

**Report on the experiment project 01-02-843
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The X-ray diffraction study of the $\text{Gd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0, 0.04, 0.10$ and 0.15) using synchrotron radiation

Introduction. In 1989, the solid solutions $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ were found to be ferroelectric at $T < T_C$ [1]. This was the first example of ferroelectricity in zinc-blende (space group $F-43m$) based systems. However, the micro-structural origin of macroscopic ferroelectricity, *i.e.* the zinc-blende structure polarisation, is still under discussion for the bulk crystals [2]. T_C was found to be dependent from the composition and changes from 383 to 538 K in the $0.04 < x < 0.45$ compositional range [1]. A polarisation hysteresis loop has been observed in all the samples from this compositional range [1]. The polarization of the ferroelectric phase was found along the $\langle 111 \rangle$ direction [1] probably with rhombohedral structure distortion [1, 2]. However, this distortion is too small to be detected by laboratory X-ray experiments [2]. A CuPt-type $\langle 111 \rangle$ ordered structure described in [3] has been observed in thin films of compositions $\text{Cd}_{0.26}\text{Zn}_{0.74}\text{Te}$ [4] and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Te}$ [5]. Extra reflections of the type $\{1/2 \ 1/2 \ 1/2\}$ have been observed in an electron diffraction pattern, pointing thus to a CuPt-type of ordering in the unit cell with parameter $a_{\text{th}} = 2a_{\text{cub}}$ [4, 5]. High-energy synchrotron X-ray measurements and pair-distribution function analysis indicated a local disorder along the $\langle 111 \rangle$ direction as the origin of macroscopic ferroelectricity in the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ bulk crystals [2]. Series of crystal structures of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ have been investigated in [6] using laboratory diffractometer, but no rhombohedral symmetry has been observed. However, the rhombohedral distortion of the unit cell with angle $89.4(1)^\circ$ and 89.94° has been reported [7] at room temperature. The temperature dependence of the unit cell constants could not be found in the available literature.

Preliminary study. A preliminary crystal structure investigation has been performed for a $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ bulk crystal at 293 K using synchrotron radiation. The crystal was probably spontaneously polarized because of $T_C = 383$ K [1, 2]. X-ray diffraction data were collected at the Swiss-Norwegian beamline BM01A of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The experimental data set was collected using the Marresearch Image Plate (345 mm diameter). According to this investigation, a Cu_3Au -type $\langle 111 \rangle$ ordered structure (also described in [3]) has been hinted for the Cd and Zn distribution on the Cd-position. The fourfold twined structure has been refined in the polar space group $R3m$ for $\text{Cd}(\text{Cd},\text{Zn})_3\text{Te}_4$. The mass coefficients obtained for the components are 0.26, 0.21, 0.29 and 0.24. These twin components can be directly associated with micro-domain structure. The directions of the domain orientations coincide with four 3-fold axes: $[111]$, $[-111]$, $[1-11]$ and $[11-1]$. This fact is consistent with all published data on $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$. Small atomic displacements from their ideal position can be associated with the lowering from cubic to rhombohedral symmetry. The absence of these displacements would result in a cubic non-polar and non-twined structure with space group $P-43m$, which would be characteristic of the paraelectric phase at $T > T_C$. Therefore, the results of our preliminary investigation could explain the micro-structural origin of macroscopic ferroelectricity, *i.e.* the polar distortion of the zinc-blende structure.

The main experimental basis of these results is the set of the very weak extra reflections with $1\sigma(\text{F}) < \text{F} < 3\sigma(\text{F})$ and $h+k, h+l, k+l \neq 2n$. These reflections contradict the F centering of the unit cell. We incorporated them into our structure refinements despite their intensity being close to the

experimental noise. In order to check the significance of the extra reflections, we performed the analogous structure investigation for pure CdTe crystal. The number of the extra reflections with $1\sigma(F) < F < 3\sigma(F)$ among all reflections with $F > 1\sigma(F)$ was about 2% for CdTe, while this number was about 20% for $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$.

The aims of the present study. The aim of the study was to clarify the structural transformations accompanying the ferro-para electric phase transition in $\text{Gd}_{1-x}\text{Zn}_x\text{Te}$ with $x = 0, 0.04, 0.10$ and 0.15 . Using synchrotron radiation, the $\text{Gd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0, 0.04, 0.10$ and 0.15) samples were tested by single-crystal and powder diffraction techniques in the $100 \text{ K} < T < 500 \text{ K}$ range.

Experimental

1. The single-crystal X-ray studies

The presence of split reflections and extra forbidden reflections in a F centred unit cell has been checked using the Oxford Diffraction KM6 diffractometer equipped with a 165mm diameter CCD area detector. Temperature control was achieved using a cooled nitrogen gas cryostream supplied by Oxford Cryosystems Ltd. A Si(111) monochromator was used to select a wavelength of 0.6991 Å. A combination of sagittally focusing monochromator crystal and vertically bent mirror in the beamline provide a focused beam of 0.5 mm diameter.

