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$Pb_{1-x}Mn_xTe$ single crystals and their structural properties

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Abstract: $Pb_{1-x}Mn_xTe$ crystals were grown by the vertical Bridgman method. Their structural properties were observed both by optical microscopy after chemical polishing and ething, and by X-ray powder diffraction analysis. A solution of 5 vol. % Br_2 in HBr at room temperatur, for an exposure of 2 min was determined for chemical polishing. A solution of 20 g KOH in 1 ml H_2O_2, 2 ml glycerol ($C_3H_8O_3$), and 20 ml H_2O at room temperature for an exposure for 6 min was found to be a suitable etching solution. The obtained results are discussed and compared with published data.

Keywords: lead manganese telluride, Bridgman method, structural properties, etching, chemical polishing.

INTRODUCTION

Lead chalkogenides are well-known materials for infrared optoelectronics. They are mainly used for the production of lasers and LEDs operating in the middle and far infrared.[1,2] In addition to this, there has been considerable success in the construction of photodiode infrared photodetecting arrays with a large number of elements matched to a silicon substrate[3] or as a substrate for the growth of $Hg_{1-x}Cd_xTe$.[4]

The doping of lead telluride and some other narrow-gap IV–VI semiconductors with certain impurities results in the appearance of a range of strong and unusual effects that are not characteristic for the undoped material. The anomalous Hall effect (AHE) is a transport phenomenon well know in ferromagnetic metals and in magnetic semiconductors.[5] Among the materials which reveal a ferromagnetic phase, crystals of $Pb_{1-x}Mn_xTe$ offer a unique possibility of controlling parameters such as the concentration of carriers and the concentration of defects.[6] $Pb_{1-x}Mn_xTe$ crystals can be employed as low-dimensional thermoelectric materials in two-dimensional (2D) quantum well system,[7] in investigations about the

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effect of negative magnetoresistance and long-term non-equilibrium processes,[8] or as materials for the analysis of the nature of phonon dispersion relation anomalies of IV–VI compounds in the high symmetry phase.[9]

Off-centering of impurity atoms was registered in the sixties in KCl doped with Li.[10] This effect means that small impurity atoms which substitute for larger ones are displaced from the regular sites in a lattice by about 0.05–0.1 nm.[11] On that way a permanent dipole is formed and local conditions near the impurity atom are changed. The $Pb_{1-x}Mn_xTe$ ternary compound is one more candidate for studying this subject. $Pb_{1-x}Mn_xTe$ is a semimagnetic semiconductor that has not been sufficiently studied.[12–16] If the Mn concentration is less than 20 at.%, Mn enters the PbTe lattice as Mn^{2+} and is not an electroactive dopant. The solibility of MnTe in PbTe is ≈30 mol. % at 1170 K and ≈ 10 mol. % at 770 K,[17] and the concentration of electrons and holes does not exceed ≈ 10^{19} cm^{-3}. Doping of PbTe with Mn gives rise to a band gap which increases at a rate of $\partial E_g/\partial x \cong 40$ meV/mol. % MnTe, but does not lead to the appearance of local or quasi-local levels in the vicinity of the actual bands.[13] The local magnetic moments in the d shell of the Mn atoms have a strong exchange interaction with the free holes. In some cases, this interaction gives rise to a small negative magnetoresistance effect.[14] The aim of this work was to investigate the structural properties of $Pb_{1-x}Mn_xTe$ compounds as necessary information about these promising materials. These results could contribute to a better understanding of the vibrational structure of $Pb_{1-x}Mn_xTe$ single crystals and indicate the possibility of new-applications.

EXPERIMENTAL

The pseudo-binary alloys PbTe–MnTe, or $Pb_{1-x}Mn_xTe$, with a rock salt structure, were synthesized in evacuated silica glass ampoules at a temperature of 1280 K during about 10 h. The synthesized material was cooled rapidly in cold water (quenching) to obtain the best possible homogeneous alloy. $Pb_{1-x}Mn_xTe$ single crystals were grown by the standard Bridgman method. The temperature of the upper part of the furnace was about 50 K higher than the melting temperature of the material. The ampoule was placed in the melting zone for about 8 h. During this time, the material melted and homogeneously mixed. Subsequently, a device enabling the ampoule to be slowly lowered at a speed of 1 mm/h was switched on. The temperature gradient in the cooling zone was equal to about 50 K/cm. The ingots had diameters of 10 mm and lengths of about 50 mm. A series of specimens were prepared with Mn contents of 0.002, 0.02, 0.2, 2 and 10 at.%. The chemical compositions of the samples were checked by an electron microprobe, which revealed good chemical homogeneity of the material. The same results were obtained by the XRD powder technique.[18]

