by the measured changes in the optical band edge and the tetragonal-to-cubic phase transition temperature. The evidence presented to support the assignment of the donor and acceptor photorefractive trapping sites combines the measurements of the effective density of photorefractive charges, the relative contributions of the electron and hole photoconductivities, the optical absorption, and the photorefractive speed. The behavior of all of these quantities near the compensation point at approximately one half atmosphere oxygen treatment pressure is consistent with the assignment. That the primary effect of the oxygen vacancies is to combine with an existing iron impurity, thus converting it from a donor to an acceptor, was established by Hageman [1980]. Finally, the direct evidence [Klein 1986] that the effective number photorefractive charges, which varied predictably with oxygen vacancy density in our experiments, scaled with the density of iron impurities established that the donors include iron atoms.

Both the speed of the photorefractive effect (and its sublinear scaling with intensity) and the strength may be improved some by reducing existing BaTiO$_3$ crystals. This is probably a worth-while technique only for "inactive" as grown crystals, like the ROCKY crystal in this work, which are unfortunate enough to be near the compensation point $N_D = N_A$ because both the speed and the strength of the photorefractive effect are significantly reduced near the compensation point (see figures V-6a and V-7a). The observed linear photoconductivity in the ROCKY crystal (Figure V-9) after the reduction treatment is the most significant such improvement observed in these studies.
and would allow operation of BaTiO$_3$-based photorefractive devices at high speed with moderately powered lasers.
References: Chapter V


VI ELECTROOPTIC AND PIEZOELECTRIC EXPERIMENTS

The linear electrooptic, or Pockels, effect is the term for the change in the optical susceptibility, or index of refraction, of a dielectric material when the change is linearly proportional to an applied electric field. Many different materials exhibit the linear electrooptic effect, the only requirement being that the material lacks inversion symmetry, but in this chapter I will only be concerned with the linear electrooptic effect in ferroelectric materials. Ferroelectric materials have a net electrical polarization to the unit cell even in the absence of an applied electric field. Most ferroelectric materials have a relatively large linear electrooptic response compared to most other electrooptic materials.

The Need for New Measurements

Because of their large linear electrooptic responses the ferroelectric materials barium titanate (BaTiO$_3$), strontium barium niobate (Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ or SBN), and lithium niobate (LiNbO$_3$) are potentially useful as photorefractive volume holographic materials (for examples see Chapter 11 of Fisher [1983] and references therein). The strength of the photorefractive effect is proportional to the linear electrooptic (Pockels) coefficients of the material. Accurate values of these coefficients are needed for quantitative device design and for interpretation of photorefractive measurements (for example two recent quantitative studies of the photorefractive material properties of BaTiO$_3$ [Ducharme 1986a and Klein 1986]). Previously reported measurements of the electrooptic coefficients in BaTiO$_3$ were made on flux-grown (Remieka Method) crystals [Kaminov 1965, 1966, Johnston 1965a,
Here we report measurements of the low frequency "unclamped" electrooptic coefficients $r_{13}$ and $r_{33}$ at $\lambda = 5145\text{Å}$ in three melt-grown $\text{BaTiO}_3$ single crystals, in a $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ single crystal, and in a $\text{LiNbO}_3$ single crystal. The measured coefficients were independent of the magnitude (in the range 0.1 to 200 V/cm) and of the frequency (in the range $10^1$ to $10^5$ Hz) of the applied electric field. The measured coefficients were also independent of the optical intensity and of the location of the probing optical beam along the crystal c-axis; therefore, space charge effects were not evident. The combined electrooptic coefficient $r_C \equiv r_{33} - (n_1/n_3)^3 r_{13}$ was measured independently in $\text{BaTiO}_3$ and agreed with the value calculated from the independently measured values of $r_{13}$ and $r_{33}$. Previously reported measurements of $r_{13} = 14\times10^{-12}$ m/V in the same crystals were in error as they did not take into account piezoelectric contributions to the phase change of a beam passing through the electrooptic crystal [Ducharme 1985, 1986a].

We have measured the piezoelectric coefficient $d_{13}$ and present the correct electrooptic coefficients in $\text{BaTiO}_3$, SBN, and $\text{LiNbO}_3$.

We have also measured the photorefractive two beam energy coupling gain and the grating diffraction efficiencies in several crystals of $\text{BaTiO}_3$ and find that the ratio of photorefractive gains for different optical polarizations $g_3/g_1 = 3.5\pm.3$ agrees with the gain predicted from electrooptic measurements;
\( n_3^3 r_{33}/n_1^3 r_{13} = 3.4 \pm 0.2 \). The theoretical relation \( g_3/g_1 = n_3^3 r_{33}/n_1^3 r_{13} \) is insensitive to the details of photorefractive transport theory. There is also good quantitative agreement between the values of \( g_1 \) and \( g_3 \) found from both coupling and diffraction efficiency measurements and the theoretical prediction from the photorefractive effect. The electooptic and two beam coupling experiments were also performed on a crystal of \( \text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6 \) with the result that \( g_3/g_1 = 5.8 \pm 1 \) and \( n_3^3 r_{33}/n_1^3 r_{13} = 4.0 \pm 2 \). In the crystal of \( \text{LiNbO}_3 \) it was found that \( g_3/g_1 = 2.1 \pm 0.3 \) and \( n_3^3 r_{33}/n_1^3 r_{13} = 2.5 \pm 2 \).

