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Research Project for Undergraduates: Ionic Thermoconductivity in Dielectrics

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Research projects for undergraduates should satisfy several conditions with regards to the physical insight, experimental manipulation, data analyses, and time for the experimental run that are required of the students. These conditions are satisfied by the study of dipole relaxations in dielectric materials using the method of ionic thermocurrents (ITC). ITC can be used to determine the concentration, activation energy, and relaxation time of dipoles in a dielectric. The necessary equipment and some possible research projects are discussed.

An essential component of the science education of undergraduate students is participation in research. However, it is difficult to find projects that are an exploration of the unknown rather than simply rediscovering some known results. This difficulty is compounded by the conditions that must be met by undergraduate research, such as:

(1) The physical models used to describe the phenomena under study must be clearly understood by the students.

(2) The manipulative skills of the students has not been well developed by laboraory experience. Experimental apparatus that is inexpensive and durable is very desirable.

(3) The analyses of the experimental data should be straightforward and within the mathematical training of the undergraduate student.

(4) The time needed for experimental runs should be geared to the time blocks likely to be available to undergaduates, not over 4 h for a single experimental run.

These conditions for undergraduate research are satisfied by the study of dipole relaxation in dielectric material using the method of ionic thermo-currents (ITC) first suggested by Bucci and Fieschi in 1964.[1]

The method of ITC is as follows:

(a) The dielectric under study is placed in a dc electric field to align the dipoles in the sample, usually at room temperature.

(b) With the electric field still on, the sample is cooled to a low temperature where the dipoles remain in alignment with the electric field.

(c) The electric field is removed, and the sample is warmed at a constant rate.

(d) The electric current (ITC) is measured as function of temperature. The current is the depolarization current which appears as the dipoles relax and become randomly oriented.

(e) From the measurements of the ITC as a function of temperature one can determine the concentration, activation energy of rotation, and characteristic relaxation time of the dipoles involved in the relaxation phenomenon.

There are many dielectrics that are well suited for ITC studies of temperature dependent dipole relaxations. Although most ITC research[2-6] has been applied to alkali halide crystals, the ITC method has also been successfully used with alcohols,[7] ice crystals,[8] and complex organic molecules.[9]

THEORY

The essential theoretical considerations are illustrated in the model of an ideal dielectric containing noninteracting dipoles.[10] These dipoles are assumed to have dipole moments, p, and temperature dependent relaxation times, τ, where τ is given by

$$\tau(T) = \tau_0 \exp(W/kT), \qquad (1)$$

where τ_0 is the characteristic relaxation time, W is the activation energy of rotation, k is the Boltzmann constant, and T is the absolute temperature. In the absence of an externally applied electric field these dipoles are randomly oriented. When an electric field is applied to the dielectric at temperature T_1, the dipoles will be aligned with the field direction and the sample will be polarized if the field is on for a time t_1 much longer than the relaxation time $\tau(T_1)$. As the dielectric is cooled

with the field on, the relaxation time of the dipoles increases rapidly. At some low temperature T_0 the external field is removed and the sample is connected to a sensitive current detector. After the field is removed the atomic and electronic depolarization current decays exponentially, but the dipoles remain aligned. When the sample is heated the dipole relaxation time becomes shorter and the dipoles begin to lose their preferred orientation. This depolarization current is measured as a function of the sample temperature.

Phenomenologically the depolarization current may be derived as follows:

$i(T) \propto$ (average polarization per dipole) (number of participating dipoles) (rate of dipole relaxation).

The first term is obtained from the classical Debye theory[10]:

$$P = p^2 E / 3kT, \qquad (2)$$

where P is the average polarization, p is the dipole moment of an individual dipole, and E is the electric field. The second term represents the number of centers at temperature T contributing to the current and is obtained from the solution of a typical relaxation equation,

$$dN/dt = -N/\tau(T), \qquad (3)$$

where N is the number of dipoles per unit volume. Therefore,

$$N = N_p \exp\left(-\int_{t_0}^{t} \frac{dt'}{\tau(T)}\right), \qquad (4)$$

where N_P is the initial number of aligned dipoles. Then,

$$N = N_P \exp\left[-\int_{T_0}^{T} (b\tau_0)^{-1} \exp\left(\frac{-W}{kT'}\right) dT'\right], \qquad (5)$$

where b is the heating rate (dT/dt). The rate of dipole relaxation is given by the inverse of the relaxation time, $\tau(T)$. Therefore, the depolarization current as a function of temperature can be

written as:

$$i(T) = \frac{Np^2E}{3kT_1\tau_0} \exp\left(\frac{-W}{kT}\right)$$

$$\times \exp\left[-(b\tau_0)^{-1} \int_{T_0}^{T} \exp\left(\frac{-W}{kT'}\right) dT'\right]. \quad (6)$$

