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High-pressure X-ray diffraction study of ternary and non-stoichiometric PbTe and PbSe crystals

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The paper reports the pressure-induced phase transitions observed in ternary PbTe and PbSe compounds ($Pb_{1-x}Sn_xTe$, $Pb_{1-x}Mn_xTe$, $Pb_{1-x}Sn_xSe$) and non-stoichiometric PbTe ones ($Pb_{0.55}Te_{0.45}$, $Pb_{0.45}Te_{0.55}$) at room temperature in the range of 0 to 14 GPa by means of angle-dispersive X-ray diffraction (ADXRD). The structure of the intermediate high-pressure phase appearing above ~6 GPa for all PbTe-based compounds was established to be Pnma (orthorhombic), like in binary PbTe. The patterns of the intermediate high-pressure phase of $Pb_{1-x}Sn_xSe$ ($x = 0.125$) were found to correspond entirely neither to GeS nor to orthorhombic Pnma, but the calculated reflections for GeS type were closer to the experimental ones. A model of the phase transformations is discussed.

1 Introduction

Lead chalcogenides PbX (X – Te, Se, S) are narrow-gap semiconductors which are applied as sensors of infrared radiation, thermoelectric devices, photoresistors, lasers and other electronic devices [1, 2]. Doping with different impurities (Sn, In, Mn, Cu, Ag, Cd, Ga, Sb, et al.) and growing of non-stoichiometric compounds have been reported to be effective tools for goal-directed variation of properties of their semiconducting phases [3].

The direct energy gaps of binary PbTe, PbSe and PbS at L-point of Brillouin zone at $T = 300$ K are $E_g \approx 0.29$, 0.27 and 0.41 eV, respectively [1, 2]. Under pressure these minerals undergo the structural transitions from ambient fcc (face-centred-cubic) NaCl lattice (space group Fm3m) to an intermediate high-pressure phase above $P \sim 2.5-6$ GPa, and then above $P \sim 12-21$ GPa to the metal bcc (body-centred-cubic) CsCl lattice [4]. The above transformations were already investigated by a set of different

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techniques, including structural X-ray diffraction [4–6], Raman scattering [7], the electrical resistance [8–12], thermopower [11–13], the Hall effect [14], and thermomagnetic Nernst–Ettigshausen effects [15, 16]. Meanwhile, until present a lattice of the intermediate high-pressure phase was not exactly detected [4, 5].

The intermediate high-pressure phase was found to be a narrow-gap semiconductor with the estimated room-temperature energy gaps around 0.1, 0.4, and 0.6 eV for PbTe, PbSe, and PbS, respectively, as obtained from the thermopower measurements [11, 12]. Due to the low transition pressures, this phase is promising for electronic applications, for example, for thermoelectric generators with the improved thermoelectric parameters [13]; this circumstance motivated investigation of its structural properties. The transformation from NaCl into the high-pressure phase is accompanied by both a sharp change of the electrical resistivity [8, 9, 11, 12] and abrupt drop of the thermopower [11–13] in PbS and PbSe single crystals, while only by the slight changes in PbTe [11–13]. Both the thermomagnetic longitudinal and transverse Nernst–Ettingshausen effects inverted their signs during the above transition in PbSe, pointing to a change of sign of scattering parameter of charge carriers [15, 16], while, no inversion was registered in PbTe [15, 16]. These results agree with the propositions about similarity of the intermediate high-pressure phases for lighter compounds PbS and PbSe, and its difference from the one of heavier compound PbTe [5, 17]. The intermediate phases of PbS and PbSe were attributed to GeS structural type [5], and only recently the intermediate phase of PbTe was deciphered near $P \sim 6$ GPa to be an orthorhombic Pnma lattice [6].

The aim of the present work is to study the structure of the intermediate high-pressure phases in some ternary ($Pb_{1-x}Mn_xTe$ ($x = 0.05$), $Pb_{1-x}Sn_xTe$ ($x = 0.29$), $Pb_{1-x}Sn_xSe$ ($x = 0.125$)) and non-stoichiometric ($Pb_{0.55}Te_{0.45}$, $Pb_{0.45}Te_{0.55}$) lead chalcogenides.