We consider and eliminate the following possible sources of systematic error in the measured coefficients: 1) space charge and electrode effects in the electooptic measurements; 2) alignment of the optical and low frequency electric fields to the crystal axes (e.g. contributions from the much larger coefficient \( r_{42} \approx 1000 \times 10^{-12} \text{ m/V } \)); 3) dependence on the specific model of charge transport in the photorefractive effect (in the photorefractive gain measurements); 4) possible incomplete poling of the crystals.

The crystals studied were grown in a top seeded melt (Chrochalski Method), cut, polished, and mechanically poled (to eliminate 90° domains) by Sanders Associates. We have electrically poled the crystals of \( \text{BaTiO}_3 \) (to eliminate 180° domains) ourselves using a technique described in Appendix A. The dimensions (\( L \times W \times H \) in Figure VI-1) of the crystals are listed in Table II-1. The crystal faces were at right angles to within \( \pm 1° \) and the c-axis oriented along the "L" dimension within \( \pm 1° \). The crystal faces were slightly
Crystal geometry and coordinate system used in the electrooptic measurements. The $x$–$y$–$x$ (or 1-2-3) axes are along the $H$–$W$–$L$ dimensions with the probing optical beam propagating along the $x$ axis. A voltage is applied along the crystal $z$-axis.
convex, producing a mildly astigmatic lensing with focal lengths of 2 to 10 meters along the x axis. The crystals were without visible flaw and had a faint olive-brown color.

**Electrooptic and Piezoelectric Measurements**

The Pockels coefficients can be determined as follows. An electric field $E$ applied across the crystal will alter the index ellipsoid by the electrooptic effect [Yariv 1975]. The change in the refractive index $\Delta n_i$ for a beam polarized along the $i^{th}$ crystal axis is:

$$\Delta n_i = - \frac{1}{2} \sum_{j=1}^{3} r_{ij} E_j$$  

Note however, that the same applied field can, by the piezoelectric effect, cause a change in the length $\Delta H_k$ of the crystal along the k direction [Nye 1967]:

$$\Delta H_k = \sum_{j=1}^{3} d_{kj} E_j$$  

If an electric field $E$ is applied to the material, there will be a distortion of the crystal by the piezoelectric effect [Nye 1967], and of the refractive index ellipsoid by the electrooptic effect [Yariv 1975]. $\text{BaTiO}_3$ is tetragonal between 5°C and 130°C and has 4mm symmetry. Letting the spatial coordinates x-y-z be numbered 1-2-3, with the c-axis along the z (or 3) direction, the nonzero
electrooptic coefficients are $r_{13} = r_{23}$, $r_{33}$, and $r_{42} = r_{51}$ and corresponding piezoelectric coefficients $d_{13} = d_{23}$, $d_{33}$, and $d_{42} = d_{51}$. The crystal is birefringent with $n_3 = 2.426$ and $n_1 = n_2 = 2.480$ at room temperature and at a vacuum wavelength $\lambda = 5145 \text{ Å}$ [Camlibel 1970]. In all the experiments described in this chapter the applied electric and space charge fields were along the c-axis, or axis of spontaneous polarization, which was along the z direction. Optical beams were propagated along the x direction and polarized along the y direction for ordinary rays or along the z direction for extraordinary rays (see Figure VI–1).

The electrooptic coefficients were determined by applying an AC electric field along the crystal's c-axis and interferometrically measuring the resulting phase change impressed on an optical beam passing through the crystal. An argon-ion laser operating in a single longitudinal and transverse mode supplied the optical beams to the homemade Mach-Zehnder interferometer [Shirane 1970] shown in Figure VI–2a. The laser, crystal, and all optical elements were mounted on a mechanically isolated optical table and enclosed with a large box to minimize turbulence and external acoustic noise sources. The reference beam passed through a Babinet-Soliel compensator, with its axes aligned parallel to the crystal axes, used here to adjust the path length of the interferometer's reference arm without altering the polarization of the reference beam. The signal beam propagated through the crystal along the x axis and was polarized along the y or z axes. The beams recombined at the second beam splitter and the output was incident on a photodetector. Since the crystals produced some lensing of the beam, a 1 meter focal length lens was placed in the reference arm of the
FIGURE VI–2 Electrooptic Modulators

(a) The Mach-Zehnder interferometer used to measure the electrooptic coefficients \( r_{13} \) and \( r_{33} \) (upper inset) and the piezoelectric coefficient \( d_{13} \) (lower inset). The crystal is placed in one arm and a Babinet-Soleil Compensator in the other (reference) arm. The crystal c-axis and the compensator slow axis are aligned in the plane of the figure. The beams in both arms are polarized either perpendicular (parallel) to the plane to have ordinary (extraordinary) polarizations in the crystal. The output polarizer was aligned parallel to the input polarizers.

(b) The polarization compensation method used to measure \( r_C \). The polarization of the beam is at 45° to the crystal c-axis at input. The Babinet-Soleil Compensator, with its slow axis parallel to the crystal c-axis, is used to adjust the polarization of the beam incident on the crossed output analyzer.
interferometer and only the intensity at the center of the resulting pattern of concentric ellipses was measured by the detector. The optical intensities of the sample and reference beams were approximately equal at the detector and the contrast of the fringes checked by adjusting the compensator.

