Low-temperature phase transitions in some quaternary solid solutions of IV–VI semiconductors

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Abstract

Samples of $PbS_xSe_yTe_{1-x-y}$, $Pb_{1-x}Sn_xTe_{1-y}Se_y$ and $Pb_{1-x}Sn_xTe_{1-y}S_y$ quaternary solid solutions were investigated in the 4–200 K temperature range using electrical and X-ray methods. The regions where low-temperature phase transitions take place were established. It is shown that phase transitions in these solid solutions are associated with off-center S and Sn ions. The dependence of the phase transition temperature on the composition of solid solutions can be qualitatively described taking into account the influence of substitutional disorder on ordering and tunneling of off-center ions.

1. Introduction

IV–VI family narrow-gap semiconductors are widely used for optoelectronic and thermoelectric device fabrication. Although ternary solid solutions are used to tune the spectral characteristics of infrared (IR) lasers and photodetectors, higher performance of these devices can be achieved on heterostructures, which use both ternary and quaternary solid solutions.

The low-temperature ferroelectric phase transitions are interesting features of some IV–VI semiconductors. Such phase transitions were observed in binary GeTe and SnTe compounds, in $Pb_{1-x}Sn_xTe$, $Sn_{1-x}Ge_xTe$, $Pb_{1-x}Ge_xTe$ and $PbTe_{1-x}S_x$ ternary and some quaternary solid solutions [1–4]. The changes in the physical properties of these semiconductors induced by phase transition may be interesting for some applications. In particular, the weak temperature dependence of the energy gap near the phase transition temperature T_c may be used for the fabrication of continuously tunable lasers [5], and the strong reduction of tunneling currents in p–n junctions near T_c may be used to improve the characteristics of photovoltaic detectors [6]. As the temperature of the phase transitions (usually 20–200 K) lies within the working temperatures of IR devices, and there is not much information on low-temperature phase transitions in quaternary solid solutions, it was important to study the low-temperature phase diagrams of quaternary solid solutions in order to find out the regions where the phase transitions can affect the physical properties of solid solutions.

2. Experimental details

Studies of three quaternary solid solutions ($Pb_{1-x}Sn_xTe_{1-y}Se_y$, $Pb_{1-x}Sn_xTe_{1-y}S_y$ and $PbS_xSe_yTe_{1-x-y}$) were performed on the samples within the whole region of the stability of the room-temperature cubic phase. Single crystals as well as polycrystalline samples of n- and p-type were studied. Single crystals were grown by the sublimation method. Polycrystalline samples were prepared by alloying the appropriate amounts of binary compounds or ternary solid solutions in evacuated silica ampoules with subsequent annealing at 600–710 °C for 25–220 h. After annealing, the samples were cooled in air or quenched in cold water to prevent the decomposition of the solid solution. In order to obtain samples of p- or n-type conductivity, a small amount of excess Pb or chalcogen was added to the alloys. The homogeneity of the samples was checked by the X-ray method. Most of the investigation was performed on polycrystals in order to know the exact sample composition.

