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PYROELECTRICITY IN CADMIUM ZINC TELLURIDE

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ABSTRACT

The dynamic method has been used to study pyroelectricity in $Cd_{0.9}Zn_{0.1}Te$. Transient currents produced in a single crystal of $Cd_{0.9}Zn_{0.1}Te$ when subjected to flashes of light are shown to be pyroelectric in origin. The pyroelectric current was found to increase with temperature until it reached a peak and dropped beyond the transition temperature which was found to be 118°C. This is the first time that pyroelectricity is reported in a material that crystallizes in the zinc blende configuration in the first approximation.

Keywords: polarization, pyroelectricity, ferrolectricity

INTRODUCTION

When certain types of crystals are heated, they develop a spontaneous polarization along a unique axis. This phenomenon is known as *pyroelectric effect*, and the ratio of the amount of polarization produced and the temperature rise of the crystal is known as the *pryroelectric coefficient*. As ferrolectrics generally have a large, temperature dependent spontaneous polarization, we expect them to be strongly pyroelectric. The spontaneous polarization changes when the temperature of the crystal changes. An excess of free charge then appears on one of the polar faces of the crystal which gives rise to current flow in the crystal and external circuit. The sense of the current depends on the direction of the polarization change.

Pyroelectric materials are studied not only because of their theoretical and experimental interest in their particular properties, but also because of their many device applications such as infrared radiation detectors.

Several techniques have been used to accurately determine the pyroelectric properties of materials. The temperature may be changed in a sinusoidal manner or in a continuous manner. The method devised by Chynowetch [1] has found many applications in the determination of the pyroelectric effect of materials. The basis of the dynamic technique is as follows: Let P_s be the spontaneous polarization of the crystal per unit area at any temperature T. Then a small temperature change dT produces a change dP_s in P_s. If this temperature change is effected in a time dt the polarization changes at the rate of (dP_s/dt) which is equivalent to a current, i, flowing in an external circuit. Thus, the current per unit area of the crystal is

$$i = \left(\frac{dP_s}{dt}\right) = \left[\left(\frac{dP_s}{dT}\right)\left(\frac{dT}{dt}\right)\right]_{T=T} \qquad (1)$$

For small ΔT, (dP_s/dT) can be regarded as a constant for that temperature and then the current depends only on the rate of change of the temperature. Eqn.1 can then be written as

$$i = \frac{dT}{dt} \qquad (2)$$

where λ is the pyroelectric coefficient.

Chynoweth's technique can be used not only to measure the pyroelectric coefficient (see Eqn.2), but also to determine the polarization of the ferrolectric in two different types of measurements. For the value of the pyroelectric constant measured in a certain interval of temperature ($T_1 - T_2$), it is possible to calculate, by means of integration, the difference $P_s(T_1) - P_s(T_2)$ between the spontaneous polarization at the temperature T_1 and T_2. The value so calculated can be compared with that determined from measurements on the hysteresis loop. Results have been found to be in good agreement [1], showing that the pyroelectric technique can be used to determine accurately the spontaneous polarization.

The existence of ferrolectricity has recently been reported in $Cd_{1-x}Zn_xTe$ from the temperature variation of the dielectric constant, and from the hysteresis loop [2]. No ferrolectricity was found in pure CdTe but all samples containing Zn had a second order ferrolectric-paraelectric transition. The polarization was in a <111> direction. $Cd_{0.9}Zn_{0.1}Te$ was found to have a transition temperature of about 120°C. Since pyroelectricity is a condition sine-qua-non for ferrolectricity, the measurements reported here were undertaken on $Cd_{0.9}Zn_{0.1}Te$ to verify that this condition is satisfied.

EXPERIMENTAL METHOD

The experiments were performed on a single crystal of $Cd_{0.9}Zn_{0.1}Te$ with electrodes on the (111) faces. The sample was prepared as indicated in reference 2.

The dynamic method originally developed by Chynoweth [1] was used for the pyroelectric measurements. A block diagram of the set-up is shown in Fig.1. The crystal was mounted inside a furnace and subjected to brief intense flashes of light by means of a rotating chopper. The current which was produced as a result of the change in temperature of the crystal was amplified by a current sensitive preamplifier and measured by a lock-in-amplifier and an oscilloscope. The output of the oscilloscope was applied to an X-Y recorder which was used to record the variation of current with time at specific temperature when the crystal was illuminated or after illumination ceased. The sample was heated and the current was measured at various temperatures.

