Ferroelectricity in Zinc Cadmium Telluride

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Ferroelectricity in $Zn_xCd_{1-x}Te$ was found from the temperature variation of the dielectric constant, and from the hysteresis loop. The Zn content varied from 4% to 45%. No ferroelectricity was found in pure CdTe but all samples containing Zn had a second-order ferroelectric transition. The transition temperature varied from 90 to 245 °C. The polarization was in a $\langle 111 \rangle$ direction. While no existing model matches the rapid rise of the Curie constant for $0 < x < 0.04$, there is some evidence to support an order-disorder transition.

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The II-VI mixed crystals, one of which is zinc cadmium telluride ($Zn_xCd_{1-x}Te$), have been the subject of a number of recent experimental[1-3] and theoretical[4] studies. We report here the measurement of ferroelectricity in these materials. This is the first time that ferroelectricity is reported in materials that crystallize in the zinc-blende configuration to first approximation,[5] and in mixed crystals in which neither of the binary constituents are known to be ferroelectric.

We believe that our observation is important because the presence of ferroelectricity in the material has serious consequences on its crystal symmetry and phonon spectrum. Furthermore, we believe that ferroelectricity in $Zn_xCd_{1-x}Te$ is probably not a freak phenomenon. In agreement with Islam and Bunker,[6] we think ferroelectricity 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, ferroelectricity has also been observed in PbGeTe (Refs. 6 and 7) and inferred in PbSnTe.[8,9] In contrast to $Zn_xCd_{1-x}Te$, these materials crystallize in the NaCl structure in their paraelectric phase.

The single crystals used in our measurements were grown in-house by the modified Bridgman technique.[10] The crystals were uncompensated; they were grown from 99.9999% purity Cd and Te, and 99.999% purity Zn. The Zn content varied from 0% to 45% for the different samples used. The composition of the samples was established by photoluminescence.[1] Sample size varied around 5 mm diam and 0.9 mm thickness.

The large surfaces of the samples were either lapped and polished or simply lapped on glass with 3-μm alumina powder. Silver paint was used for the contacts. We found that the results reported were insensitive to the surface treatment.

At low frequencies the samples behaved as if their room-temperature dielectric constant was of the order of 10^4. We found that this effect was due to the high bulk conductivity of our samples, which was in the range of 10^{-2} to 10^{-1} $(\Omega\,\mathrm{cm})^{-1}$ at room temperature. The high bulk conductivity, combined with a thin, high-resistivity surface layer, caused the effect, which was first described by J. C. Maxwell and by K. W. Wagner, and more recently by Koops.[11] Our samples conformed well with the frequency dependence of the resistivity and dielectric constant predicted by the Maxwell-Wagner model. Our measurements could be fitted with a surface zone of the order of 1 μm thick with a resistivity of 10^6 Ω cm. The only assumption was that the dielectric constants of the bulk and of the surface zone are the same. The origin of this region could be a depletion layer at the contacts. We found that with Au or graphite contacts the Maxwell-Wagner behavior persisted, but other fitting parameters were needed. We fitted the measured resistance and dielectric constant as a function of frequency by the Maxwell-Wagner model and calculated the bulk dielectric constant from the model.

Measurements were made with Hewlett-Packard type 4815 and type 4801A impedance meters.

Figure 1 is representative of the data we obtained for all the zinc-bearing samples when the applied field was in a $\langle 111 \rangle$ direction. In it we present a plot of the dielectric constant ϵ of a sample containing 10% Zn as a function of temperature, at 100 MHz (where the correction to obtain ϵ_{bulk} is less than 10%). In the same figure we also present a plot of $1/(\epsilon-\epsilon_\infty)$ as a function of temperature. ϵ_∞ was calculated for every composition x from a linear extrapolation between 7.21, the ϵ_∞ of pure CdTe,[12] and 7.26, the value for pure ZnTe.[12] ϵ_∞ was taken to be temperature independent.

In Fig. 1, ϵ at 20 °C is 13.0; this is larger than that which would be expected from a linear interpolation between the values measured by others[13,14] for pure CdTe (11.0) and pure ZnTe (10.1). For 10% Zn content the interpolation yields $\epsilon = 10.9$. The larger value is due to the dipoles' contribution.