A fragment of the $\text{Gd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0, 0.04, 0.10$ and 0.15) crystals with a plate shape of dimensions about 0.3 mm x 0.3 mm x 0.1 mm were selected and mounted on a glass fiber. These large size crystals have been used in order to recognize even very weak extra reflections. The reciprocal space limited by $0 \leq h \leq 4, 0 \leq k \leq 4, 0 \leq l \leq 4$ has been tested at 293 K and 100 K with 4 different composition. The temperature dependent behaviour of the diffuse scattering has been qualitatively checked by cooling from 293 K to 100 K and then by heating from 100 K to 420 K with the speed 100 K per hour.

2. The powder diffraction X-ray studies

Synchrotron powder diffraction data were collected using the mar345 image plate detector for $\text{Gd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0, 0.04, 0.10$ and 0.15) in the temperature range $100 \text{ K} \leq T \leq 500 \text{ K}$. The wavelength 0.70023 was selected using a Si(111) double crystal monochromator, and the synchrotron beam was focused onto a spot size of 0.3 mm x 0.3 mm using a combination of curved mirrors and sagittally bent second crystal. All powder samples were filled into borosilicate capillaries of 0.2 mm diameter. A mar345 image plate detector was used to register the powder patterns. The sample-to-detector distance of 110 mm was calibrated using a LaB_6 reference powder. Exposure times were 30 s per image, and the speed of heating was 100 K per hour. The sample was rotated during the data collection at a speed of 1 degree per second. Exposure times were chosen to avoid any pixel saturation.

The main experimental results obtained

1. Despite our expectation, neither split nor extra reflections have been detected in the compound under consideration. No satellite reflections pointing to structure modulations could be observed.

2. Strong diffuse scattering were observed in all samples. The diffuse scattering areas have shape of $\{hh0\}$ walls crossing the Bragg reflections. Intensity of diffuse scattering is less in the sample without Zn and the intensity fall down by decreasing temperature. However, it is still clearly recognisable at 100 K.

3. Temperature dependence of the cubic unit cell parameter a and isotropic atomic displacements (Fig. 1) do not show any indication of a phase transition at any temperature within the $100 \text{ K} < T < 500 \text{ K}$ range.

4. 250 powder diffraction profiles obtained for each composition in the $100\text{ K} < T < 500\text{ K}$ range will be used for the analysis of the temperature- and composition dependence of intensity of the Bragg reflections and diffuse scattering.

5. The powder diffraction data obtained at 150 K, 300 K, 380 and 450 K for each composition will be used for the characterization of the anharmonic atomic displacements in the corresponding crystal structure.

The main temporary conclusions of the study

1. Diffuse scattering has been observed in $\text{Gd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0, 0.04, 0.10$ and 0.15) for the first time.

