Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

Ferroelectric Behaviors in Semiconductive $Cd_{1-x}Zn_xTe$ Crystals.

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From the re-examination of the dielectric constants of $Cd_{1-x}Zn_xTe$ crystals, the phase transitions were confirmed. X-ray studies and the structure analysis of $Cd_{1-x}Zn_xTe$ were carried out in the temperature range of 10K to 600K in order to clarify the nature of phase transitions microscopically. It was found that the phase transition of $Cd_{1-x}Zn_xTe$ was second order-like. The temperature factor of $Cd_{1-x}Zn_xTe$ indicated that the transition was an order-disorder-type.

1. INTRODUCTION

Recently alloy semiconductors have been investigated by the measurement of the electrical resistivity, mobility, carrier concentration and so on, for application to wavelength-tunable infrared detectors and lasers. But one of our greatest interests of semiconductive alloy is a ferroelectric behavior. It is well known that IV-VI (averaged V) compound semiconductors such as SnTe, GeTe, PbTe and their ternary alloys exhibit an apparent ferroelectric phase transition, which has been confirmed by the temperature change of the Bragg intensities of the neutron diffraction and by the dielectric measurements [1-3]. This phase transition of SnTe-GeTe-PbTe alloys occurs with a structural change from a high-temperature NaCl (cubic) structure to a low-temperature As-like (rhombohedral) structure, and the stability of low temperature structure is discussed in terms of the electron - phonon coupling [4,5].

In semiconductive II-VI compounds, CdTe and ZnTe, the phase transition does not occur down to low temperatures, however the phase transitions are found in the mixed crystal $Cd_{1-x}Zn_xTe$ [6,7]. The possibility of the ferroelectric phase transitions in CdTe-ZnTe alloy has been confirmed by the measurements of the spontaneous polarization, birefringence and specific heat. We have measured the EXAFS spectra to clarify the local structure of $Cd_{1-x}Zn_xTe$ [8]. The Cd-Te and Zn-Te nearest neighbor distances deviated from the Vegard's law but the weighted average of the two distances agreed with the law [9].

2. EXPERIMENTAL

The $Cd_{1-x}Zn_xTe$ single crystals were prepared in the Bridgman furnace [10]. They were grown from 99.999% purity Cd, Zn and Te which were etched in order to take away oxide compounds. The temperature of the furnace was kept at 970K for kept 24 hours in the first stage and was kept over the melting point of $Cd_{1-x}Zn_xTe$ and for 24 hours, then cooled to room temperature for one or two weeks. The composition of the $Cd_{1-x}Zn_xTe$ crystals was confirmed by x-ray powder diffraction.

Dielectric measurements were made with Hewlet Packard type 4284A LCR meter. The frequencies were from 20Hz to 1MHz and the temperature range was RT to 550K. The x-ray diffraction experiments were carried out using a four-circle and a double axis diffractometer. Mo-Kα or Cu-Kα radiation monochromatized by a pyrolytic graphite crystal was employed as the x-ray source.

3. RESULTS AND DISCUSSION

3.1 Dielectric measurements

Figure 1 shows dielectric constant ε at 10kHz with the electric field in a < 111 > direction for $Cd_{0.95}Zn_{0.05}Te$ as a function of temperature. The closed circles are ε(T) on first heating the sample and the open circles are ε(T) on 4th heating the sample.

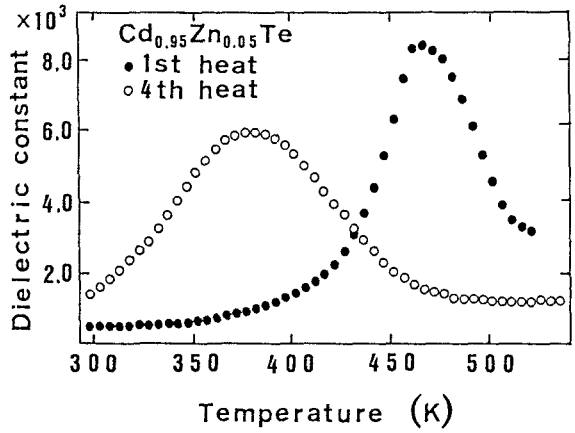

Fig. 1. Dielectric constant as a function of temperature for $Cd_{0.95}Zn_{0.05}Te$ with the electric field in a <1 1 1> direction measured at 10kHz on first heating (the closed circles) and 4th heating (the open circles).