The results displayed in Fig. 1 clearly show that the material has characteristic ferroelectric behavior, with a Curie temperature of 120 °C. Note that the ratio of the

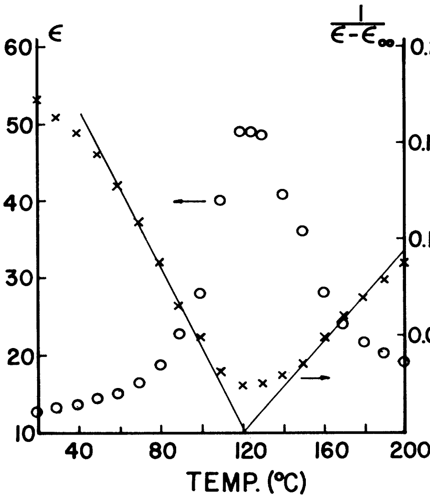

FIG. 1. Dielectric constant (o) and inverse dielectric constant (×) as a function of temperature for Zn$_{0.1}$Cd$_{0.9}$Te with the electric field in a $\langle 111 \rangle$ direction, measured at 100 MHz.

slopes of the two straight lines is 1.84, which is close to the value of 2.0 expected for a second-order transition from thermodynamic considerations.[15] The transition temperature is the same as the Curie temperature. This is also characteristic of a second-order transition.

We have made plots such as shown in Fig. 1 from measurements at six frequencies spaced down to 60 Hz on the sample containing 10% Zn. We found the same qualitative behavior. Quantitatively, the peak dielectric constant showed a monotonic decrease of roughly 20% from 60 Hz to 100 MHz. The ratio of the slopes was 1.91 ± 0.17 over the whole range. The transition temperature was constant within the accuracy of the graphs.

Figure 2 is a plot of the Curie temperature T_C and the Curie constant, both as functions of Zn content of the samples. A cursory extrapolation of T_C would lead to the conclusion that pure CdTe should be ferroelectric at about 70 °C. However, we found no ferroelectric effect in CdTe above room temperature.

In Fig. 3 we show the dielectric constant of the same material of Fig. 1, but measured with the electric field in a $\langle 110 \rangle$ direction. We also show in Fig. 3 the dielectric constant of our pure CdTe samples in a $\langle 111 \rangle$ direction. No ferroelectric behavior is evident, and the temperature coefficient of the dielectric constant, $(2.5 \pm 0.2) \times 10^{-4}$ $°\mathrm{C}^{-1}$, of the CdTe agrees well with the value found by Strzalkowski, Joshi, and Crowell.[12] Furthermore, the values of bulk ϵ at room temperature agree with what is expected for nonferroelectric material. Comparison of Figs. 1 and 3 makes it clear that the dipoles are aligned in a $\langle 111 \rangle$ direction. Comparison of the two figures also proves that the ferroelectric effect we see is not an artifact caused by the interface of the high-resistivity layer on the low-resistivity bulk material, since these layers were also in full evidence in both samples of Fig. 3.

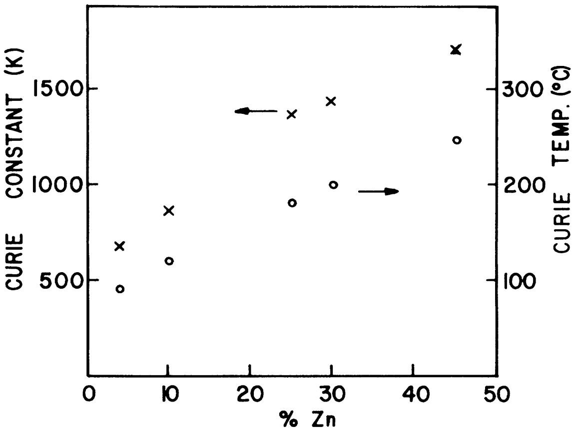

FIG. 2. Curie constant (×) and transition—or Curie—temperature (o) as functions of zinc content in Zn$_x$Cd$_{1-x}$Te with the electric field in a $\langle 111 \rangle$ direction, measured at 100 MHz.

We observed a polarization hysteresis loop in all the samples containing Zn. A representative loop, taken at 50 Hz is shown in Fig. 4. The curve is typical of those measured in ferroelectrics.[16] Because of the rather high conductivity of the samples we could not apply high fields without destroying them.