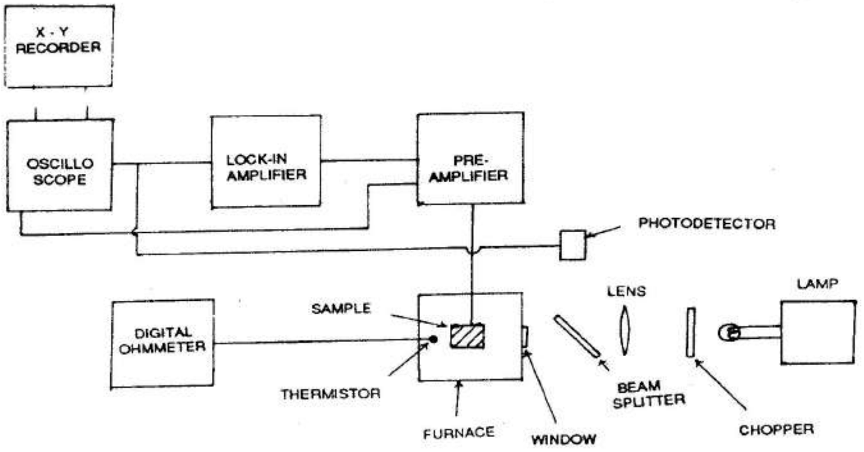

Fig.1: A block diagram of the arrangement for pyroelectric measurements

RESULTS AND DISCUSSIONS

Figure 2 shows the wave form for the signal obtained at 80°C, a temperature below the reported transition temperature of 120°C. The nature of the wave form may be explained as follows: When the illumination of the crystal is commenced at time t = o, its temperature rises initially at the rate $(dT/dt)_{t=0}$. As the temperature increases towards its new steady value, the rate of change of temperature, (dT/dt), decreases, reaching zero at equilibrium. This decrease is reflected in the pyroelectric current as shown in Fig.2. When the light is cut off the crystal begins to cool. Initially, its rate of cooling is at a maximum and proceeds smoothly to zero as the original temperature is regained. This is also reflected in the current. However, the current, while cooling, has a direction opposite to that when warming. The current cycles shown in Fig.2 bear out the pyroelectric effect as given by Eqn.1.

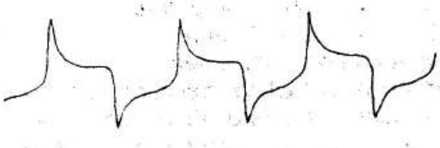

Fig.2: Waveform exhibited by output signal at 80°C

It would be relevant, however to discuss whether any other processes would produce such behaviour. The possibility of photoconduction was considered. To eliminate photocurrent and increase heat absorption, the exposed face of the sample was painted black with a layer of conducting graphite.

A change in the temperature of a crystal could also result in an electrical change of a thermoelectric nature. In this case, the electrical manifestation would proceed as dT and not as

(Dt/dt). Under illumination, therefore, the thermally-stimulated current would grow steadily towards a new equilibrium value corresponding to the new equilibrium temperature. On the other hand, when the illumination is cut off, the current would decay smoothly to its original value without any change of sign. This, of course, is completely contrary to the observed behaviour.

The pyroelectric current is found (Fig.3) to increase with temperature until it reaches a peak and then decreases. At low temperatures the change in the polarization is small as a result of the saturation of the polarization. However, as the temperature increases, the rate of change of polarization increases, since the tendency towards complete disorder of the dipoles increases. This leads to the increase in the pyroelectric current. The temperature at which the pyroelectric current reaches a maximum is 118°C. This transition temperature agrees quite well with that obtained from dielectric constant measurements [2]. The nature of the pyroelectric current versus temperature curve is similar to those obtained for other ferrolectrics [1,3].