The important features of this function $i(T)$ have been summarized as follows[3]:

(1) $i(T)$ is represented by an asymmetric band (see Fig. 1) with a maximum at a temperature T_m which is independent of T_1 and E is given by

$$T_m^2 = bW\tau(T_m)/k. \quad (7)$$

(2) The low temperature tail of this band is represented by the equation

$$\ln i(T) = \text{const} - W/kT. \quad (8)$$

(3) The area under the ITC band is proportional to the initial dipole moment per unit volume for $t_1 \gg \tau(T_1)$:

$$\int_{T_0}^{T_1} i(T) dT = P_0 A = \frac{Np^2E}{3kT}, \quad (9)$$

where A is the area of the sample and P_0 is the polarization at T_0. The activation energy W may be obtained from Eq. (8) and τ_0 from Eq. (7). The determination of the number of dipoles is made from Eq. (9), and this can be studied as a function of polarization conditions. Another feature of Eq. (6) is that the activation energy can be determined by using the whole ITC curve. Such a result may be derived from noticing that the time rate of change of the polarization, or $P(T)/\tau(T)$, is equal to the current density, $J(T)$. However, the polarization that is left in the sample at any temperature T will manifest itself in the electric current that is measured as the sample is warmed, so

$$P(T)A = \int_{T}^{T_f} J(T')A dT' = \int_{t(T)}^{\infty} i(t') dt'. \quad (10)$$

This equation is then combined with the expression for the rate of change of $P(T)$,
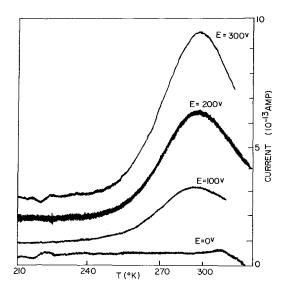
$$P(T)A/\tau(T) = J(T)A \quad (11)$$

FIG. 1. Typical ITC curves. These data were obtained by Mellema, senior physics major at GAC, on a 2 mm thick sample of electrolytically colored CsI using a heating rate of 6°C/min and a voltage E across the sample.

so that

$$\tau(T) = \tau_0 \exp\left(\frac{W}{kT}\right) = \int_{t(T)}^{\infty} i(t') dt' \Big/ i(T), \quad (12)$$

and the following equation results:

$$\ln \tau(T) = \ln \tau_0 + \frac{W}{kT}$$

$$= \left(\int_{i(T)}^{\infty} i(T') dT'\right) - \ln[i(T)]. \quad (13)$$

The integral in Eq. (13) can be replaced by a graphical integration of the ITC curve with fairly good accuracy: By plotting $\ln \tau$ as a function of $1/kT$ one gets a straight line. The slope of this line gives W, the intercept gives in τ_0, and the heating rate is not in this equation. This model and approach to ITC provides a good application for the physics knowledge of undergraduates. It involves classical physics from electricity and magnetism and statistical thermodynamics. There are obvious uses for computers in the data analyses that provide additional learning experiences for the students. As the students develop their under-
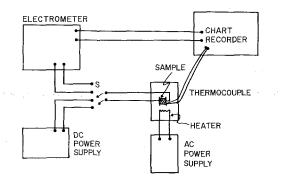
FIG. 2. Block diagram of an ITC system.

standing of ITC they begin to generate projects that interest them and the applicability of ITC to such projects is broad.

EXPERIMENTAL PROCEDURES

A typical ITC experimental set up is shown in Fig. 2. The system used at Gustavus Adolphus College consists of a Keithley Model 640 electrometer (this instrument is capable of measuring 10^{-17} A, but in all cases currents were greater than 10^{-14} A), a Keithley Model 240 A power supply, a sample cell (with liquid nitrogen cooling capability), a dual pen Sargent Model DSR recorder or a Hewlett–Packard X–Y recorder. The temperature of the sample cell is measured with a Cu–constantan thermocouple, and the heater is a soldering pencil connected to a variable ac power supply to adjust the heating rate.