The specimens were cut parallel to (100) (the cleavage plane) with an inner blade diamond cutter and then mechanically polished. Chemical polishing was carried out with an exposure time of a 2 minute to solution of HBr containing 3 or 5 vol.% Br_2 at room temperature. Two etchants gave suitable etch-pits for optical investigations. One was a solution of 20 g KOH in 1 ml H_2O_2, 2 ml glycerol ($C_3H_8O_3$), and 20 ml H_2O at room temperature with an exposure time of 6 min and the other was a mixture of KOH saturated aqueous solution, ethylene glycol, and H_2O_2 with an exposure time of one minute. The presence of low-angle boundaries was observed by means of microscopic examination on chemically etched samples.

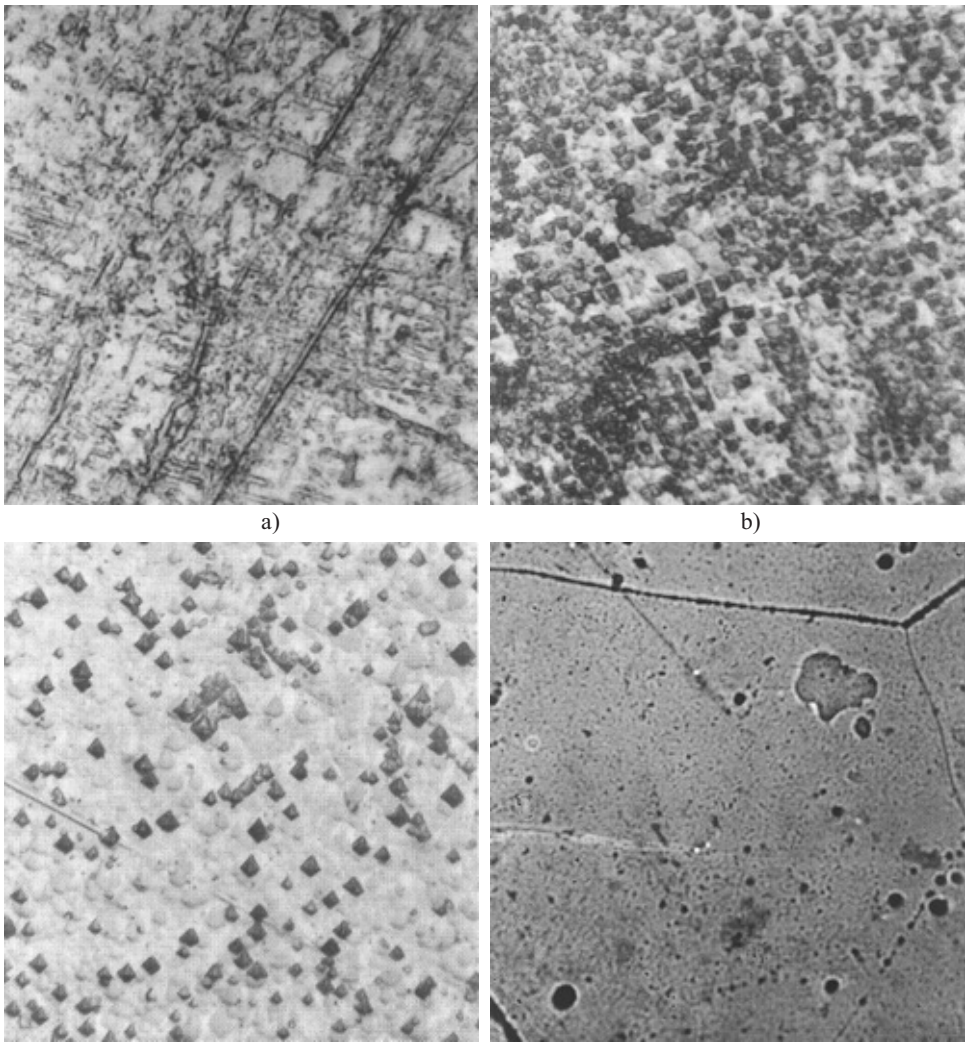
The chemical compositions of the products were determined by the XRD powder technique. All the samples were examined under the same conditions, using a Philips PW 1729 X-ray genera-

tor, a Philips 1710 diffractometer and original APD software. The radiation source was an X-ray LLF tube with copper radiation and a graphite monochromator. The radiations were $\lambda CuK\alpha_1$ = 0.154178 nm and $\lambda CuK\alpha_2$ = 0.154438. The anode tube load was 40 kV and 30 mA. Slits of 1.0 and 0.1 mm were fixed. The samples were pressed into standard aluminium frames and measured in the 2θ range from 10° to 100°. Each 1/50° (0.02°) was measured for 0.5 s. For product identification, the MPDS program and JCPDS (ASTM) card files were used.

