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P 38

HIGH-TEMPERATURE STUDIES OF $Pb_{1-x}Cd_xTe$ SOLID SOLUTION: STRUCTURE STABILITY AND CdTe SOLUBILITY LIMIT

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1. Introduction

The solid solution of lead telluride with cadmium telluride constitutes an attractive system for developing of the mid-IR optoelectronic devices based on quantum dots. The thermo-electric properties of $Pb_{1-x}Cd_xTe$ solution are also considered as a basis of other possible devices. These applications are powered by extremely low solubility of both materials [1] resulting from the difference in their crystal structure - rock-salt (RS) for PbTe and zinc-blende (ZB) for CdTe. It was a reason that only polycrystalline ternary $Pb_{1-x}Cd_xTe$ bulk samples obtained by Bridgman growth technique were so far available. Recently, the successful growth of $Pb_{1-x}Cd_xTe$ single crystals of 1 ccm volume with (100) natural crystal facets, and Cd content up to 11 at.% by self-selecting vapour transport method (SSVG) [2] has been reported [3]. In the latter paper the X-ray diffraction revealed the single-phase RS crystal structure of obtained samples and their relatively high crystal quality confirmed by FWHM of 004 X-ray rocking curve of about 100 arcsec. The decrease of the lattice parameter with increasing Cd content x had linear character with $da/dx \approx -0.43$ Å for studied samples. The results of Hall effect and electrical conductivity measurements as well as the photoluminescence measurements were also obtained in the temperature range from 4.2 K to 300 K [3].

The goal of the present work was to study the structure properties of $Pb_{1-x}Cd_xTe$ solid solution at high temperatures (HT) and to get new information about the phase diagram corresponding to the system above mentioned.

2. Experimental details

In this work the analysis of selected structure properties of $Pb_{1-x}Cd_xTe$ (where x = 0; 0.013; 0.056; 0.096) were studied by X-ray diffraction measurements performed at temperatures ranging from 301 K to 1073 K. First, good quality single $Pb_{1-x}Cd_xTe$ crystals grown by SSVG method were powdered and analysed at room temperature (RT) using X'Pert Philips diffractometer and Cu $K_{\alpha 1}$ radiation. Later on, the HT measurements using a synchrotron radiation were carried out taking advantage of a powder diffractometer installed at the B2 beamline at Hasylab/DESY. The instrumental parallel-beam set-up included a Ge(111) double monochromator, and a curved on-site readable imaging plate [4]. The samples were prepared as a mixture of powdered $Pb_{1-x}Cd_xTe$ crystals and fine diamond powder. For sample mounting a thin-wall quartz capillary was applied. During all measurements the capillary rotates inside a graphite hitter. The radiation wavelength, λ = 0.5276 Å, was calibrated *in situ*, using the diamond standard (advantages of such calibration method have been described in Ref. [5]). For the analysis of the diffraction patterns Rietveld method using the Fullprof.2k (v. 2.70) program was applied [6].

3. Results and discussion

The results of preliminary X-ray diffraction measurements performed at RT confirmed a single-phase (RS) character of all investigated $Pb_{1-x}Cd_xTe$ solid solutions. Figure 1 presents the composition dependence of the lattice parameter value determined in Ref. [3] (shown by the dashed line), values of the lattice parameters corresponding to the samples investigated in the present paper are marked by the open circles in this figure.

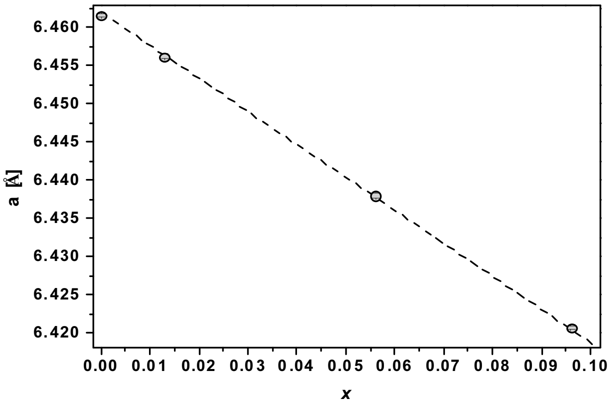

Figure 1. The initial lattice parameter value (determined by X-ray diffraction) versus the chemical composition of $Pb_{1-x}Cd_xTe$ solid solutions analysed in this paper. The dashed line was taken from Ref. [3].