The peaks of ε(T) appeared at different temperatures. Near *Tc*, the dielectric constant of $Cd_{1-x}Zn_xTe$ showed a round anomaly which is characteristic to the diffuse transition [11,12].

3.2 X-ray studies

The x-ray diffraction studies can provide information of the phase transition and the structure of $Cd_{1-x}Zn_xTe$ crystal in the view point of average structure. The phase transition was manifested by a change in integrated intensities of the Bragg reflections of x-ray with temperature. Figure 2 shows the temperature dependence of the integrated intensities of the (2 2 8) Bragg reflection. The zinc concentration of the sample is 0.3. The integrated intensity decreased with increasing temperature. The change of integrated intensity as a function of temperature showed no jump when the transition was occurred. Therefore, the phase transition of $Cd_{1-x}Zn_xTe$ is almost second order

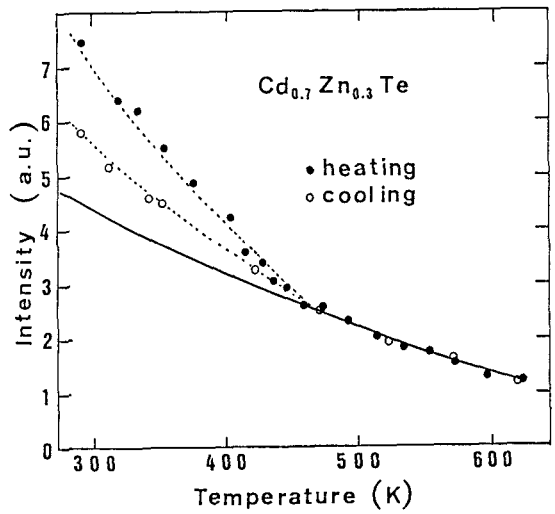

Fig. 2. Temperature dependence of the integrated intensities of (2 2 8) reflection in $Cd_{0.3}Zn_{0.7}Te$ on heating (closed circles) and cooling (open circles). Solid line shows the temperature dependence of the integrated intensity in the case of no phase transition.

diffuse transition nature. On the contrary, on cooling process, the slight change of the integrated intensity was observed when the phase transition was occurred.

The difference in the transition temperature between on heating sample and on cooling

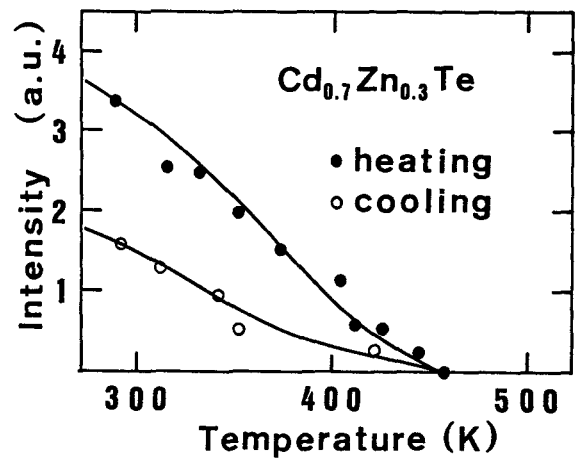

Fig. 3. Subtracted intensities from the case of no phase transition of (2 2 8) reflection in $Cd_{0.7}Zn_{0.3}Te$.

was observed in dielectric measurement, too. Benguigui *et al.* suggested a two-state configuration-coordinate diagram in order to explain the behavior of dielectric constant. Our works of the dielectric measurements and the x-ray studies were good agreement with their model. Benguigui *et al.* measured the spontaneous polarization of $Cd_{1-x}Zn_xTe$ and concluded that the phase transition of $Cd_{1-x}Zn_xTe$ was diffuse, second order and order-disorder type. Figure 3 shows the temperature dependence of x-ray integrated intensities that is subtracted the value in the case of no phase transition. The subtracted intensities are decreasing gradually in proportion to the Ps^2 which were measured by Benguigui *et al.*

The profile of powder x-ray diffraction of $Cd_{0.8}Zn_{0.2}Te$ at room temperature is shown in Figure 4. At room temperature, $Cd_{0.8}Zn_{0.2}Te$ is in the low temperature phase in which the structure of $Cd_{0.8}Zn_{0.2}Te$ is rhombohedral. In this x-ray powder diffraction profile, the splits of (220) or (311) Bragg peaks were observed indicating the rhombohedral phase . The lower panel shows the calculated 2θ-angle assuming the rhombohedral structure with a = 90.5°. Figure 5 shows the temperature change of powder x-ray diffraction profiles near (311) peak. The intensity of one of the split peak decreases with increasing temperature. Because the $Cd_{1-x}Zn_xTe$ alloys have a two-state