2   Experiment

The measurements were carried out at room temperature in a high-pressure chamber with diamond anvils [18, 19] on a station of the fourth channel of the VEPP-3 accelerator at the Budker Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences [19] in 0.3675-Å monochromatic synchrotron radiation. An MAR-3450 image plate detector was used to detect diffracted radiation. To improve the quality of powder diffraction patterns, the chamber was swung around one axis by angle from $-3°$ to $+3°$. A sample was placed in a hole of ~ 0.2 mm diameter in a stainless-steel compressible gasket. Pressure in the transmitting medium (4 : 1 mixture of methyl and ethyl alcohols) was determined both by change in the silver lattice parameter with an accuracy ~ 0.1 GPa [18, 19] and from the shift of the ruby luminescence line [20]. The ruby luminescence spectra were excited by the 514.5-nm line of an argon laser. The diffraction data were analyzed by means of the FULLPROF program for the profile analysis (Rietveld method) [21] and the unit cell parameters were refined also using the XLAT program [21].

3   Results and discussion

The ADXRD patterns of some PbTe- and PbSe-based ternary crystals are presented in Fig. 1a and b, respectively. Figure 2 shows the ADXRD pattern of the non-stoichiometric $Pb_{0.45}Te_{0.55}$ crystal at a selected pressure. The initial NaCl (Fm3m) lattice was conserved in all PbTe crystals until $P \sim 5$ GPa. An appearance of the intermediate high-pressure phase was found at ~ 6.05, ~ 6.73, ~ 5.31, and ~ 6.53 GPa in $Pb_{1-x}Sn_xTe$ ($x = 0.29$), $Pb_{1-x}Mn_xTe$ ($x = 0.05$), $Pb_{0.55}Te_{0.45}$ and $Pb_{0.45}Te_{0.55}$, respectively. The transition was completed in ~ 2 GPa after the beginning. So, for case of $Pb_{1-x}Sn_xTe$ ($x = 0.29$), a heterophase region was found to exist from 6.05 GPa up to 7.82 GPa. Shifts in transition pressures P_t of non-stoichiometrics compounds agreed with the thermopower data [13] confirming that excess of Pb decreases P_t, while excess of Te increases that in comparison with stoichiometric binary PbTe. According to the thermopower data [13], the beginning of the phase transition in $Pb_{1-x}Mn_xTe$ ($x = 0.05$) was expected to occur at less pressure than in binary PbTe [6], but this divergence might by explained by a wide pressure step in synchrotron diffraction study (Fig. 1a). It is remarkably to note that a strong substitution
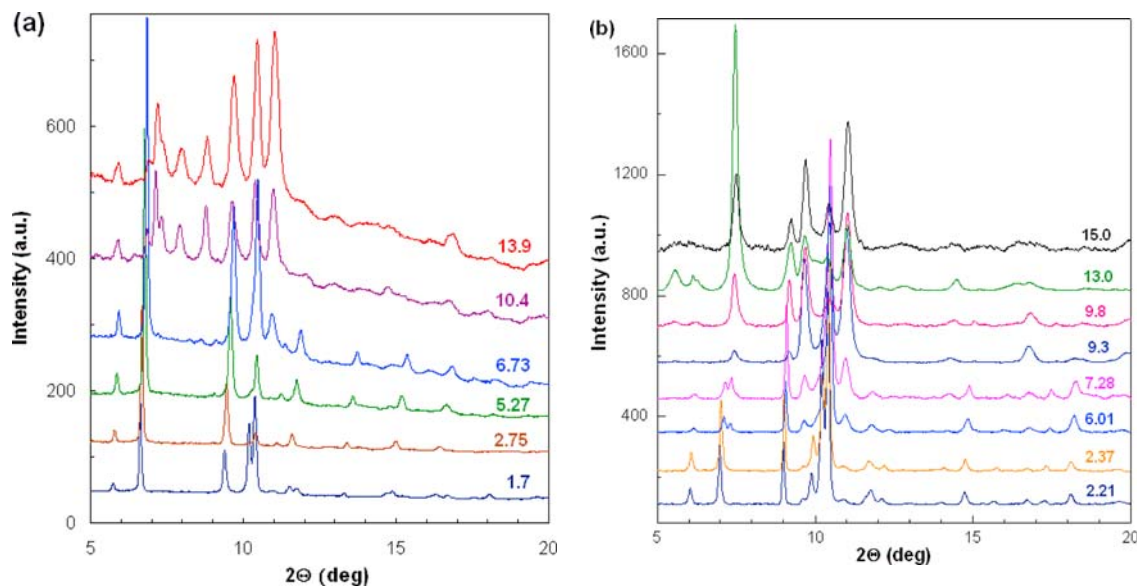
Fig. 1 (online colour at: www.pss-b.com)   Room-temperature diffraction patterns of $Pb_{1-x}Mn_xTe$ ($x = 0.05$) (a) and $Pb_{1-x}Sn_xSe$ ($x = 0.125$) (b) at selected pressures (in GPa near the curves) under pressurization.