A DC voltage (0 to 100 V/cm) plus a small AC voltage (0.1 to 200 V/cm) at frequencies ranging from 10 Hz to 100 kHz were applied to the silver-paint electrodes on the c-axis faces of the crystal (Figure VI–1). The applied voltage caused refractive index of the crystal to change and therefore caused the phase of the beam passing through the crystal to change. The modulation of the intensity at the interferometer output due to the AC applied voltage was monitored by the optical detector (Figure VI–2a) and lock-in amplifier. The Babinet-Soliel compensator was adjusted to set the relative optical path lengths of the two interferometer arms to make the intensity at the center of the interference pattern at the interferometer output halfway between a minimum and a maximum, so that the interferometer was operated at its most sensitive point. This bias point was monitored during each 10-second experiment to insure that the interferometer phases did not drift due to drifts in the positions or orientations of the optical elements.

The voltage source was a Hewlett-Packard Model 3314A programmable function generator terminated at its output with 50 Ω (see Figure VI–3). The output of the function generator was a DC bias voltage plus a small, low frequency, sinusoidal voltage with peak-to-peak amplitude V. The function generator was connected to the crystal via a coaxial cable (type RG-58-U). In all the measurements described below, the magnitude and phase of the applied field measured using separate contacts on the silver
Block schematic of the electronic equipment used in the measurement of the electrooptic coefficients. The function generator output is applied to the silver paste crystal electrodes through a coaxial cable of total length 2 meters. The DC and AC components of the optical signal were displayed on the oscilloscope and the AC signal measured by a lock-in amplifier.
paint electrodes was the same as at the function generator output. The intensities of the optical beams in figures 2a & 2b were measured with either a photomultiplier or with a photodiode. The output of the PMT was terminated with 10kΩ to 50kΩ and connected to the oscilloscope and the lock-in amplifier. The output of the photodiode was amplified by either an NRC Model 820 meter unit or a UDT model 101C transimpedance amplifier. The AC component of the interferometer signal was measured with a high-impedance averaging meter: either a Tektronix model 468 digital oscilloscope (1 MΩ averaging ~1000 periods of the AC signal) or a lock-in amplifier (Stanford Research model 510 with an input impedance of 100 MΩ, and with time constants ~10 sec). The frequency response of all of the above detection configurations was checked carefully in all measurement situations, particularly with respect to the linearity of the small AC signal imposed on the DC average intensity (see Equation VI–4). The calibrations of the function generator and the lock-in amplifier were checked against the TEK 468 scope. Since all measurements of the electrooptic coefficients involve the ratio of the AC signal to the function generator output only relative calibration was necessary. The frequency response and linearity of the function generator, cables, detector, and lock-in amplifier were all carefully checked.

The optical wavefront at the output of the interferometer, whose intensity is measured by the detector, is the coherent sum of the wavefronts in the two arms. The phase φ of the optical wavefront in the interferometer arm containing the crystal (the upper inset of Figure VI–3) changes due to the combined refractive index (electrooptic) and length (piezoelectric) changes
induced in the crystal by an applied electric field. The phase change of the optical wavefront in the crystal arm of the interferometer due to an applied AC electric field $E_3 = V/L$ for a beam polarized along the $i^{th}$ axis is:

$$\Delta \phi_i = (2\pi/\lambda)\Delta(n_iH)$$

$$= (2\pi/\lambda)(\Delta n_iH + n_i\Delta H) = (2\pi n_iH/\lambda)(-n_i^2 r_{i3}/2 + d_{i3})E_3 , \quad (VI-3)$$

where $H$ is the length of the crystal along the 1-direction traversed by the optical beam, $i = 2$ for ordinary rays and $i = 3$ for extraordinary rays, and $\lambda$ is the vacuum wavelength. A small phase change $\Delta \phi$ in one arm of the interferometer will cause an intensity change $\Delta I$ at the output of the interferometer:

$$I = I_1 + I_2 + 2\sqrt{(I_1/I_2)} \cos(\phi_0 + \Delta \phi) = I_1 + I_2 - 2(I_1/I_2)^{1/2} \Delta \phi \quad (VI-4)$$

when $\phi_0 = \pi/2$, the maximum sensitivity point of the interferometer. The compensator was adjusted so that the average output intensity was $I_1 + I_2$ thus assuring that $\phi_0 = \pi/2$.

To determine the electrooptic coefficients, a separate measurement of the piezoelectric coefficient $d_{13}$ was made. The technique was similar to that for the electrooptic measurement except that the signal beam was reflected off of the outside of the crystal instead of passing through it as shown in the
lower inset in Figure VI–2a. Then the signal in the detector is given by Equation VI–4 with $\Delta \phi = 2\pi d_{13}(V/L\lambda)$.