There are the usual experimental procedures that should be followed when measuring such small currents. Coaxial cables are used, and connections with the electrometer are as short as possible. The sample cell is designed so as to insulate the two electrodes of the sample capacitor by a very large resistance (i.e., clean insulating material must be used), and any insulator should be subjected to as small amount of thermal cycling as possible so as to avoid ITC from the insulating material.[11] In all of our cells Teflon is used with no problems. The Gustavus Adolphus College sample cell is a liquid nitrogen cold finger with a compartment for the sample capacitor in a vacuum chamber. The pressure in the chamber was maintained below 5 μ of Hg throughout the experimental runs. The simple heater used gave very

linear heating rates. With 80 V applied to the heater the heating rate was approximately 5°C/min, and this proved to be a very convenient heating rate. The typical time needed for an experimental run, starting with the mounting of the crystal in the sample capacitor and finishing the run with the sample heated back to room temperature was less than 2 h. A sample of the experimental data received is shown in Fig. 1.

One sample cell is such that the sample can be irradiated with light. This is made possible by using a quartz window on the cell and cutting a slot in one of the electrodes. This feature makes it possible to study the optical properties of the dipoles involved in the ITC study. In principle it would also allow for thermoluminescence studies simultaneously with ITC, although this has not been attempted.

SAMPLES

Alkali halide crystals are good materials with which to work and can serve to check out the experimental system. Commercially grown alkali halide crystals, e.g., we have used crystals of CsBr, CsI, and KBr purchased from the Harshaw Chemical Company, give large ITC bands (I_{max} greater than 10^{-11} A) around 300°K.[3]

A more precise test of the experimental system can be obtained by studying the dipoles associated with color centers in alkali halide crystals.[11] The crystals can be colored by electrolytic coloring where the sample is heated in an oven with an electric field applied between point and plate electrodes on opposite sides of the sample, or by radiation coloring where the sample is subjected to ionizing radiation at room temperature, or by additive coloring where the sample is heated in an atmosphere of alkali metal vapor. These colored samples are well suited to combination optical absorption and ITC measurements.

A good project for the beginning student is the study of the ITC bands in samples of an alkali halide containing various concentrations of a bivalent impurity. The ITC bands in these materials have been well documented,[3] and the student's results can readily be compared with the results of others. For example, samples of potassium chloride containing strontium have a prominent ITC band with a T_{max} at 223°K and an activation energy of 0.657 eV.[3]

Some experimental difficulties may be encountered with the alkali halide samples. Water vapor on the surface of a sample will produce an additional ITC signal many times larger than the signal of interest. The sample should be placed between the electrodes of the sample chamber and carefully dried by heating the sample and pumping the moist air from the sample chamber. Good electrical contact whould be maintained between the sample and the electrodes. Platinum or silver electrodes are recommended. If necessary silver may be painted directly on to the surface of the sample to facilitate the conduction of electrical current from the sample to the electrodes.

UNDERGRADUATE RESEARCH PROJECTS

The method of ITC has been used to examine the aggregation process of divalent impurities in ionic crystals,[3,4,6] to observe changes in the divalent-impurity–cation-vacancy complex concentrations,[6] and to study the kinetics of color center formation.[2] Simple extensions of these works to other materials and impurities would appear to be suitable for undergraduate projects.

The preliminary work that has been done on alcohols,[7] ice,[8] and organic materials[9] could well be repeated and extended in a profitable way by diligent students.

In more unexplored areas there is the problem of the properties OH impurity dipoles in the alkali halide crystals.[12] Perhaps even more interesting is the possible existence of metastable HCl molecules in NH_4Cl crystals.[13] The method of ITC might provide a way of determining the concentration and the activation energy of such a specie.

SUMMARY

We have suggested ionic thermoconductivity as an area of investigation that meets some important criteria for undergraduate research. The model used to explain ITC is straightforward and understandable by undergraduates. It provides computer applications and data analyses that stimulate students to further work. The experimental apparatus is relatively inexpensive and durable. The time needed for experimental runs is around 2 h and is well suited for undergraduate schedules. Finally, ITC may be used in many different research projects that will stimulate the creativity and curiousity of the students.

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