RESULTS AND DISCUSSION

Lead telluride containing manganese as an impurity belongs to a group of materials called semimagnetic semiconductors.[19] Semimagnetic semiconductors contain transition group metals or rare earths. The interaction of the electrons and holes with the electron spins of the d and f shells of the magnetic impurity induces a modification of the electron band structure of these materials. The widely known etch pit technique is very suitable for the studying crystalline solids. For such studies, cleavage planes are often preferred to the mature surface, because the former are free from the usual growth features and the characteristic surface marking which affect each of the patterns produced. It was found[20] that a mixture of 25 ml saturated aqueous solution of KOH, 25 ml ethylene glycol and 1 ml H_2O_2 is a suitable etching solution (etchant) for $Pb_{1-x}Sn_xTe$ crystals. As no etchant for $Pb_{1-x}Mn_xTe$ crystals was found in the literature, the above solution was used. The etchant produced sizable pits with the characteristic shape of the (100) plane in about 1 minute at room temperature. Microscopic observation of the chemically etched (100) surfaces also revealed other structural characteristics. It was confirmed that $Pb_{1-x}Mn_xTe$ single crystals and low-angle grain boundary free crystals were obtained in the cases of 0.002, 0.02, 0.2 and 2 at.% Mn. In the case of 10 % Mn, a polycrystaline material was obtained. Also, no cellular structure or metal inclusions were observed. A common procedure for the estimation of densities was used,[21–24] and the dislocation denstiy was estimated to be about 10^{-4} cm^{-2} which is lower than those cited in the literature. Another etchant,[25] also formulated for $Pb_{1-x}Sn_xTe$, consisting of a solution of 20 g KOH in 1 ml H_2O_2, 2 ml glycerol ($C_3H_8O_3$), and 20 ml H_2O at room temperature was used and it was found that after an exposure time of 6 min well developed etch pits could be seen. Square pits with the characteristic shape for the (100) plane were clearly visible. Comparing the two mentioned solutions, it was concluded that the second etching solution gives better etch-pits picture of $Pb_{1-x}Mn_xTe$ crystals. Figure 1 shows the etch pits for $Pb_{1-x}Mn_xTe$ samples with 0.002 (a), 0.2 (b), 2 (c) and 10 % (d), respectively. The sample with 10 % Mn is polycrystaline and in Fig. 1 (d) boundaries between three grains can be dearly seen. The estimated dislocation densities were about 10^6 cm^{-6} which are in accordance to the values reported in the literature.

Prior to the chemical etching, the samples were chemicaly polished to remove surface damage using solutions of 3 % Br_2 or 5 % Br_2 in HBr. The best results were obtained using the solution of 5 % Br_2 in HBr at room temperature after an exposure time of 2 min.



a) b)

c) d)

Fig. 1. Photographs of the etch-pits for $Pb_{1-x}Mn_xTe$ samples with 0.002 %Mn (a), magnification 2920×; 0.2 %Mn (b), magnification 4600×; 2 % Mn (c), magnification 3100×, and 10% Mn (d), magnification 860×.

The structural properties were obtained using X-ray diffraction analysis of powdered samples. A Philips PW 1710 difractometer was used in the 2θ ranges from 10° to 100°. The unit cell of $Pb_{1-x}Mn_xTe$ was calculated by the least square method and, for example, for the $Pb_{0.98}Mn_{0.02}Te$ single crystal grown by Bridgman method, using 12 reflections including more $K\alpha_2$ for 1 reflection. All the reflections corresponded to PbTe crystals[26] and gave the parameter of the cubic unit cell a = 0.6459 (5) nm and $V = 0.26946$ nm^3. Some divergence of the compared results can be explained by the fact that X-ray powder diffraction analysis gives a statistical result