Light propagating along the x axis and polarized at an angle of 45° with respect to both the y and z axes will experience linear birefringence $\delta n = 0.07$ at 5145Å and room temperature. A voltage applied along the z axis will induce an additional birefringence $\Delta(\delta n) = -[(n_3^3 r_{33} - n_1^3 r_{13})/2]V/L$. A Babinet-Soliel compensator was placed in the beam following the crystal (Figure VI–2b) to compensate for the change in polarization due to the linear birefringence $\delta n$. The transmitted intensity through the crossed polarizers is given by Equation VI–4 with $\Delta \phi = (2\pi H/\lambda)[d_{13}(n_3 - n_1) - (n_3^3 r_{33} - n_1^3 r_{13})]V/L$ when the phase $\phi_0 = \pi/2$.

Table VI–I shows the results of the low frequency electrooptic and piezoelectric measurements in the various crystals. The measurements reported in Table I reflect the following experimental conditions: 1) frequency 1000 Hz; 2) AC voltage 10V peak-to-peak; 3) DC voltage 0V; 4) detector, the PMT; 5) electrical signal measured with the the lock-in amplifier with a 10 second time constant: 6) temperature $T \equiv 23 \degree C$. In addition the numerous tests described in the next paragraph were made on three of the crystals (the CAT, SWISS, and the SBN:60 crystals) to determine the effect of surface layer, space-charge, and photorefractive effects on the measured values of the electrooptic coefficients.
### TABLE VI-1: ELECTROOPTIC COEFFICIENTS

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<th>Crystal</th>
<th>$r_{13}$</th>
<th>$r_{33}$</th>
<th>$r_c = r_{33} - (n_1/n_3)^3 r_{13}$</th>
<th>$n_3^3 r_{33}$</th>
<th>$g_3/g_1$</th>
<th>$d_{13}$</th>
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<td>measured</td>
<td>computed</td>
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<td>SWISS</td>
<td>32±2</td>
<td>118±8</td>
<td>87±5</td>
<td>84±10</td>
<td>3.5±3</td>
<td>3.6±2</td>
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<td>CAT</td>
<td>34±1</td>
<td>126±6</td>
<td>------</td>
<td>89±7</td>
<td>3.4±2</td>
<td>3.3±2</td>
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<tr>
<td>DOYLE</td>
<td>-----------</td>
<td>------</td>
<td>----------------------------------</td>
<td></td>
<td>3.5±2</td>
<td>------</td>
</tr>
<tr>
<td>FREE</td>
<td>-----------</td>
<td>------</td>
<td>----------------------------------</td>
<td></td>
<td>3.4±5</td>
<td>------</td>
</tr>
<tr>
<td>ROCKY</td>
<td>32±2</td>
<td>110±10</td>
<td>------</td>
<td>76±8</td>
<td>3.2±2</td>
<td>2.8±5</td>
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<td>SBN:60</td>
<td>55±3</td>
<td>224±7</td>
<td>-----------</td>
<td>4.0±2</td>
<td>5.8±1</td>
<td>47.3±4</td>
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<td>28.5±1</td>
<td>10.1±3</td>
<td>------</td>
<td>17.4±1.3</td>
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* Takizawa [1982] at $\lambda = 6398\text{Å}$

**TITLE:** Electrooptic measurements in photorefractive crystals at 5145Å, 1000 Hz, 23 °C (except as noted).
Space charge limited conduction occurs at frequencies below the dielectric relaxation rate which is < 10 Hz in our BaTiO₃ crystals at the optical intensities used. We looked for possible space-charge effects on the measured electrooptic coefficients \( r_{13} \) and \( r_{33} \) in five ways: 1) The frequency change in the detected signal. 2) The magnitude of the detected interferometer signal was linear in the applied AC field which was varied from 0.1 to 100 V/cm; Figure VI–4 shows the interferometer signal vs the applied AC field. 3) The signal was independent of the position and size of the probe beam within the crystal. 4) The signal was independent of the intensity of the probe beam and independent of the intensity of uniform illumination of the crystal by a beam incoherent with the probe; 5) The signal was independent of the presence of of a photorefractive grating created simultaneously within the crystal by two beams coherent with each other but incoherent with the measuring probe beam. Any space-charge effects due to charge injection at the electrodes would have shown up in tests 1) – 4) above. Test 5) was also designed to check for possible electrostrictive effects caused by the presence of the large (~1000 V/cm) photorefractive fields present during photorefractive experiments.

Comparison With Photorefractive Measurements

We also used photorefractive measurements to check the consistency of the measured electrooptic coefficients. Two-beam energy coupling experiments were performed with an argon-ion laser operating at 514.5 nm on a single longitudinal TEM\(_{00}\) mode. Two coherent Gaussian beams with intensities \( I_1 \sim 10^{-3} \) W/cm\(^2\) and \( I_2 \sim 10^{-1} \) W/cm\(^2\) and diameters of 3mm were
The interferometer signal vs. the amplitude of the applied AC field in the electrooptic measurements in the SWISS crystal.
aligned so that the direction of the grating wavevector \( k \) was parallel to the c-axis of the BaTiO\(_3\) crystal. The half crossing angle in air was \( \theta = 5^\circ \) in these experiments.

The increase in the transmitted intensity of the weak beam \( I_1 \) due to the presence of the strong beam \( I_2 \) was measured. Only the peak value of \( I_1 \) was recorded as the signal fluctuated in time during the experiment due to shifts in the optical paths of the two beams. Such shifts usually tend to reduce the magnitude of the coupling. The small-signal gain coefficient \( g \) was determined from Equation 11-14a for each of the two polarizations. The measured values of \( g \) were independent of the ratio of the beam intensities.