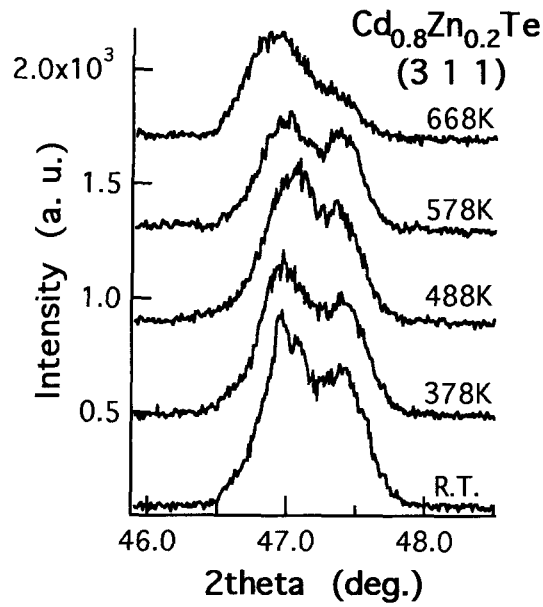

Fig. 5. Temperature dependence of x-ray diffraction profile near (3 1 1) of $Cd_{0.8}Zn_{0.2}Te$.

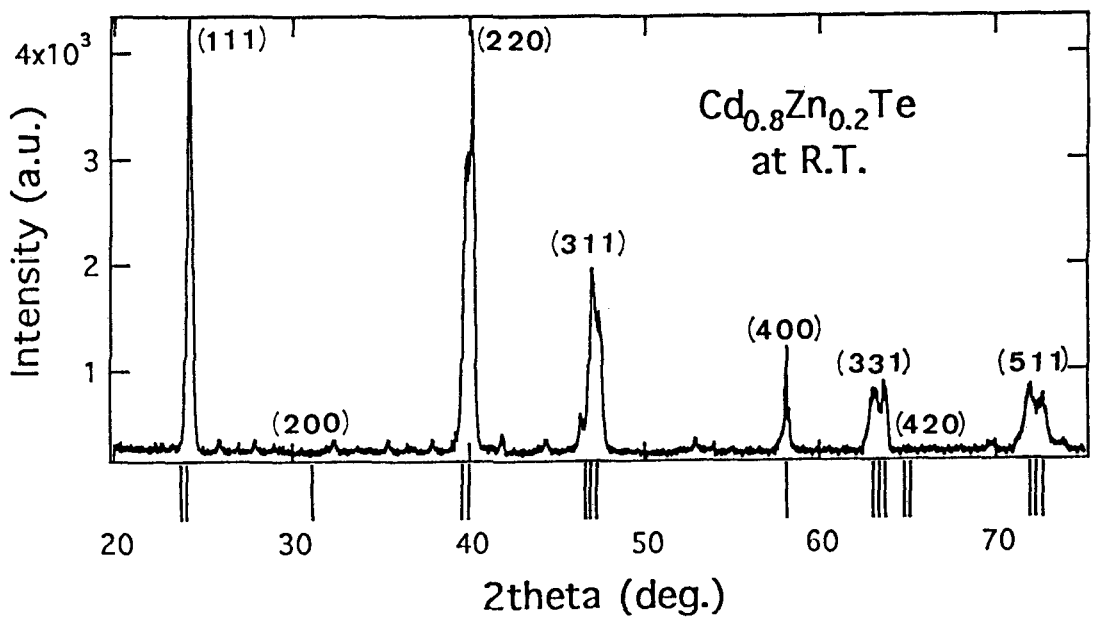

Fig. 4. Diffraction pattern of powder $Cd_{0.8}Zn_{0.2}Te$ at room temperature. Rhombohedral splittings are indicated at the down part

Table 1
Structure data of CdTe and ZnTe

	lattice	space group	lattice parameter at R T (Å)
ZnTe	zinc-blende	F43m	6.104
CdTe	zinc-blende	F43m	6.481

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configuration coordinate diagram system, the peak from the rhombohedral phase remained at 668K in the high temperature phase.