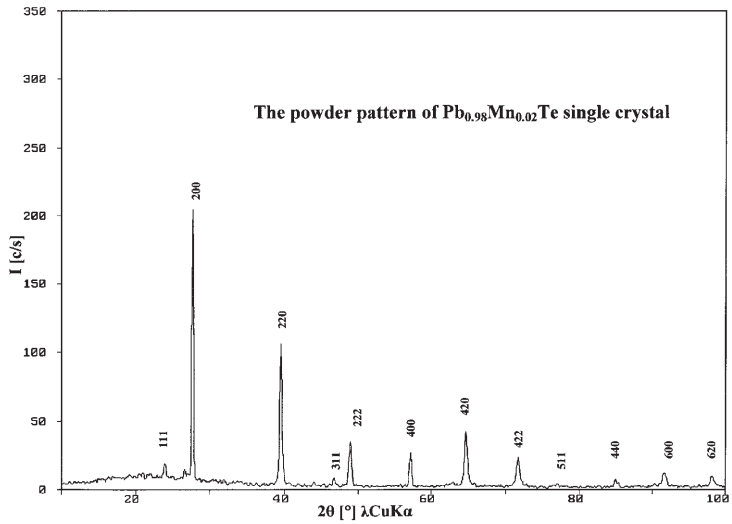


Fig. 2. Powder pattern of $Pb_{0.98}Mn_{0.02}Te$ single crystals grown by the Bridgman method.

and that the Mn atoms entering the unit cell produce some contractions as the Mn atom is smaller than the Pb atom. Our calculated results for the lattice parameters are a = 0.6448 (3) nm and V = 0.2681 (4) nm^3, which are in good agreement with the published data. An X-ray difractogram of powdered $Pb_{0.98}Mn_{0.02}Te$ is given in Fig. 2.

The small peaks in Fig. 2 at 2θ = 21.23° and 26.615° belong to quartz (silica glass) as the ampoule was made from this material. This can be avoided by using graphitised ampoules during the crystal growth run.[27] Some divergences between the experimentally obtained 2θ values and the literature values could be explained as being the consequence of the used wavelength $\lambda CuK\alpha_1$ and $\lambda CuK\alpha_2$ (0.154178

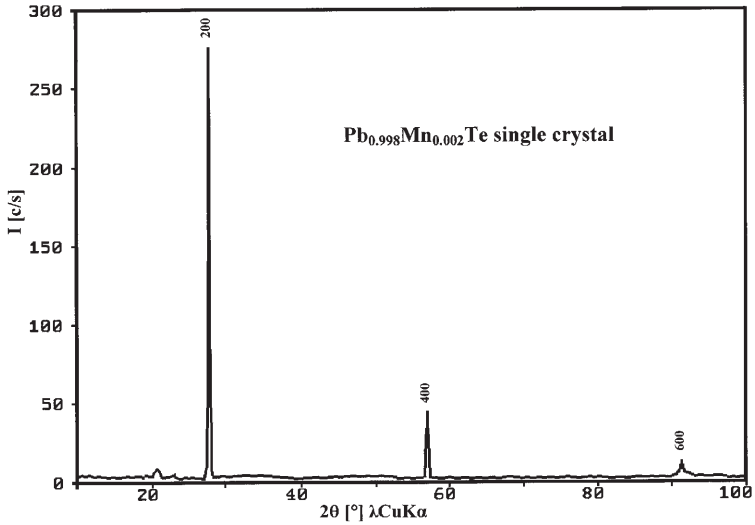


Fig. 3. Reflection spectrum of a $Pb_{0.998}Mn_{0.002}Te$ single crystal growth by the Bridgman method.

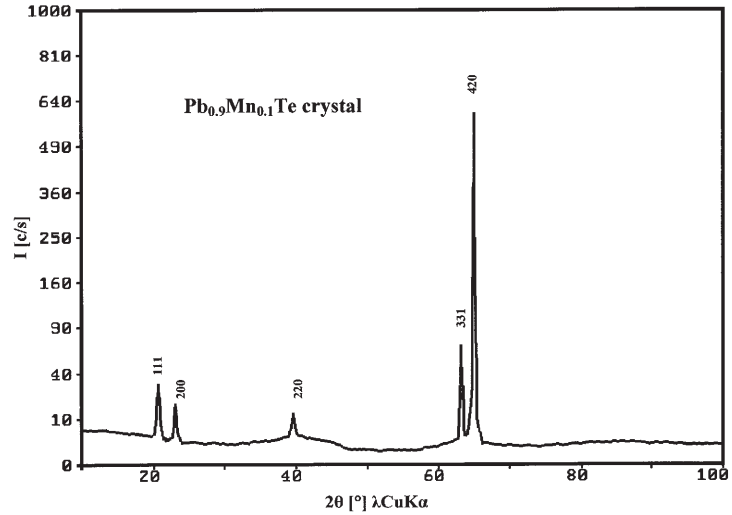


Fig. 4. Reflection spectrum of a $Pb_{0.9}Mn_{0.1}Te$ crystal grown by the Bridgman method.

nm and 0.154438 nm) and the CuKα_1 cited in the literature[28] (0.15405 nm). Also, it should be noted that X-ray difraction analysis confirmed that $Pb_{1-x}Mn_xTe$ single crystals were obtained.