by Sn (29 at%) did not result in any significant difference in high-pressure structural behaviour of PbTe. While from the thermopower S study, this composition is a p-type semimetal in the range of $0-15$ GPa in contrary to all the others [13], and the phase transition was hardly noticeable by $S(P)$ [13].

The diffraction patterns of the intermediate high-pressure phase of the all PbTe-based ternary crystals were satisfactorily described by the orthorhombic Pnma structural type as for binary PbTe (Fig. 1a) [6]. However, the peak intensities were not completely identical to the ones calculated for Pnma structural type. The difference was small and might be explained by elastic strains in powdery sample [6]. Compressibility of $Pb_{1-x}Mn_xTe$ ($x = 0.05$) was found to be higher than in the others tellurides (Table 1).

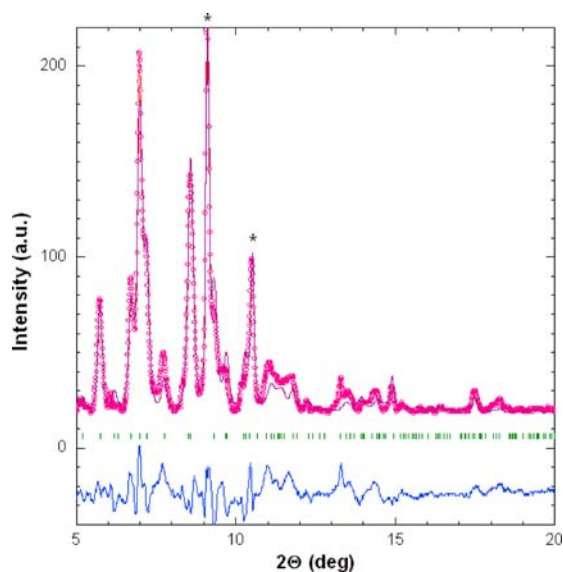**Fig. 2** (online colour at: www.pss-b.com)   Room-temperature diffraction patterns of the intermediate high-pressure phase of $Pb_{0.45}Te_{0.55}$ at $P = 7.44$ GPa. The dashes show the reflectance position for the orthorhombic Pnma phase, the stars point to the Ag reflections, the lower line denotes the difference between experimental and calculated intensities.

Lattice parameters of Pnma structure are related to the NaCl ones by the following ratios: a(Pnma) $= \sqrt{2} \cdot a$(NaCl), b(Pnma) $= (\sqrt{2}/2) \cdot a$(NaCl), c(Pnma) $= a$(NaCl); the coordinate origin of the unit cell is at the point (1/4, 1/2, 3/4), the a- and b-axes are oriented along the (110) direction of the NaCl phase. Estimated from the patterns a and b parameters were, respectively ~5–6% smaller and ~1.5–2% larger than the respective calculated data, while c was ~1% larger than parameter a of the NaCl lattice (Table 1).

Table 1 Lattice parameters of the samples investigated.