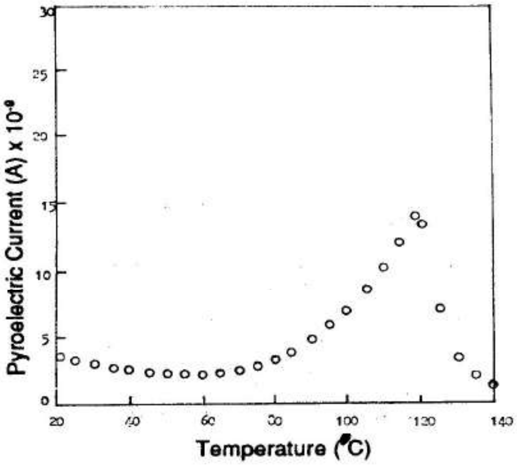

Fig. 3: Temperature dependence for pyroelectric current

Above the transition temperature the pyrocurrent should have dropped to zero since the polarization goes to zero at the Curie point. However, some residual current is observed. this can be explained by imagining that below the transition temperature there is a rapid formation of a domain structure in which there are discontinuities in the polarization vectors. According to Chynoweth [3], compensation charges accumulate on these domain boundaries. This compensation supposedly takes place fairly slowly. Above the Curie point, the spontaneous polarization disappears everywhere leaving behind the remaining compensation charge. These free charges give rise to electric fields which in turn induce a polarization P_1 throughout the bulk of the crystal and a net polarization P_2 within the regions formerly occupied by the domains. The two polarizations act in opposite directions. It can be assumed that the residual pyroelectric signal for which P_2 is responsible is much greater than that caused by P_1. In other words, the fields persisting within the old domain location are very much greater than the fields produced in the bulk by the interface charges. However, as the temperature increases, the two fields become equal and the residual signal disappears.

For a second-order ferrolectric-paraelectric transition, the spontaneous polarization may be obtained (in arbitrary units) by the direct integration of the dP_s/dt versus temperature curve[4], that is,

$$P_s^T = \int_{T_c}^{T} (dP_s/dT)dT. \qquad (3)$$

Fig.4 shows the P_s versus T curve obtained for $Cd_{0.9}Zn_{0.1}Te$. It is observed that the spontaneous polarization decreases continuously until it vanishes at the Curie temperature.

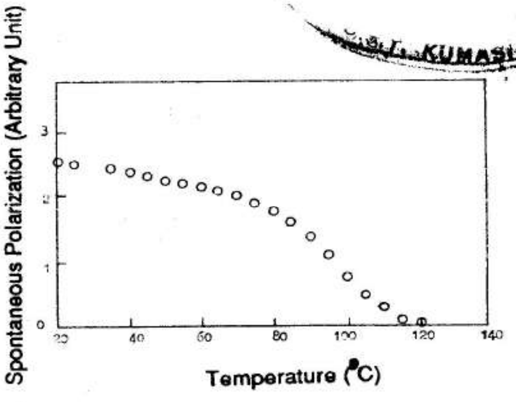

Fig. 4: Temperature dependence of the spontaneous polarization

CONCLUSIONS

The dynamic method has been used to investigate pyroelectricity in $Cd_{0.9}Zn_{0.1}Te$. The current produced as a result of small temperature changes has been found to be pyroelectric in origin at temperature below the transition temperature. The spontaneous polarization obtained from the pyroelectric measurements showed a smooth decrease with temperature. This gives evidence of a second-order transition.

As far as we know, this is the first time that pyroelectricity is reported in materials that crystallize in the zinc blende configuration to the first approximation. This observation is very important because it confirms the presence of ferrolectricity in the material studied, and the presence of ferrolectricity in a material has serious consequences on its crystal symmetry and phonon spectrum. Furthermore, ferrolectricity in $Cd_{0.9}Zn_{0.1}Te$ is probably not a freak phenomenon. In agreement with Islam and Bunker [5], ferrolectricity could occur generally in simple binary mixed crystals. They suggest that the required condition is that the substitutional atoms be of appreciably different size from that of the host atoms they replace. Thus, ferrolectricity has been observed in $Ph_{1-x}Ge_xTe$ and inferred in $Pb_{1-x}Sn_xTe$. In contrast to $Cd_{1-x}Zn_xTe$, these materials crystallize in the NaCl structure in their paraelectric phase.

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