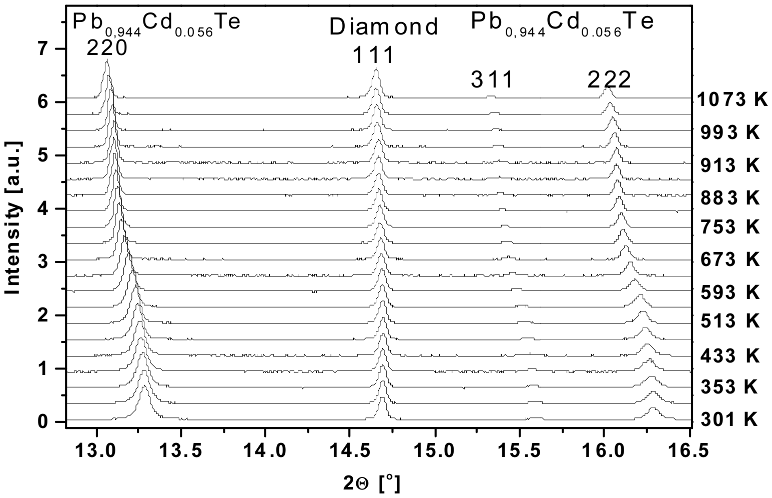

Figure 2. The temperature-dependent peak shift for the sample containing $Pb_{0.944}Cd_{0.056}Te$ solid solution (the diffraction patterns at limited angular range are shown).

Figure 2 shows a part of the temperature evolution of X-ray diffraction pattern taken with the use of synchrotron radiation for $Pb_{0.944}Cd_{0.056}Te$ sample. As one can see, the angular shift of Bragg peaks corresponding to the solid solution under studies is slightly different below and above the temperature of about 650 K. The 111 reflection from diamond powder being the internal standard in the analyzed sample is also seen in this figure. The similar data were obtained for other investigated samples.

The example of the result of Rietveld refinement, performed for the diffraction pattern collected at $T = 301$ K is shown in Fig. 3. The high quality of the analysis taking into consideration the single phase character of $Pb_{0.904}Cd_{0.096}Te$ solid solution and the diamond powder only excluded possible presence of other crystal phase in the investigated sample.

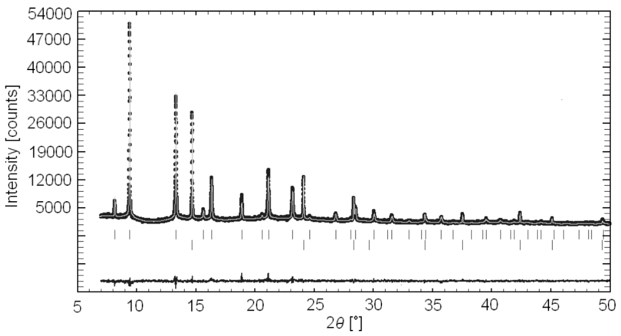

Figure 3. The Rietveld analysis of powder diffraction pattern obtained for the sample containing $Pb_{0.904}Cd_{0.096}Te$ solid solution and the diamond powder. Points: the experimental data taken with the use of synchrotron radiation, solid line: theoretical curve. The first and the second set of vertical bars correspond to $Pb_{0.904}Cd_{0.096}Te$ and diamond, respectively.

Due to the application of procedure above mentioned it was possible to demonstrate unexpected, non-monotonous temperature dependence of the lattice parameter value corresponding to every $Pb_{1-x}Cd_xTe$ sample with the initial x value different from zero. The comparison of dependences found for all measured samples is given in Fig. 4.