substance	pressure	lattice parameters (Å) of					atom positions at (Pnma/GeS) phase			
		NaCl	intermediate (Pnma for PbTe, GeS for PbSe)			CsCl	Pb (Sn, Mn)		Te (Se)	
	(GPa)	a	a	b	c	a	x	z	x	z
$Pb_{1-x}Sn_xSe$	2.21	6.0337								
($x = 0.125$)	2.37	6.0007								
	6.01	5.926	11.51	4.272	4.4157		0.1668	0.1381	0.7072	0.6879
	7.28	5.897	11.24	4.34	4.06		0.1604	0.1275	0.6826	0.587
	9.3		11.05	4.36	3.95		0.1668	0.1381	0.7072	0.6879
	9.8		11.04	4.35	3.955	3.86	0.1668	0.1381	0.7072	0.6879
	13.0		11.18	4.36	3.92	3.82	0.1668	0.1381	0.7072	0.6879
	15.0		10.98	4.34	3.91	3.79	0.1668	0.1381	0.7072	0.6879
$Pb_{1-x}Sn_xTe$	1.96	6.3505								
($x = 0.29$)	2.86	6.3169								
	3.34	6.302								
	4.58	6.262								
	6.05	6.241	8.157	4.505	6.337		0.5768	−0.1118	0.8427	0.9074
	7.82	6.174	8.117	4.44	6.269		0.5691	−0.1791	0.8416	0.8861
$Pb_{1-x}Mn_xTe$	1.7	6.3483								
($x = 0.05$)	2.75	6.303								
	5.27	6.2183								
	6.73	6.1493								
	10.4		8.031	4.369	6.152		0.5668	−0.1790	0.8309	0.8584
	13.0		7.858	4.462	6.141		0.5806	−0.1733	0.8680	0.8572
	13.9		7.998	4.345	6.144		0.5672	−0.1733	0.8177	0.8671
$Pb_{0.55}Te_{0.45}$	0.95	6.4121								
	1.09	6.4061								
	2.4	6.3584								
	3.87	6.3052								
	4.46	6.2815								
	5.31	6.2644	8.2286	4.5070	6.344					
	6.39		8.158	4.521	6.306					
	8.94		8.117	4.512	6.278					
$Pb_{0.45}Te_{0.55}$	0.58	6.4238								
	2.9	6.3520								
	4.41	6.3026								
	6.53	6.2554	8.2779	4.4562	6.3445					
	6.72	6.237	8.153	4.516	6.332					
	7.44		8.151	4.505	6.286					

In Pnma structure [6], the period of the initial NaCl lattice is doubled along the $[\bar{1}10]$ axis and the largest atomic displacement occurs in the [001] direction. Thus, new phase is formed from NaCl lattice by a distortion resulting in two-fold enlargement in period. So, a mechanism of the transition is probably a Peierls distortion [11, 12, 22, 23], and an energetic profit during the transformation is achieved by a splitting of conduction band and formation of forbidden gap at Fermi level [13].

In $Pb_{1-x}Sn_xSe$ ($x = 0.125$), the initial NaCl phase was conserved up to $P \sim 7.28$ GPa but the beginning of the transition into the high-pressure phase was missed because of a wide pressure step. Meanwhile, by the electrical resistivity and thermopower, this transition was seen above $P \sim 3$ GPa [11]. Appearance of the second high-pressure phase with CsCl lattice was noticed near $P \sim 9.8$ GPa (Table 1). The transition into CsCl lattice was not completed to 13 GPa, and the lattice parameters of this phase extracted from the patterns are approximate (Table 1). The patterns of the intermediate high-pressure phase existing at least in the range of $6.01-15$ GPa were not described entirely neither by GeS nor Pmna types, but the calculated reflections for GeS type were closer to experimental ones. The lattice parameters were determined for GeS (Table 1). So, either Sn substitution resulted in a diverse intermediate phase or lattice of the transient phase of PbSe is not exactly GeS as supposed [5, 24]. GeS structure may be obtained by a two-fold enlarging of lattice parameter of NaCl along the [001] axis [6], and the Peierls distortion mechanism of the transformation is also applicable [11, 12, 22, 23]. Notice, that the values of semiconductor gap of the intermediate high-pressure phases of PbSe and PbS with the proposed GeS structure are larger [11, 12], than one of PbTe at Pnma lattice implying a different type of distortion.

4 Conclusion

The high-pressure phase appearing above $P \sim 5.5-6$ GPa in PbTe-based crystals was established to have orthorhombic Pnma lattice, as in binary PbTe [6]. We found Sn dopant influences on high-pressure transport properties of PbTe but does not lead to a significant change of structural ones. Neither GeS nor Pnma lattices fit the ADXRD patterns of the intermediate high-pressure phase of $Pb_{1-x}Sn_xSe$ ($x = 0.125$).

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