In separate experiments, the diffraction efficiency of a grating was measured directly, with particular attention to the ratio of diffraction efficiencies for different polarizations. Figure VI–5b shows the diffraction of beam 1 incident on the grating at the Bragg angle. The ratio of the diffracted intensity to the transmitted intensity yields the diffraction efficiency:

\[
\eta = \frac{I_1}{I_2} = \left[ \tan(2Rm\gamma L\sin\theta) \right]^2 = (2Rm\gamma L\sin\theta)^2
\]

(VI–9)

Here \( m = 2\sqrt{(I_1/I_2)/(1+ I_1/I_2)} \) is the modulation of the beams used to write the grating. The grating was written as in Figure VI–4a with beam 2 polarized along either the z or the y axes and beam 1 polarized at 45° to the z axis. Beam 2 was blocked when \( I_1 \) (which was too weak to erase the grating on its
In the two-beam energy coupling experiments a) a strong beam, with optical wavevector \( \mathbf{k}_1 \), and a weak probe beam, with optical wavevector \( \mathbf{k}_2 \), crossed at an angle \( \theta \) (measured in air) and were oriented so that the interference grating, with wavevector \( \mathbf{k}_g \), was oriented parallel to the entrance face. Both beams were polarized perpendicular (parallel) to the plane to have ordinary (extraordinary) polarizations in the crystal. In the diffraction efficiency experiments b) the photorefractive grating was first written as in Figure VI–4a. During writing, the weak beam 1 was polarized at 45° to the crystal c-axis and the strong beam 2 polarized either parallel or perpendicular to the c-axis. The diffraction efficiency of the grating was measured in the absence of beam 2.
FIGURE VI-5a

\[ \vec{k} = \vec{k}_1 - \vec{k}_2 \]

grating planes
FIGURE VI–5b
own) was maximum, as in the coupling experiments, and the diffraction efficiencies of the o and e components measured by rotating the output polarizer parallel to the y and z axes, respectively. There are several nice features of this method for measuring the diffraction efficiencies: 1) Polarizing beam 1 at 45° allowed the diffraction efficiencies of both o and e rays to be measured simultaneously 2) from the same index grating without changing the alignment of the beams. Both the o and e ray components of beam 1 are automatically Bragg-matched to the grating independent of the polarization of beam 2 during writing. 3) The ratio of diffraction efficiencies \( \eta_3/\eta_1 \) is independent of the actual value of the grating modulation \( m \), which may differ from \( m = 2\sqrt{(I_1/I_2)/(1+ I_1/I_2)} \) due to the fluctuation effects mentioned above (Though the photorefractive gain coefficients determined in the simultaneous coupling and the diffraction efficiency measurements in the DOYLE crystal agreed with each other). 4) Repeating the experiment with beam 2 in both polarizations checked for possible bending of the grating planes during writing as reported by Odulov.

**Conclusions**

We have measured the low frequency ("unclamped") electrooptic and piezoelectric coefficients in barium titanate crystals using interferometric techniques. The electrooptic and piezoelectric measurements were linear in the magnitude of the applied voltage in the range 0.1 to 200 V/cm, and independent of its frequency in the range 10 Hz to 100 kHz. Therefore these crystals were behaving like ideal electrooptic insulators, with no measurable space-charge effects (which are important below the dielectric relaxation rate
~ 10 Hz) or piezoelectric resonances (which are important above 250 MHz). The average unclamped electrooptic coefficients of two poled, melt-grown, BaTiO₃ single crystals were $r_{13} = 33\pm 2 \text{ pm/V}$ and $r_{33} = 120\pm 7 \text{ pm/V}$ measured at a wavelength of 5145Å and at T=23°C. The combined Pockels coefficient $r_{cd} = 84\pm 5 \text{ pm/V}$ was measured independently and is in good agreement with the value $r_{cd} = r_{33} - (n_1/n_3)^3 r_{13} = 84\pm 5 \text{ pm/V}$ computed from the above values of $r_{13}$ and $r_{33}$, where $n_1$ and $n_3$ are the ordinary and extraordinary indices of refraction, respectively. The piezoelectric coefficient $d_{13} = 57\pm 4 \text{ pm/V}$ was determined from the same two crystals, and the contribution of the piezoelectric effect to the Pockels measurements is discussed. We also measured the photorefractive coupling of two optical beams in the crystals, and we show that the dependence of the coupling strength on beam polarization predicted by photorefractive theory agrees with the measured values of the Pockels coefficients.
References: Chapter VI


Appendix A: Ferroelectric principles

BaTiO₃ is a tetragonal ferroelectric (symmetry 4mm or C₄ᵥ depending on the notation system used) between approximately ~6 °C and ~130 °C, and cubic above 130 °C. The structure of the cubic unit cell is shown in Figure A-1a. The barium Ba²⁺ ions form the corners of the cube, the three oxygen O²⁻ ions are located on the cube faces in a tetrahedral structure, and the titanium Ti⁴⁺ ion resides at cell center. In the tetragonal phase, the unit cell distorts into a stretched cube by increasing the length of one edge and decreasing the lengths of the other two edges. The Ti⁴⁺ ion is shifted from the body center of the tetragonal unit cell (Figure A-1b); therefore, the tetragonal unit cell has a net polarization which manifests itself in numerous phenomena such as the linear electrooptic (Pockels), piezoelectric and pyroelectric effects. A thorough discussion of the interrelationships of these phenomena and their dependence on the crystal symmetry is found in Nye [1957]. (Note that these phenomena are not restricted to materials with a tetragonal unit cell but also occur in other materials such as InP, GaAs, BSO, and BGO which have cubic zincblende unit cells and are electrooptic and photorefractive but have no net polarization of the unit cell.