The temperature dependence of resistivity $\rho(T)$ for these crystals was studied in the range 4.2–200 K [7]. Figure 1 shows typical $\rho(T)$ curves for $PbS_xSe_yTe_{1-x-y}$ and $Pb_{1-x}Sn_xTe_{1-y}Se_y$ samples. The anomalous resistivity peaks associated with the scattering of free carriers by the ferroelectric fluctuations near the phase transition [8] are seen on most of the plots. The curves $\rho(T)$, obtained during heating and cooling (the directions of temperature change are shown by arrows in Fig. 1), differ in a wide temperature range around an anomalous resistivity peak. The difference between the peak po-
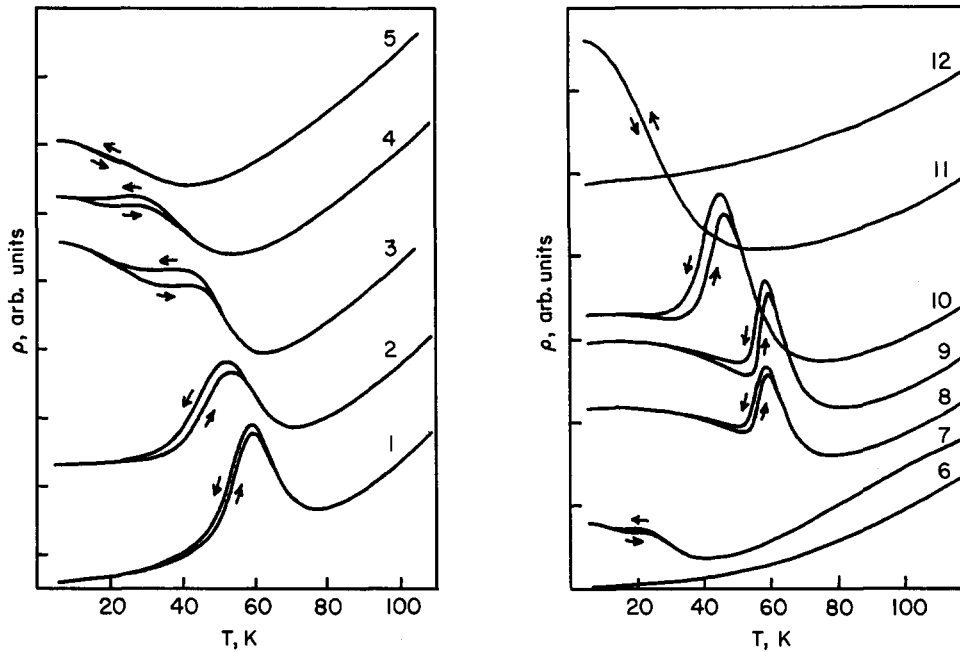
Fig. 1. Typical $\rho(T)$ plots for $PbS_xSe_yTe_{1-x-y}$ and $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solutions. Curves 1–5 correspond to the samples of $PbS_xSe_yTe_{1-x-y}$ with constant $x = 0.08$ and $y = 0.21$, 0.27, 0.34, 0.40 and 0.46, respectively. Curves 6–12 correspond to the samples of $Pb_{1-x}Sn_xTe_{1-y}Se_y$ with constant $x = 0.2$ and $y = 0$, 0.05, 0.25, 0.33, 0.5, 0.67 and 0.83, respectively. The curves are shifted arbitrarily along the vertical axis. The arrows show the direction of temperature change during recording of the curves.

sitions on heating and cooling was usually 1–3 K, so the phase transition temperature T_c was taken as the mean value of the anomalous resistivity peak temperatures. At low temperatures some $\rho(T)$ curves exhibited the enhancement of ρ with decreasing the temperature, so-called additional low-temperature scattering. The causes of the appearance of hysteresis and additional low-temperature scattering accompanying the phase transition in crystals were discussed in detail in our other papers [4, 9–11].

The phase transitions in $Pb_{1-x}Sn_xTe_ySe_{1-y}$ and $Pb_{1-x}Sn_xTe_yS_{1-y}$ crystals were studied by a low-temperature X-ray technique, which revealed the rhombohedral distortion of the lattice below T_c.

Figures 2–4 show the dependence of T_c on the composition of three quaternary systems studied (Pb–S–Se–Te, Pb–Sn–Te–Se and Pb–Sn–Te–S). The points in these figures correspond to compositions of samples. The solid curves are isotherms which are drawn after computer approximation of the experimental data.