Figure 6. shows the so called "side band" of x-ray diffraction profile near the (3 3 1) reciprocal lattice point of $Cd_{0.3}Zn_{0.7}Te$ single crystal. The side bands are very weak peak that exist at the foot of main Bragg peak. In the case of $Cd_{1-x}Zn_xTe$ crystal, because of the two - state configuration coordinate diagram, the cubic phase and the rhombohedral phase that are co-existing at same temperature, construct modulated structure. The period of this modulated structure is about 10 times as large as the unit cell of $Cd_{1-x}Zn_xTe$.

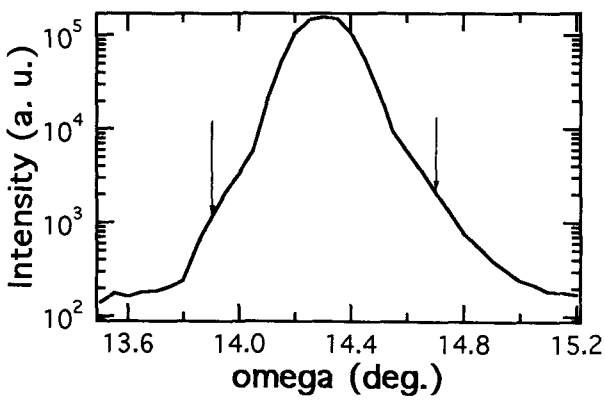

Fig. 6. X-ray diffraction profile near the (3 3 1) of $Cd_{0.3}Zn_{0.7}Te$ single crystal. The arrows point to the side bands.

3.3 Structure analysis

Table 1 gives the structure data of CdTe and ZnTe. $Cd_{1-x}Zn_xTe$ mixed crystals may be also zinc-blende structure like CdTe or ZnTe. The structure analysis were carried out under the space group of F43m. If Zn atoms shift along the <1 1 1> direction in the low temperature phase as Benguigui suggested, the F43m symmetry is broken. Next, we tried structure analysis under rhombohedral (R3m) symmetry. The sample was not difficult to carry out the calculations. It was spherical with a diameter of 0.30(1)mm. Measurements of independent Bragg intensities were made at room temperature (ferroelectric phase) by means of a 2θ-ω scanning method for the ($h \geq 0, k \geq 0, l \geq 0$) region with $2\theta max = 70.0°$. The result of structure analysis is shown in Table 2. Because each atom places at zinc-blende atomic position, the R-factors ($S \mid\mid F_0 \mid - \mid F_C \mid\mid / S \mid F_0 \mid$) of under the space group of F43m and R3m are almost same. The difference is not significant improvement which is essentially caused by choosing between two models [13]. We added a parameter δ that was the off-center atomic

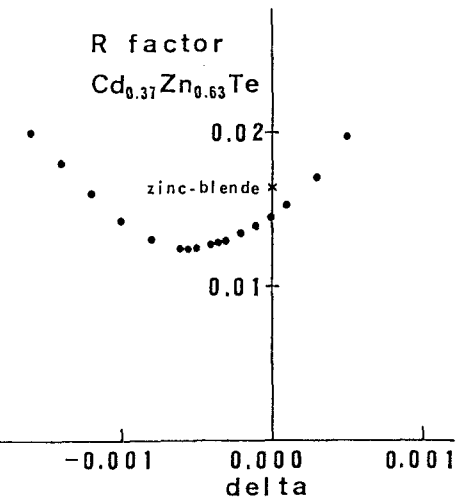

Fig. 7. Discrepancy factors R as a function of atomic displacement δ. (x) is calculated under the space group of F43m.

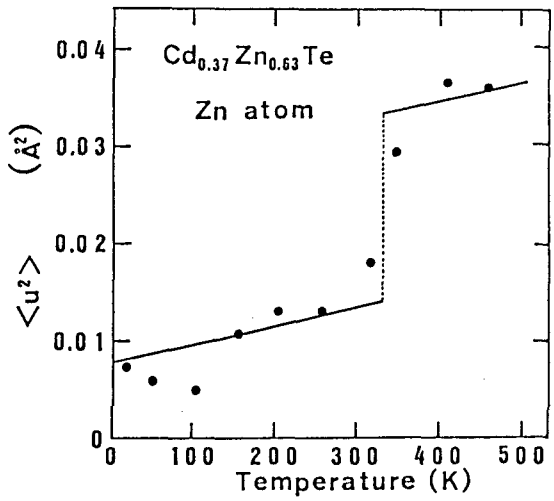

Fig. 8. Temperature dependence of the isotropic thermal parameter of the Zn atom in $Cd_{0.37}Zn_{0.63}Te$.

displacement of Zn from zinc-blende position along the <1 1 1> direction. The results are given in Fig. 7. A off-centerminimum which is shifted along the <1 1 1> direction from zinc-blende position indicating the possibility of structural phase transition. The displacement of Zn atoms determined from the value of δ was about 0.01Å.