The variation of the Curie temperature with the concentration (Fig. 2) merits some comments. As mentioned above, a smooth extrapolation of the curve $T_C(x)$ to $x=0$ cannot be made. This implies that $T_C(x)$ de-

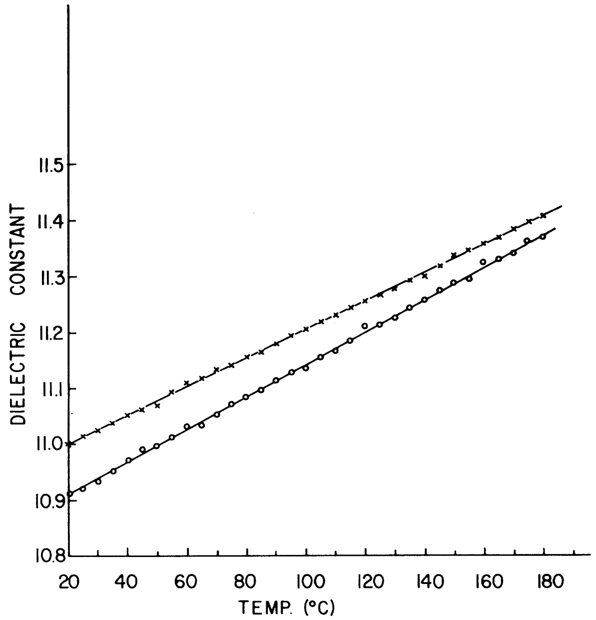

FIG. 3. Dielectric constant as a function of temperature for pure CdTe with the electric field in a $\langle 111 \rangle$ direction (×) and for Zn$_{0.1}$Cd$_{0.9}$Te with the electric field in a $\langle 110 \rangle$ direction (o), measured at 100 MHz.

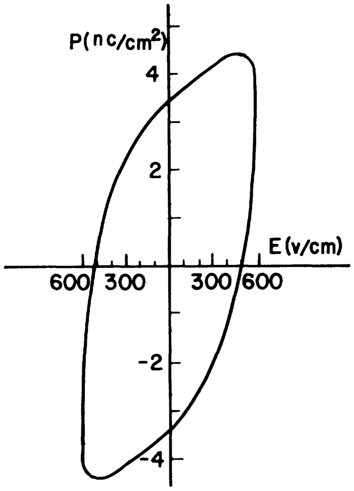

FIG. 4. Polarization as a function of applied field, for $Zn_{0.1}Cd_{0.9}Te$ with the electric field in a ⟨111⟩ direction. The measurement was performed at 50 Hz and room temperature.

creases steeply for $x < 0.04$, whatever the value of T_C for $x = 0$ turns out to be, if it is real.

It is usual to distinguish between two basic mechanisms for ferroelectricity:[15] a displacive transition with the softening of an optical mode, or an order-disorder transition of a pseudospin system. Nevertheless, this distinction is not very sharp, and several examples of mixed cases are known.[6]

We tried to apply the two basic models (using the detailed derivations given in Ref. 15) to find how the various parameters of each model might depend on the concentration x in order to fit the experimental curves $T_C(x)$ and $C(x)$. These attempts were unsuccessful because it turned out to be impossible to match the rapid decrease in $T_C(x)$ for $x < 0.04$, in the computed values. This seems to constitute the main problem. Although there is an apparent similarity with $Pb_{1-x}Ge_xTe$, the situation is different precisely in the strong variation of T_C for low values of x. Another question that has to be addressed is the low value (for ferroelectrics) of the peak dielectric constant as shown in Fig. 1. However, this behavior is not unknown in ferroelectrics.[17]

It is clear that a more elaborate model is necessary, maybe in the spirit of the model of Katayama and Murase.[18] They proposed a modification of the pseudospin model, introducing coupling between the dipoles and the optical phonons. However, their model is limited to low temperatures.

Probably an order-disorder model is the most suitable. The TO phonon dispersion curves[19] of CdTe at 300 K do not show any trend—even small—toward a softening. Then, one finds that $C(x)$ is close to $3\times T_C$ in our samples, especially for $x > 0.1$. This is further evidence of an order-disorder mechanism. Finally, the difference between the covalent radii (Cd = 1.48 Å, Zn = 1.31 Å)[20] or the ionic radii (Cd^{2+} = 1.03 Å, Zn^{+2} = 0.83 Å)[20] is large enough to give the possibility for the Zn atom to move in a double-well potential. There is little doubt that from a microscopic point of view ferroelectricity in $Zn_xCd_{1-x}Te$ has its origin in the alloying effects which cause differences in bond lengths and in local symmetry.[4]

We have gathered additional evidence of ferroelectricity in our samples. We have detected the pyroelectric effect below the transition temperature of the Zn-bearing samples, and we have preliminary x-ray diffraction results showing that the ferroelectric phase is rhombohedral. Furthermore, the resistivity of the samples was found to have a peak anomaly exactly at the ferroelectric transition temperature. This behavior is similar to that found[9] in PbGeTe and PbSnTe, even though these systems are metallic in character, while ours is a semiconductor. These results will be presented in a more detailed report which is in preparation.

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