XAFS and XRD Studies of the Cd$_{1-x}$Zn$_x$Te Crystal Fine Structure

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Abstract. Cd$_{1-x}$Zn$_x$Te crystal is a new kind of room temperature semiconductor radiation detector material developed in recent years. Cd$_{1-x}$Zn$_x$Te is zinc-blende structure, which is similar to CdTe, but the fine structure of Cd$_{1-x}$Zn$_x$Te ternary compound semiconductor is different from CdTe and ZnTe binary compound semiconductors. In this contribution, the fine structure of Cd$_{1-x}$Zn$_x$Te has been studied by the synchrotron radiation X-ray absorption fine structure (XAFS) technology and X-ray diffraction (XRD) technology. The K-edges XAFS spectra of cadmium, zinc and tellurium in Cd$_{1-x}$Zn$_x$Te have been obtained, and the differences between the structures of binary and ternary compound crystals have also been analyzed. The Fourier transform of the $k^2$-weighted absorption spectra prove that Zn atoms occupy the position of the Cd atoms. The bond lengths of Cd$_{1-x}$Zn$_x$Te have also been obtained by extended X-ray absorption fine structure (EXAFS), and the results imply that the local atomic structure of Cd$_{1-x}$Zn$_x$Te is distorted. The doping of Zn in the structure contributes to the distortion, which should be responsible for the different properties in Cd$_{1-x}$Zn$_x$Te. Normalized X-ray absorption near-edge structure (XANES) spectra on Cd K-edge, Zn K-edge and Te K-edge in CdTe, Cd$_{0.96}$Zn$_{0.04}$Te, Cd$_{0.9}$Zn$_{0.1}$Te and ZnTe are also shown.

1. Introduction

II - VI ternary compound semiconductor Cd$_{1-x}$Zn$_x$Te is a new kind of room temperature semiconductor radiation detector material developed in recent years. In 1989, R. weil et al. found that Cd$_{1-x}$Zn$_x$Te is ferroelectric[1]. This is the first example of ferroelectricity in zinc-blende-based systems. D. J. Fu et al. [2] found the hysteretic behaviour of the electrical polarization and the electrical conductivity of this material. However, ferroelectricity is forbidden in the zinc-blende structure adopted by pure CdTe, and it implies that Zn doping provokes a lattice distortion and reduces the symmetry[3]. Most of the polarization hysteresis measurements reported in the literature have been performed on compositions with low Zn content, such as Cd$_{0.96}$Zn$_{0.04}$Te, but no structural distortions have been reported for such low Zn concentration. Recent diffraction studies employing synchrotron radiation of Cd$_{0.7}$Zn$_{0.3}$Te crystals revealed an undistorted zinc-blende structure[4].

Cd$_{1-x}$Zn$_x$Te was thought as a solid solution semiconductor mixed by CdTe and ZnTe, so the lattice constant can be adjusted by the value of x. Because of Zn doping, Cd$_{1-x}$Zn$_x$Te has a more covalent bonding and higher stacking fault energy compared to CdTe crystal, which reduces the dislocation density and twin formation[5].
Here, the fine structures of Cd$_{1-x}$Zn$_x$Te crystals have been studied by XRD and XAFS techniques. As XAFS signal is sensitive to the local structure and chemical state of X-ray absorbing atom, this experimental technique constitutes a powerful tool for the objective of this study.

2. Experimental

The samples of CdTe, Cd$_{0.96}$Zn$_{0.04}$Te, Cd$_{0.9}$Zn$_{0.1}$Te and ZnTe were grown by the modified vertical Bridgman (MVB) method in our laboratory. Powder samples with a grain size in the micrometer range were obtained by grinding single crystal samples.

XRD studies were made with PANalytical's X'Pert PRO Materials Research Diffractometer using Cu K$_\alpha$ radiation (λ=0.15406 nm).

The X-ray absorption data of the samples were recorded at room temperature at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The Cd K-edge, Te K-edge and Zn K-edge were measured in transmission mode using ion chambers or in the fluorescent mode with silicon drift fluorescence detector. XAFS data were analyzed using the IFEFFIT code$^6$. A non-linear best fit of theoretical to experimental spectra has been performed by using FEFF8 code$^7$ and the graphical interface Artemis$^8$.

3. Results and discussion

![Figure 1. XRD diffraction patterns of CdTe, Cd$_{0.96}$Zn$_{0.04}$Te, Cd$_{0.9}$Zn$_{0.1}$Te, and ZnTe powder samples](image)

From Fig.1, we found that the average bond length of Cd$_{1-x}$Zn$_x$Te crystal decreased with the increase of x. The results are agreed with the VCA model, Vegard’s law$^9$.

| Crystal          | Spacing of (400)/Å | Lattice constant/ Å | Average bond length/ Å |
|------------------|--------------------|---------------------|------------------------|
| CdTe             | 1.6200             | 6.480               | 2.8059                 |
| Cd$_{0.96}$Zn$_{0.04}$Te | 1.6196             | 6.478               | 2.8051                 |
| Cd$_{0.9}$Zn$_{0.1}$Te  | 1.6145             | 6.458               | 2.7964                 |
| ZnTe             | 1.5252             | 6.101               | 2.6418                 |
Fig. 2. The lines are Fourier transform of the k^2-weighted absorption spectra on Cd (a) in CdTe, Cd_{0.96}Zn_{0.04}Te, Cd_{0.9}Zn_{0.1}Te, and ZnTe, and the circles represent the fitting results.