3. Discussion

Our results show that in all three systems there are regions where low-temperature phase transitions take place. The manifestations of the phase transition in the electrical properties of these solid solutions were similar to that in ternary $Pb_{1-x}Ge_xTe$ and $PbTe_{1-x}S_x$ solid solutions, where the phase transitions are un-

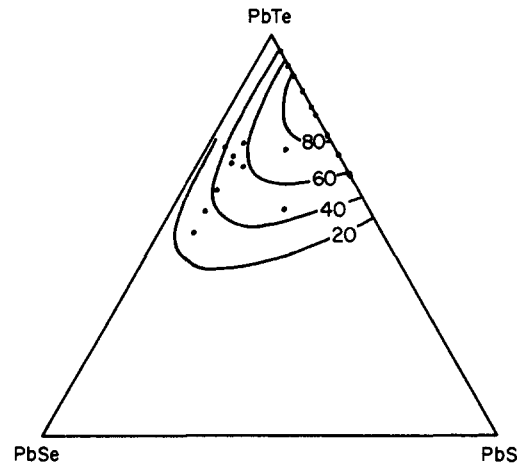

Fig. 2. The dependence of T_c (in K) upon composition for PbS_xSe_y-Te_{1-x-y} solid solution.

ambiguously associated with the presence of off-center ions [12, 13]. This enabled us to suppose that phase transitions in investigated quaternary solid solutions have the same origin and are induced by off-center ions. Following the results of ref. 3, one could suppose that the S atom is off-center in $PbS_xSe_yTe_{1-x-y}$, while according to refs. 10 and 11, Sn is off-center in $Pb_{1-x}Sn_xTe_{1-y}Se_y$, and Sn and S are both off-center in $Pb_{1-x}Sn_xTe_{1-y}S_y$.

The individual features of off-center ions and host crystals, into which off-center ions are built, result in a different dependency of T_c on composition. Figure
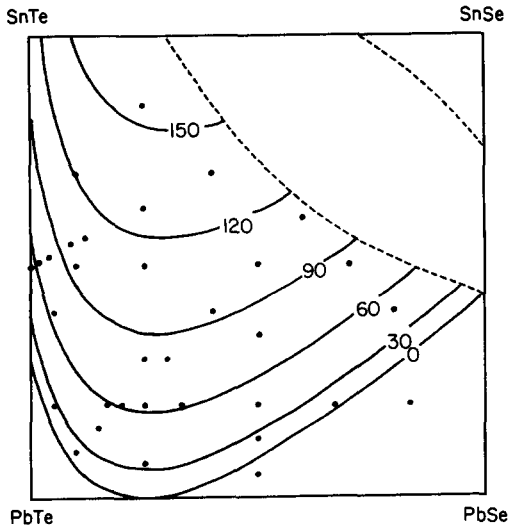
Fig. 3. The dependence of T_c (in K) upon composition for $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solution. The dotted lines show the stability limits for a solid solution.
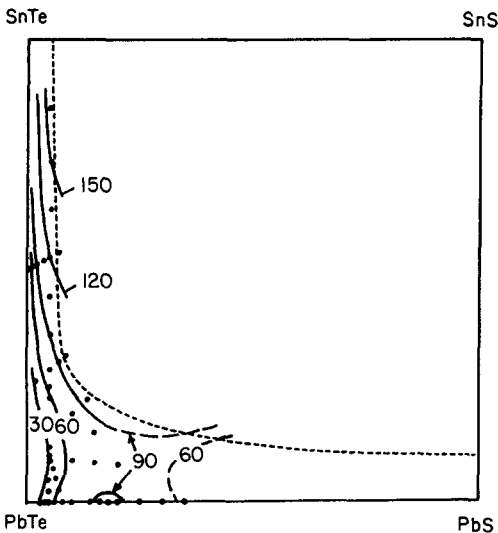

Fig. 4. The dependence of T_c (in K) on composition for $Pb_{1-x}Sn_x Te_{1-y}S_y$ solid solution. The dotted line shows the stability limits for a solid solution according our data.