The X-ray spectrum of the reflections for a $Pb_{0.998}Mn_{0.002}Te$ single crystal is shown in Fig. 3. Three peaks, belonging to the (*h* 00) family can be seen. These are from the (200), (400) and (600) planes. The plane (100) has no reflections[26] and, as a consequence of this, the (*h*00) family appears. This is in accordance with the general principles of X-ray diffraction.[29]

The X-ray spectrum of the reflection for a $Pb_{0.9}Mn_{0.1}Te$ crystal is shown in Fig. 4. It can be seen from Fig. 4 that the crystal has 5 reflections, *i.e.,* from the (111), (200), (220), (331) and (420) planes, which do not belong to the same family, and it was not a single crystal. This picture confirms a previous observation that the sample with 10 % Mn does not agree with the Vegard rule.[18] The diagram of the lattice constant *vs*. the mole faction of manganese *x* for $Pb_{1-x}Mn_xTe$ single crystals obtained by the Bridgman method also showed (relative errors were about, 0.1%) that the samples obey the Vegard rule. It was found in the literature[30] that the content of Mn can be extended up to 12 %, and for this reason the employed concentrations were chosen. The lowering rate was the same (1 mm/h) for all contents of Mn in the Bridgman grown crystals, as cited in the literature,[19,31] but this rate was suitable especially for the sample with 2 % Mn (this can be seen from Fig. 1). From the well known Burton–Prim–Slichter theory and the equation for the distribution of constituents along the growth axes[32]

$$c_S = k_{eff} c_0 (1 - g)^{k_{eff}^{-1}} \quad (1)$$

where c_S, c_0, k_{eff} and g are solute concentration in the solid, original melt concentration, effective distribution coefficient and solidified fraction, respectively, k_{eff} can expressed by:

$$k_{\text{eff}} = \frac{1}{1 + \left(\frac{1}{k_0} - 1\right) \exp\left(-\frac{R\delta}{D}\right)} \tag{2}$$

where k_0 – equlibrium distribution coefficient, R – crystal growth rate, δ – thickness of diffusion layer, D – diffusion coefficient. Hence, it is clear that the crystal growth rate (lowering rate in the case of the Bridgman method) has to be changed if single crystals with various contents of Mn are to be obtained. Our specimen with the lowest concentration of Mn was the worst, although the lattice parameter is not bigger enough to change the material from being single crystal to polycrystalline.

CONCLUSION

$Pb_{1-x}Mn_xTe$ single crystals with $x \leq 0.02$ were grown by the Bridgman method with a lowering rate of 1 mm/h and their lattice constants agreed with the Vegard rule. This was confirmation of the results of previous experiments.[18]

A solution of 5 vol. % Br_2 in HBr at room temperature after an exposure of 2 minutes was shown to be suitable polishing solution.

A solution of 20 g KOH in 1 ml H_2O_2, 2 ml glycerol ($C_3H_8O_3$), and 20 ml H_2O at room temperature after an exposure for 6 min was found to be a suitable etching solution.

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ИЗВОД

МОНОКРИСТАЛИ $Pb_{1-x}Mn_xTe$ И ЊИХОВЕ СТРУКТУРНЕ ОСОБИНЕ

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Кристали $Pb_{1-x}Mn_xTe$ су добијени методом раста по вертикалном Брицману. Структурне особине су посматране оптичком микроскопијом после хемијског полирања и нагризања и рендгенском дифракцијом праха. За хемијско полирање је одређен раствор од 5 зап.% Br_2 у HBr на собној температури при излагању од 2 минута. Раствор од 20 g KOH у 1 ml H_2O_2, 2 ml глицерола ($C_3H_8O_3$) и 20 ml H_2O на собној температури при излагању од 6 минута се показао као погодно средство за нагризање. Добијени резултати су дискутовани и упоређивани са подацима из литературе.

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