The ordering of the spontaneous polarization is analogous to ferromagnetic ordering; hence the term "ferroelectric." The ferroelectric crystal can form independent regions, or domains, each with its own local orientation of the spontaneous polarization. The domains can be oriented in six equivalent directions corresponding to the crystal axes. In Figure A-2a the domains are all aligned and the crystal is poled. If surface and bulk defects are ignored, this structure is the only stable one. There are two types of domain walls, which are the boundaries between neighboring domains,
FIGURE A–1 The BaTiO$_3$ Unit Cell

Schematic of the BaTiO$_3$ unit cell in the a) cubic phase (above $\sim$130 °C) and b) tetragonal phase ($\sim$6 °C to $\sim$130 °C). The tetragonal unit cell is about 1% longer along the c-axis. The Ti$^{4+}$ ion is shown displaced toward one end of the unit cell.
a. cubic

b. tetragonal

Figure A-1
Domain types in a ferroelectric. The individual arrows represent the orientation of the c-axis of the unit cell in a small region (domain) of the crystal. In a) all the unit cells are aligned along the same axis; the crystal is "poled". In b) 180° domain walls form the boundaries between domains of opposite c-axis orientation. The 180° domain walls are only 1 unit cell thick and are themselves invisible. In c) a 90° domain wall forms at the boundary between domains oriented 90° to each other. The 90° domain walls are typically 1000 unit cells thick due to the large strain energy of the mismatched unit cell dimensions. The 90° domain walls are visible as reflective plains oriented 45° to the crystal axes.
a. poled

b 180° domains  
c 90° domains

FIGURE A–2
as shown in Figures A–2a and b. The 180° domain walls forming the boundaries between domains of opposite polarization are shown in Figure A–2b. The 180° domain walls are thin, only one unit cell thick, so the local polarization direction changes abruptly across the walls and they are generally invisible. The 180° domain walls have a small creation energy of electrostatic origin proportional to the polarization of the unit cell: the energy per unit area of a 180° domain wall is $LP_s^2/\varepsilon_0 = 0.02 \text{ J/m}^2 = 0.02 \text{ eV/unit cell}$ with $L = 4 \text{ Å}, P_s = 0.25 \text{ C/m}^2$. The 180° domain walls are only one unit cell thick because thicker domain walls would have a prohibitively large strain energy. The 90° domain walls shown in Figure A–2c are the boundaries between domains whose polarizations are oriented 90° with respect to each other. The ~1% mismatch of the unit cell dimensions for the neighboring domains cause significant strain in the 90° domain wall, whose thickness is determined by the balance between strain and polarization energies. The 90° domain wall thickness at room temperature is of the order of several thousand unit cells and is readily visible to the naked eye as a reflective plane oriented at a diagonal in the crystal. In single crystals both 180° and 90° domain walls are metastable, forming planes which extend the full width of the crystal. Figure A–3 depicts the domain structures of a typical crystal.

The dielectric constant of BaTiO$_3$ shown in Figure A–4 shows the Curie-Law behavior of the dielectric constant in the cubic phase leading to the ferroelectric phase below about 130 °C. There is also a large anisotropy in the dielectric constant due to the spontaneous polarization.

Stoichiometric BaTiO$_3$ single crystals have been grown successfully by three different methods, as described by Rosenberger [1979]: potassium flux growth, top seeded melt growth, and floating zone growth. Here we only
FIGURE A–3  Domain Structures

Diagram of a ferroelectric crystal showing the typical shapes of domains surrounded by 90° and 180° domain walls. The 180° domains are tubes of arbitrary cross-section which extend the entire length of the crystal. The 90° domains are bounded by diagonal planes which intersect the crystal surfaces. Figure Courtesy of Marvin Klein, Hughes Research Laboratories, Malibu, California.

FIGURE A–4  Dielectric Constants of BaTiO₃

Temperature dependence of the low frequency (1 kHz) dielectric constants in single-domain BaTiO₃. From Camlibel [1970].
discuss the basic method and details pertinent to photorefractive applications of the crystals. The earliest and easiest method used to grow BaTiO$_3$ single crystals is the potassium flux, or Remeika, method. BaO and TiO$_2$ dissolve in equal concentrations in a liquid KF "flux", and cubic "butterflies" grow as the solution is cooled below 833 °C. This method has the advantage of low growth temperatures and it automatically yields stoichiometric crystals. However, the crystals which solidify at the bottom of the crucible are thin (<1 mm) "butterflies", or butterfly-shaped wafers, and contain high concentrations (a few %) of impurities, particularly iron, which dissolve readily in the KF flux. The high iron concentrations give the flux grown crystals a strong yellow-brown color and have undesirably large optical absorption and dark conductivity. A comparison of the impurity content of flux and melt-grown crystals is found in Godefroy [1977].