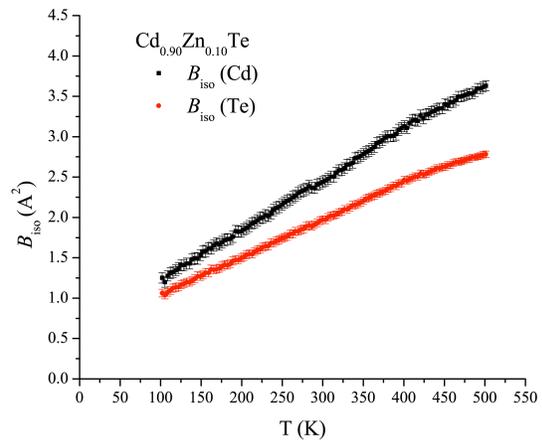
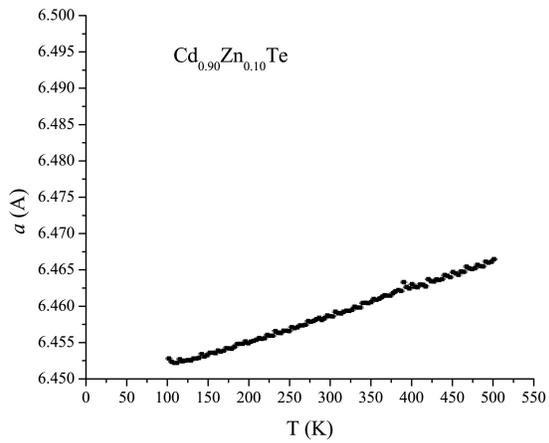
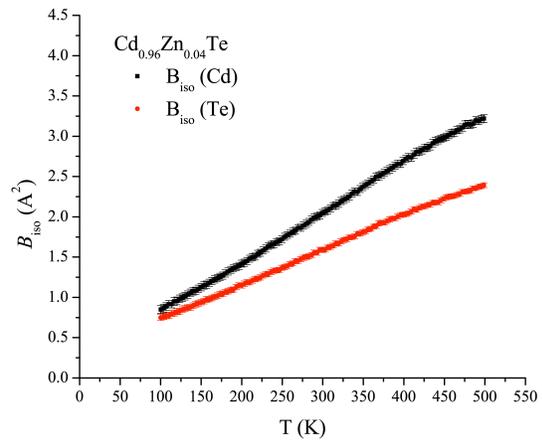
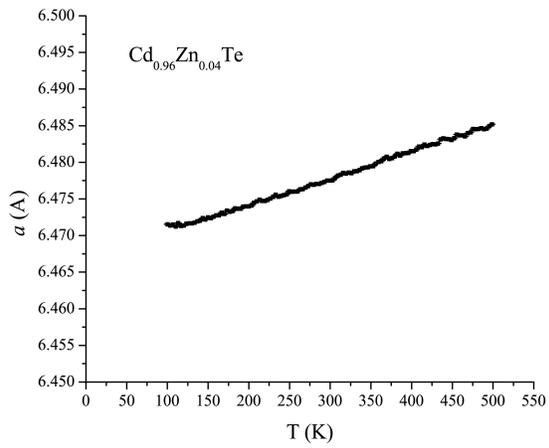
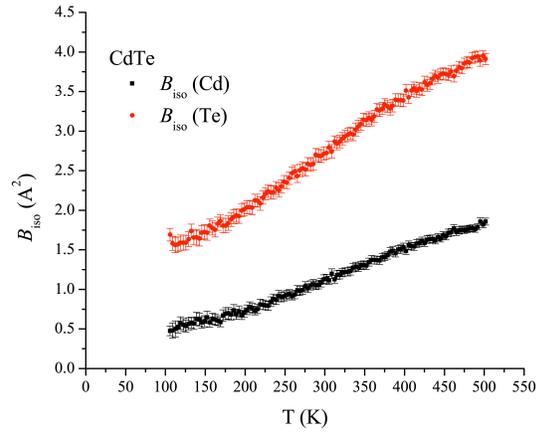
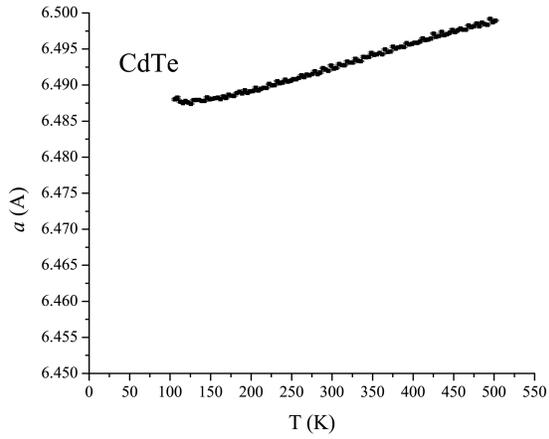
2. The temperature dependence of the cubic unit cell parameter and atomic displacements have been obtained for the first time for $\text{Gd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0, 0.04, 0.10$ and 0.15).

3. The ferroelectric - paraelectric phase transition at about 400 K could not be confirmed with the studied samples of $\text{Gd}_{1-x}\text{Zn}_x\text{Te}$ with $x = 0, 0.04, 0.10$ and 0.15 .

Treatment and analysis of the experimental results are in a progress.

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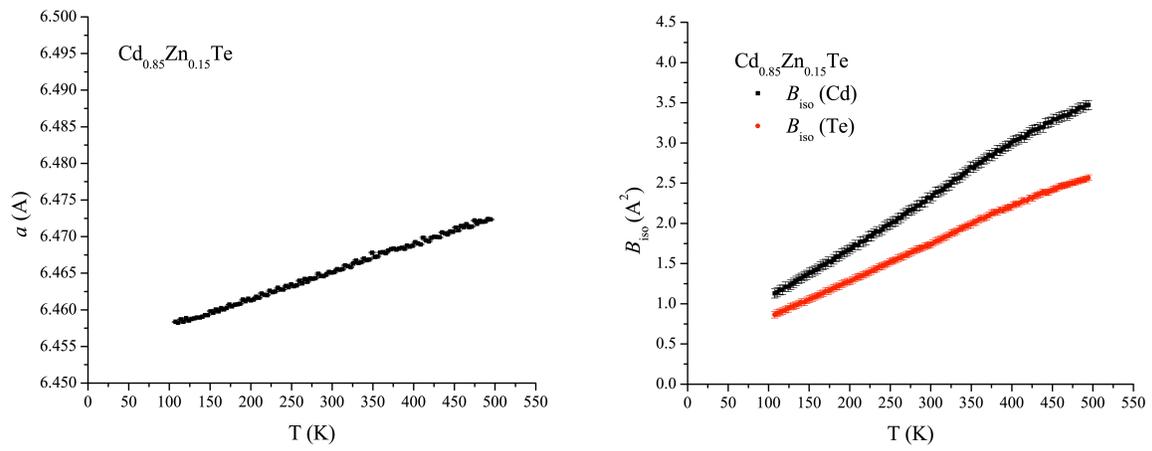


Fig. 1. Temperature dependence of the cubic unit cell constant a (left) and isotropic atomic displacements (right) for GdTe, $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$, $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ and $\text{Cd}_{0.85}\text{Zn}_{0.15}\text{Te}$ (from top to bottom, respectively).