Phase transition in heat-treated $(PbTe)_{0.4}(SnSe)_{0.6}$ crystals

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A phase transition has been observed in $(PbTe)_{0.4}(SnSe)_{0.6}$ crystals after high-temperature heat treatment. The transition is diffuse and is accompanied by a clearly expressed thermal hysteresis in the electrical conductivity and the thermal emf.

Several papers have recently been published on phase transitions in IV–VI systems. It has been established that the nature and temperature of these transitions depend on the composition and density of the charge carriers in the crystals. In the present letter we are reporting the first (to the best of our knowledge) observation of a dependence of the nature of phase transitions in IV–VI crystals on the history of their synthesis.

We observed this dependence in a study of the temperature-induced changes in the electrical conductivity σ and the thermal emf α of $(PbTe)_{0.4}(SnSe)_{0.6}$ crystals. The crystals were grown by the Bridgman method. We studied two lots of samples: "raw" samples, made directly from the ingots that were grown, and samples which were annealed for 10–12 days at 903 K. To avoid errors stemming from a possible variation in the concentrations of the components along the length of the ingots, we compared the results for the raw and annealed crystals on the basis of samples fabricated from the same disk, cut from an ingot in the direction perpendicular to its growth direction. The annealing was carried out in order to relieve the stresses that arose in the crystals during their growth because of the influence of the grown containers and temperature gradients on them. The annealing conditions were chosen to keep the density of holes in the samples, about 1×10^{20} cm^{-3}, from changing.

The results of this study are shown in Figs. 1 and 2. We see that the temperature dependence of σ and α for the raw samples is the customary temperature dependence of group IV–VI crystals and is completely reproducible when the thermal cycling is

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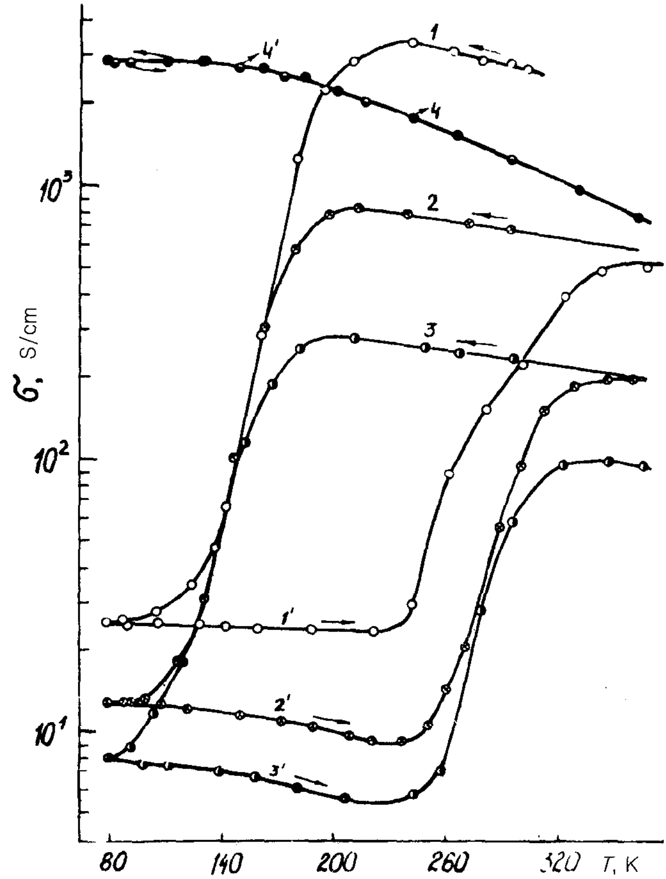

FIG. 1. Temperature dependence of the electrical conductivity of (1–3, 1'–3') an annealed sample and (4,4') an unannealed sample. The curve labels for the annealed samples show the order of the thermal cycling. 1–4—Cooling; 1'–4'—heating.

repeated. The corresponding behavior for the annealed samples is fundamentally different: In a certain temperature interval we see sharp changes and a thermal hysteresis. We find the following:

1) The temperature T_0, at which σ begins to fall off (and α is increasing) during the cooling, becomes lower during each successive thermal cycling (for the sample shown in Fig. 1, T_0 decreased from 240 K to 200 K from the first to the third cooling cycles).