The local structure of CdTe, Cd_{0.96}Zn_{0.04}Te, Cd_{0.9}Zn_{0.1}Te, and ZnTe were studied with EXAFS at the Cd K-edge, Zn K-edge and Te K-edge, and the Fourier transform of the k^2-weighted absorption spectra on Cd (Fig. 2 a), Zn (Fig. 2 b), and Te (Fig. 2 c) are presented. The Fourier transformed spectra do not change its character significantly with different Zn contents in our samples. The similarity in shape of the first-neighbor Te peak with the cation Zn or Cd as central atom (with R between 1.5 and 3 Å) can be observed in Fig. 2. So the Zn atoms occupy the position of the Cd atoms can be educed.

In Fig. 2, simulated EXAFS spectra were also generated using Aterm is, based on the known lattice constants calculated by XRD. The bond lengths were fixed according to FEFF8 code. The absorption spectra of Cd and Zn are best fitted with first neighbour Te-shell to the Zn and Cd as central atom in terms of width, amplitude, and position as seen in the Fourier transformed spectra. The Fourier transformed spectra of Te have are best fitted with two distinct bond lengths (Te-Cd and Te-Zn). The results list in Table 2.

### Table 2. The results of the EXAFS data fits for first shell around Cd atom and Zn atom

| Bond length/Å | Coordination number | σ²        | ΔE₀/eV  |
|---------------|---------------------|-----------|---------|
| Cd-Te(CdTe)   | 2.798               | 4         | 0.005890| 1.841   |
| Cd-Te(Cd_{0.96}Zn_{0.04}Te) | 2.798 | 4 | 0.006309| 1.978   |
| Cd-Te(Cd_{0.9}Zn_{0.1}Te) | 2.797 | 4 | 0.006019| 1.746   |
| Zn-Te(ZnTe)   | 2.635               | 4         | 0.006759| 3.325   |
| Zn-Te(Cd_{0.96}Zn_{0.04}Te) | 2.658 | 4 | 0.006361| 3.286   |
| Zn-Te(Cd_{0.9}Zn_{0.1}Te) | 2.654 | 4 | 0.006778| 3.161   |
The results imply that the local atomic structure of ternary compound semiconductor is distorted. It can be observed that the local bond lengths are deviated strongly from Vegard’s law as given by XRD data. The results imply the bond lengths retain the values of pure compounds than to the average bond length measured by XRD. As we know above, Zn atoms take place of the Cd atoms in Cd_{1-x}Zn_xTe crystal. So one (or more) of the four chemical bonds connected with Te is short than the others, and this leads to the distortion of local structure. The distortion reduces the symmetry of Cd_{1-x}Zn_xTe crystal. Because of the asymmetry of the Cd_{1-x}Zn_xTe crystal, the centers of positive and negative charges cannot coincide, and the crystal has a spontaneous electric polarization. So structural distortion exists in Cd_{1-x}Zn_xTe with low Zn content, and it may be related with the hysteresis of the electric polarization and ferroelectricity.

The Zn-Te bond is stretched with doping of Zn, so it is reasonable to consider the Cd-Te bond is compressed. Cd-Te bond-length of the Cd_{1-x}Zn_xTe is shorter than that of pure CdTe, so the Cd-Te bond in Cd_{1-x}Zn_xTe is stronger, which should be responsible for the low density of dislocation and twin formation in Cd_{1-x}Zn_xTe.

Fig.3 shows the comparison of X-ray absorption near-edge structure (XANE) spectra on the Cd K-edge, Zn K-edge and Te K-edge in CdTe, Cd_{0.96}Zn_{0.04}Te, Cd_{0.9}Zn_{0.1}Te and ZnTe. The XANES of Cd K-edge (Fig.3 a) are similar, which shows the Cd atoms have the same chemical state in CdTe, Cd_{0.96}Zn_{0.04}Te and Cd_{0.9}Zn_{0.1}Te. By comparing the XANES spectra of the Zn K-edge (Fig.3 b), we have found that state of valence electrons in Zn atoms are changed in ZnTe compared with Cd_{0.96}Zn_{0.04}Te, Cd_{0.9}Zn_{0.1}Te. The XANES of Te K-edge in ZnTe is different from that in CdTe, Cd_{0.96}Zn_{0.04}Te and Cd_{0.9}Zn_{0.1}Te (Fig.3 c). That means the states of the valence electrons of Te are similar in CdTe, Cd_{0.96}Zn_{0.04}Te and Cd_{0.9}Zn_{0.1}Te, but change a lot in ZnTe crystal. The spectra show above reveal the original state of Zn-Te bond has changed in Cd_{1-x}Zn_xTe. The XANES spectra of CdTe, Cd_{0.96}Zn_{0.04}Te, Cd_{0.9}Zn_{0.1}Te and ZnTe need further study to find out the differences.
4. Conclusion
From the XRD and XAFS data analysis, we can conclude that Zn atoms occupy the position of Cd atoms in Cd$_{1-x}$Zn$_x$Te crystal. Because of Zn doping, local atomic structure is distorted, and this distortion reduces the symmetry of Cd$_{1-x}$Zn$_x$Te crystal. Structural distortion exists in Cd$_{1-x}$Zn$_x$Te with low Zn content. Such distortion may be the reason of some special properties in Cd$_{1-x}$Zn$_x$Te crystal, such as ferroelectricity, low density of dislocation and twin formation. The XANES spectra show the different chemical states of Zn-Te bond in Cd$_{0.96}$Zn$_{0.04}$Te, Cd$_{0.9}$Zn$_{0.1}$Te and ZnTe.

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