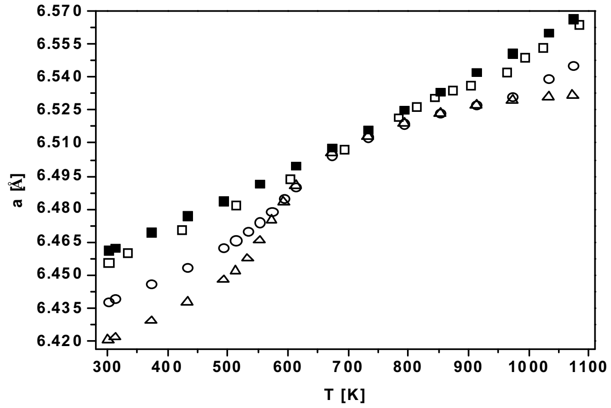

Figure 4. The lattice parameter value versus temperature for all $Pb_{1-x}Cd_xTe$ solid solutions analysed in this paper. Full squares: $x = 0$; open squares: $x = 0.013$; circles: $x = 0.056$; triangles: $x = 0.096$.

The scenario of the temperature evolution of sample structure, corresponding to $Pb_{1-x}Cd_xTe$ samples with $x > 0$ may be understood in the following manner. Due to a very rapid sample cooling from the growth temperature (being close to about 1100 K) to room temperature, applied in SSVG method [2, 3], a metastable solid solution was obtained. The exact chemical composition of this solution, determined prior to the accompagned by the HT studies with the use of synchrotron radiation, was far from that corresponding to the solubility limit. Thus, the 'initial' sample composition reflected the HT,'frozen' equilibrium state of the solid solution. A partial decomposition of the sample was clearly observed as the result of increasing sample temperature from about 500 K to 650 K. This effect was indicated by the increase of the lattice parameter significantly higher than the linear one expected on the basis of our data determined for pure PbTe (see Fig. 4). It means that some part of Cd present at the beginning in $Pb_{1-x}Cd_xTe$ solid solution is missing at higher temperatures. The same time possible creation of the second crystal phase (like, *e.g.*, Cd, Te, or ZB CdTe) was not observed. Due to the lack of new crystal phase at this temperature range one may suppose a creation of an amorphous CdTe precipitates or clusters in the sample. The minimal chemical composition of every solid solution, observed in the present studies, was close to $x = 0.01$ and corresponded to the temperature of about 650 K. It should be stressed that this composition value does not depend on the 'initial' sample composition, as it was demonstrated in Fig. 4. This finding may be interpreted as the real CdTe solubility limit in PbTe for the temperature indicated above. Further increase of temperature resulted in a partial dissolution of CdTe in $Pb_{1-x}Cd_xTe$ and finally at some, high temperature the final solid solution composition was about the same as that at the beginning of measurements. One may suppose that at this last temperature the second phase (not visible in the diffraction patterns) disappears and the solid solution under investigation starts to be once more one-phase and uniform material. The only exception was the sample initially determined as $Pb_{0.904}Cd_{0.096}Te$ solid solution. After the measurements performed at high temperatures and cooling down this sample back to RT the ZB CdTe precipitates were observed and the chemical composition of the final solid solution was estimated as equal to $x \approx 0.08$.

The scenario described above is not new. The possible creation of temperature activated precipitates in systems composed of two substances characterized by a broad miscibility gap has been reported and discussed in the literature for a few systems composed of selected II-VI and IV-VI semiconducting compounds exhibiting ZB (or wurtzite) structure and RS structure, respectively [7-10]. The new results presented in this paper completed published previously phase diagram for PbTe-CdTe system [8, 11] limited in the past to temperatures above 870 K and solid solution compositions exceeding the value $x = 0.05$.

4. Conclusions

Due to the access to bulk $Pb_{1-x}Cd_xTe$ solid solution it was possible to contribute to the phase diagram of this system for $x < 0.1$ and $T < 1100$ K. In particular, new information concerning the CdTe solubility limit in PbTe was obtained. Such findings may have important influence on the optimization of material devoted to possible future applications.

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