2) The temperature T_H, at which σ begins to increase sharply (and α decreases) in the course of the heating, is essentially the same for all of the thermal cycles and for both coefficients. Its value is about 230 K.

3) During the cooling and heating of a sample, its conductivity decreases with each successive thermal cycle, just as it decreases during a cooling-heating cycle. The

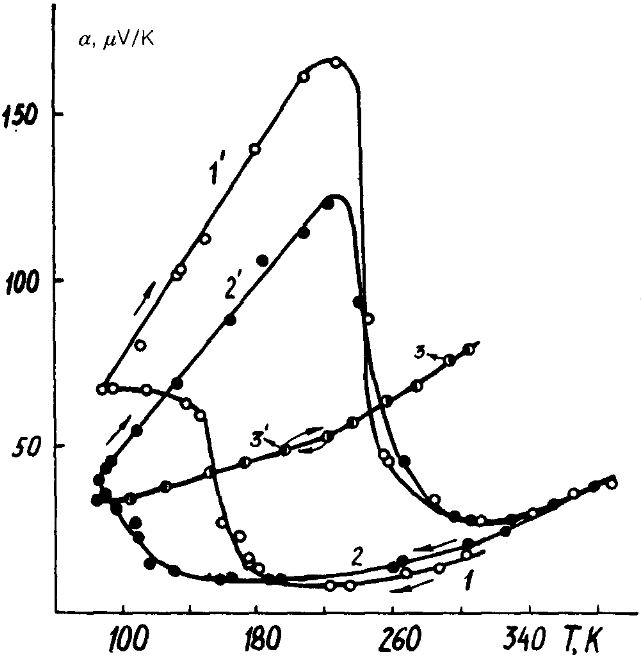

FIG. 2. Temperature dependence of the thermal emf of (1, 2, 1′, 2′) an annealed sample and (3,3′) an unannealed sample. The curve labels have the same meaning as in Fig. 1.

corresponding drop in the values of α also decreases with each successive cycle.

Abrupt changes in σ, similar to those which we have observed in the SnSe-PbTe system, have been observed in a study of the SnSe-PbTe system,[1] but the transitions which we observed are not accompanied by corresponding changes in the carrier density. In the crystals of the present experiments the Hall coefficient exhibited no structural features anywhere over the temperature range and depended only slightly on T. In the SnSe-PbSe system, a hysteresis was also seen in the temperature dependence of σ (Ref. 2), but in those materials the hysteresis was not accompanied by any structural features on the temperature dependence of the thermal emf. It can thus be concluded that a new set of structural features, determined by the history of the synthesis of the crystals, has been observed on the temperature dependence of the kinetic parameters of group IV–VI crystals in our study. The presence of these structural features is evidence that a phase transition occurs in the annealed crystals of this system. The fact that these features are spread out along the temperature scale indicates that the phases between which the transition occurs coexist in a certain temperature interval.[3]

We would like to suggest that the transition detected here is a transition from a commensurate phase to an incommensurate phase, which may precede the transition of IV–VI crystals from a cubic phase to an orthorhombic phase during cooling[4] (as has been pointed out previously,[5] the material studied is a single-phase material at room temperature, and it crystallizes in a cubic lattice of the NaCl type). The suggestion of an incommensurate phase can explain the direction of the temperature-induced changes in the characteristics studied: σ decreases because of an additional scattering of charge carriers, and α changes because of a change in the energy dependence of the probability for a scattering of the carriers. The hysteresis in σ and α can apparently be attributed to a corresponding hysteresis in the differential transient function which determines the nature of the transition.[3] The existence of this hysteresis and the constancy of T_H during the thermal cycling indicate that the reversible transition from a structure with incommensurate phases to a cubic structure requires a certain energy, which is determined by the value of T_H.

The fact that anomalies are not seen in the behavior of σ and α of the samples which were not annealed may indicate that the probability for the appearance of an incommensurate phase depends strongly on the stress level in the crystal and may be zero at a certain stress level. In our opinion, evidence in favor of this suggestion is the decrease in the temperature T_0 during the thermal cycling, since in the course of each thermal cycle the degree of mechanical stress should naturally increase because of the changes which occur in the crystal.

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