The temperature factor of Zn atom determined from structure analysis under the space group of R3m is shown in Fig. 8. The behavior of the temperature factor indicates that the phase transition of $Cd_{1-x}Zn_xTe$ is order-disorder type. In the high temperature phase, Zn-atom jumps between off-center minimum through tunneling and the average structure of $Cd_{1-x}Zn_xTe$ crystal keeps zinc-blende structure. Below the transition temperature, Zn-atoms' jumping is frozen and relative position of Zn-atom shifted along the <1 1 1> direction. The anomalous behavior of the temperature factor is similar to that in the case of the order-disorder type phase transition of ferroelectric materials.

Table 2
Discrepancy factors R and R_w at room temperature

symmetry	R	R_w
F43m	0.01492	0.02036
R3m	0.01445	0.02030

3.4 Optical absorption analysis

From the studies of x-ray diffraction and dielectric measurement, it becomes clear that the $Cd_{1-x}Zn_xTe$ mixed crystal undergoes a ferroelectric structural phase transition. We anticipated that the origin of the phase transition is the coupling between electron system and phonon system on the analogy of ferroelectric phase transition of IV-VI (averaged V) semiconductive mixed crystals. Figure 9 shows the optical absorption edges of $Cd_{0.7}Zn_{0.3}Te$ and $Cd_{0.3}Zn_{0.7}Te$ crystals that were measured as a function of temperature. But no anomaly was observed around *Tc*. We suggest that the phase transition of $Cd_{1-x}Zn_xTe$ mixed crystal is a simple order-disorder type.

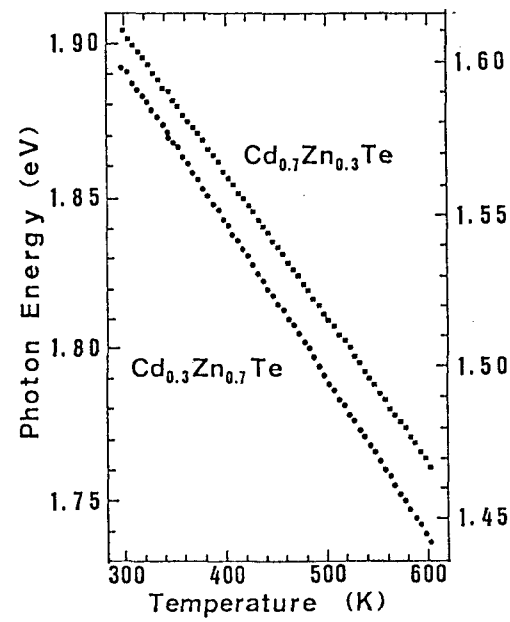

Fig. 9. Optical absorption edges of $Cd_{0.3}Zn_{0.7}Te$ (closed circles) and $Cd_{0.7}Zn_{0.3}Te$ (open circles) as a function of temperature.

4. CONCLUSIONS

The structural phase transition in $Cd_{1-x}Zn_xTe$ mixed crystals has been

investigated by means of the dielectric measurements, the x-ray studies and the optical absorption analysis. We summarize our experimental results and analysis as follows:
a) The dielectric anomaly has been observed in $Cd_{1-x}Zn_xTe$ near Tc. The anomaly was very round peak which is characteristic to glass or diffuse transition.
b) The structure of $Cd_{1-x}Zn_xTe$ changed from the cubic to the rhombohedral when the phase transition occurred. The different behaviors near Tc between heating process and cooling process were almost explained by two state configuration coordinate diagram. This possibility was also suggested by the observation of the "side band".
c) We could not detect the phonon - electron coupling observed in $Sn_{1-x}Pb_xTe$. The phenomenon indicated the phase transition of $Cd_{1-x}Zn_xTe$ was a simple order - disorder type.

It is desirable to carry out more experimental and theoretical studies, for example, x-ray measurements under high pressure.

ACKNOWLEDGMENTS

The authors are grateful to Dr. S. Sugai and Prof. S. Nakashima for their fruitful discussion.

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