Top seeded melt growth, often called the Czochralski method, is the only method now producing large optical quality single crystals [Linz 1965, Belrus 1971]. In melt growth, a small seed crystal of cubic BaTiO$_3$ held at the top of a solution of BaO and TiO$_2$ (with a ~14% excess of TiO$_2$) is slowly pulled and rotated to allow the liquid to condense onto the seed. The temperature, pull rate, and rotation rate must be carefully controlled to insure uniform, large single crystals. The crystals, now available commercially from Sanders Associates of Nashua, New Hampshire, are typically (5 mm)$^3$ and are free from visible defects, having a faint olive-brown color (absorption ~0.5 cm$^{-1}$) and are highly insulating (>10$^{11}$ Ω cm).

To my knowledge, there was only one boule of BaTiO$_3$ grown by a flame fusion method (a variant of the floating zone technique used to grow
and refine single crystal silicon) and little is known about this boule [Tien 1972].

Table III-1 lists the dimensions of the crystals studied in this work. The BaTiO$_3$ crystals were melt-grown, cut parallel to the crystal axes, pressure polled, and polished by Sanders Associates. The SBN:60 crystal was melt-grown, cut parallel to the crystal axis and poled by Ratnakar Neurgaonkar of Rockwell International Science Center, Thousand Oaks, California. The LiNbO$_3$ crystal was melt-grown, cut parallel to the crystal axis and poled by Crystal Technology.
References


APPENDIX B: Poling of BaTiO$_3$ single crystals

When a BaTiO$_3$ single crystal cools through the cubic-to-tetragonal phase transition temperature multiple domains form, each with a different orientation of the axis of spontaneous polarization with either 180° or 90° domain walls separating them. A crystal cut parallel to the crystal axes can be electrically poled. The poling procedure consists of heating the crystal to ~1 °C above the tetragonal-to-cubic phase transition temperature (~130 °C), applying a DC electric field of ~250 V/cm, and slowly cooling the crystal to room temperature with the field applied. When the crystal cools through the cubic-to-tetragonal transition the ferroelectric domains align parallel to the applied electric field. The 90° domain walls, because of their dependence on strain energy, can usually be eliminated at room temperature by squeezing the crystal along two of the lattice directions thus forcing the domains to align along the third axis – now the c-axis. After mechanical poling the crystal will be free from the visible 90° domain walls and will exhibit uniaxial birefringence, though there may be little or no measurable electrooptic effect due to the presence of 180° domain walls which must be eliminated by electrical poling.

The 180° and 90° domains can be eliminated and the crystal made single domain by electrical poling. Here we describe our procedure for poling BaTiO$_3$ crystals cut parallel to the crystal axes.

The direction of the c-axis must first be found. This can be done by a simple visual technique. First, an incandescent or other broad band light source is used to illuminate two polarizers which are oriented with their transmission axes mutually perpendicular (crossed). The crystal is placed
between the crossed polarizers with one crystal axis oriented along the path of the illumination and slowly rotated about this axis. If the crystal appears dark when its axes are aligned with the transmission axes of the polarizers and transparent otherwise, the c-axis is oriented perpendicular to the path of the illumination. The crystal is birefringent for light propagating perpendicular to the c-axis but not polarized along either crystal axis: therefore the crystal will appear transparent because it alters the polarization of the light as it passes through.

If the crystal appears consistently multicolored as it is rotated then the c-axis is oriented along the direction of illumination. There should, ideally, be no transmission through the polarizers when the c-axis is oriented along the direction of illumination because the crystal is not birefringent for light propagating along the c-axis. But, in general, because the crystal surfaces are not flat and the white light not perfectly collimated, the light propagating along the c-axis will experience a small birefringence and the crossed polarizers will produce perfect extinction only for certain colors along each path through the crystal; the crystal appears multicolored when viewed through crossed polarizers.

Poling Apparatus

The crystal is placed between two chrome-plated brass electrodes and held with light spring pressure in a spectroscopic cuvette (1×2×4 cm), as shown in Figure B–1. The cuvette is filled with DOW Corning 200 silicon fluid to provide a temperature bath and to prevent electrical arcing in the cell. The purpose of the spring is to hold the crystal securely, but it should not be too strong or the pressure might produce domains oriented 90° to the c-axis.
Diagram of the crystal electrodes and cuvette (1×2×4 cm³) for holding the crystal during poling. The spring is made just strong enough to hold the crystal securely. The electrodes are made of chrome-plated brass.
The cell is suspended in a larger bath of mineral oil (~1 liter) placed on a hot plate as in Figure B–2. The hot plate power is controlled by a variable transformer. The temperature is measured with a thermometer immersed in the silicon fluid and the hot plate power adjusted to adjust the temperature. There is a relatively large thermal mass in the system to prevent rapid changes in the temperature. In addition an enclosure of clear plexiglass surrounds the apparatus to eliminate drafts. The thermal and electrical characteristics of the system are thoroughly tested before installing a crystal; there is little room for error.