2 shows that maximum values of T_c on the PbS_x-Se_yTe_{1-x-y} phase diagram are achieved in ternary $PbTe_{1-x}S_x$ solid solutions; in other ternary solid solutions ($PbS_{1-x}Se_x$ and $PbTe_{1-x}Se_x$) there are no phase transitions. This emphasizes the key role of substitution of Te by S in the appearance of phase transitions in $PbS_xSe_yTe_{1-x-y}$. The region where phase transitions take place is located near PbTe whose lattice is known to be softest among the different lead chalcogenides. Adding Se to $PbTe_{1-x}S_x$ lowers T_c; one of the causes of this lowering may be the influence of random fields (resulting from the substitutional disorder in the quaternary solid solution) on the ordering of off-center ions [4].

A qualitatively different behavior was observed in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ solid solution. As follows from the phase diagram shown in Fig. 3, the substitution of Te by Se in $Pb_{1-x}Sn_xTe$ crystals with low tin concentration ($x < 0.35$) results in the onset of phase transition. When increasing Se concentration in crystals with constant x, the phase transition temperature first increased quickly, then reached a maximum (at about $y \approx 0.25$) and decreased again down to zero when approaching $Pb_{1-x}Sn_xSe$. At constant $y = 0.25$, the phase transition could be observed starting from Sn concentrations as low as $x = 0.08$. According to our computer approximation of experimental data, the maximal value of T_c should be achieved near $x = 1$ and $y \approx 0.25$, but another phase transition took place in $SnTe_{0.75}Se_{0.25}$ at a higher temperature [10]. The maximal value of T_c in this quaternary solid solution was 1.5 times higher than in the best single crystals of SnTe [14]. The unusual rise of T_c with increasing the substitutional disorder in $Pb_{1-x}Sn_xTe_{1-y}Se_y$ was explained in ref. 10: the substitutional disorder does not only produce random fields, but it can depress strongly the tunneling motion of off-center ions and so may result in an increase of T_c. We suppose that the latter effect is predominant in $Pb_{1-x}Sn_xTe_{1-y}Se_y$.

$Pb_{1-x}Sn_xTe_{1-y}S_y$ is the most interesting system investigated in this work. There are two different off-center ions in this system — S and Sn. As follows from Fig. 4, their simultaneous influence on T_c is more complicated than in $Pb_{1-x}Sn_xTe_{1-y}Se_y$. The substitution of small amounts of Pb by Sn in crystals with fixed S concentration first strongly decreased T_c so that the phase transition disappeared at about $x \approx 0.1$. With further increasing Sn concentration, the phase transition appeared again. Thus, the low-temperature phase diagram consists of two regions; in one of these (at low Sn concentration) the ferroelectric phase is induced by S off-center ions, and in the other it is associated with Sn off-center ions. The phase diagram is so complicated (it even has a saddle point) because the substitutional disorder depresses the ordering of S off-center ions (by random fields) and at the same time enhances the cooperative motion of Sn off-center ions due to decreasing their tunneling.

The comparison of phase diagrams in Figs. 3 and 4 shows that they are similar in the region of high Sn concentration. The substitution of Te by S results in a stronger increase of T_c than in the case of substituting Te by Se; we suppose that it is associated with a stronger perturbation produced in the former case. The similarity between these phase diagrams confirms that the origin of the rise of T_c in both cases is the same — the depression of the tunneling motion of Sn off-center ions by the substitutional disorder [11]. Unfortunately, the composition stability limits for $Pb_{1-x}Sn_xTe_{1-y}S_y$ are

not very large; the boundaries of the single phase region (according to our data) are indicated by the dotted line in Fig. 4.

4. Conclusions

1. The samples of $PbS_xSe_yTe_{1-x-y}$, $Pb_{1-x}Sn_xTe_{1-y}Se_y$ and $Pb_{1-x}Sn_xTe_{1-y}S_y$ quaternary solid solutions were investigated at low temperatures using electrical and X-ray methods. The regions where low-temperature phase transitions take place were established.

2. It is shown that low-temperature phase transitions in all three systems investigated are associated with off-center S and Sn ions.

3. The dependence of the phase transition temperature on the composition of solid solutions may be qualitatively described by taking into account the influence of substitutional disorder on the ordering and tunneling of off-center ions.

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