**Heating the Crystal**

The assembly is heated *slowly* to minimize thermal stresses which can crack the crystal. The rate of heating or cooling should not exceed 20 °C per hour for temperatures up to 100 °C, 5 °C per hour for 100 to 120 °C, and 2 °C per hour above 120 °C.

The transition temperature of the crystal ranges from $T = 120 \, ^\circ C$ to $T = 130 \, ^\circ C$ depending on the impurity [Godefroy 1981], and defect [Ducharme 1986a] densities. Therefore the approach of the tetragonal to cubic transition is monitored by two methods. In the first, the capacitance of the crystal, which is proportional to the dielectric constant, is monitored with a capacitance bridge. The room temperature dielectric constant along the c-axis is about 135 [Camlibel 1970] and increases to about 7800 at the transition (Figure A–4). Figure B–3 shows the crystal capacitance during a typical poling procedure.

The crystal capacitance should triple between 80 °C and 120 °C. If not there is a layer of silicon oil between the electrodes and the crystal thus
Diagram of the heat bath. A large thermal mass is used to minimize temperature fluctuations.
The crystal capacitance along the c-axis of a typical BaTiO$_3$ crystal before poling. There were no 90° domain walls observed in the crystal before poling. The phase transition is at ~128 °C. The voltage applied at 123 °C squeezed excess oil from between the chrome electrodes and the crystal. Before squeezing, the measured capacitance was limited to that of the oil layers at the electrodes.
limiting the maximum capacitance of the system to that of the oil layers, approximately 10 pf in our system. The oil layers can be "squeezed" out by applying \(-500\) Volts to the electrodes. If the squeezing was successful the capacitance should increase dramatically and continue to rise as the temperature increases. This is demonstrated in Figure B–3 where the squeezing voltage was applied at \(123^\circ\)C.

The second method of anticipating the transition consists of monitoring the visual appearance of the crystal between crossed polarizers as it is heated. Some \(90^\circ\) domain walls may appear when the crystal temperature is several degrees below the actual transition temperature and striking colors suddenly appear at the transition temperature as the crystal abruptly changes from its birefringent tetragonal to its isotropic cubic phase. The colors appear because the crystal is no longer birefringent in the cubic phase. Often many diagonal stripes will appear at temperatures just below the transition temperature, possibly forming a tight, fabric-like weave. The \(90^\circ\) domain walls are forming and changing due to fluctuations near the transition. When domain walls are present, the transition is marked by a distinct and thorough clearing of these domain walls, usually beginning from one side of the crystal and sweeping slowly across the crystal.

Poling the Crystal

After the transition to the cubic phase has occurred, a DC electric field of \(~250\) Volts/mm is applied gradually (over a few minutes). The applied field induces a phase transition back into the ferroelectric phase with the domains aligned along the positive c-axis. The crystal is cooled starting with a rate of \(2^\circ\)C per hour. Though \(90^\circ\) domain walls often appear when the field is applied, they usually disappear as the crystal is cooled. (We have often
observed domain walls to remain visible until the crystal has cooled to 115 °C.) The applied electric field is removed when the crystal is at room temperature. If the crystal retains 90° (diagonal) domain walls after cooling below 100 °C, the procedure is repeated with a higher poling field. Domain walls may also appear if the crystal squeezed or handled roughly, even at room temperature.

Small cracks, probably nucleated by surface defects and scratches, often develop in the positive electrode face during poling. They should not be polished or cut off after poling as this procedure will cause the formation of domain walls and thus depole the crystal. The small cracks on the positive electrode face can be minimized and often eliminated by keeping the poling field small and minimizing the time spent near or above the phase transition. We have successfully poled crystals by applying the DC electric field while the crystal is still tetragonal (0.5 to 2 °C below the transition temperature) and cooling without allowing the phase transition to take place. This alternate technique may inhibit the formation of the cracks on the positive face, though we find no difference in the crystals we have poled.

It is also possible to pole the crystal by heating it only to 115 or 120 °C [Marvin Klein, private communication]. The main advantage to poling well below the transition temperature is that it may minimize the small surface cracks which frequently appear on the positive electrode face of the crystal. The main disadvantage is the increased likelihood that the crystal won't pole completely and the entire procedure would have to be repeated.

We have also poled crystals with electrodes made of silver paint applied to the c-faces of the crystal. Our success at poling and the number and size of the small cracks which develop on the positive electrode face is
about the same as with the chrome-plated electrodes. But silver atoms diffuse into the positive electrode face quite readily, even at room temperature, when a voltage is applied to the silver paint electrodes [Branwood 1962].

Occasionally a melt-grown single crystal of BaTiO₃ will be poled without resorting to the above procedure. But this situation is rare so I recommend that crystals be purchased poled. The savings in purchasing an unpoled crystal is offset by the time (several days) required for a "beginner" who needs to build and test his own equipment and pole the crystal. We have not poled any individual crystal more than three times, but we believe that each poling procedure slightly and irreversibly damages the positive electrode face of the crystal. The procedure outlined in this chapter is relatively straightforward and probably unnecessarily strict. We have found some variations of the poling conditions to have no noticeable effect, but the high cost of errors kept us from exploring the actual limits of heating rate, poling field, poling temperature, electrode material, etc.
References: Appendix B


References


