

Amorphous-to-crystalline transition in $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ phase change materials



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INTRODUCTION

Chalcogenide phase change materials are characterized by significant changes in optical parameters during reversible phase transitions between crystalline and amorphous states, which are caused by the action of ultrashort laser pulses. Among these materials, a group of Sb- and Se-containing semiconductor chalcogenides are distinguished as optical phase change materials. It is worth noting that GeSb(Bi)Se alloys can be expected to exhibit significant differences in refractive index and reflectivity during phase transformations, combined with low optical losses over a wide spectral range. The high glass-forming ability of the aforementioned phase change materials contributes to the stability of their characteristics when used as optical switches and modulators.

EXPERIMENTAL

Bulk samples of $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ alloys ($0 \leq x \leq 0.4$) were synthesized from stoichiometric elemental components in a vacuumed quartz ampoule, which was heated at a rate of 30 K/h to a temperature of 973 K, and after an hour of isothermal treatment the ampoule with the mixture was heated again at the rate of 20 K/h until a temperature of 1243 K was reached, and then an eight-hour isothermal treatment was carried out. Then the ampoule with the melt was cooled at a rate of 25 K/h down to a temperature of 943 K or (in another variant) to a temperature of 853 K, then the melt was quenched by immersing the ampoule in cold water. We designated these two modes of synthesis of $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ alloys as rapid quenching (RQ) mode and slow quenching (SQ) mode, since the final stage of isothermal holding (before quenching the alloy) occurred at temperatures that differed by ~ 90 K.

X-ray diffraction (XRD) studies were performed using an AXRD Benchtop diffractometer.

We focused on the kinetic analysis of non-isothermal crystallization processes in $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ glasses, using the possibilities of differential thermal analysis technique (DTA). The glass heating rate was varied from 3 to 15 K/min.

RESULTS AND DISCUSSION

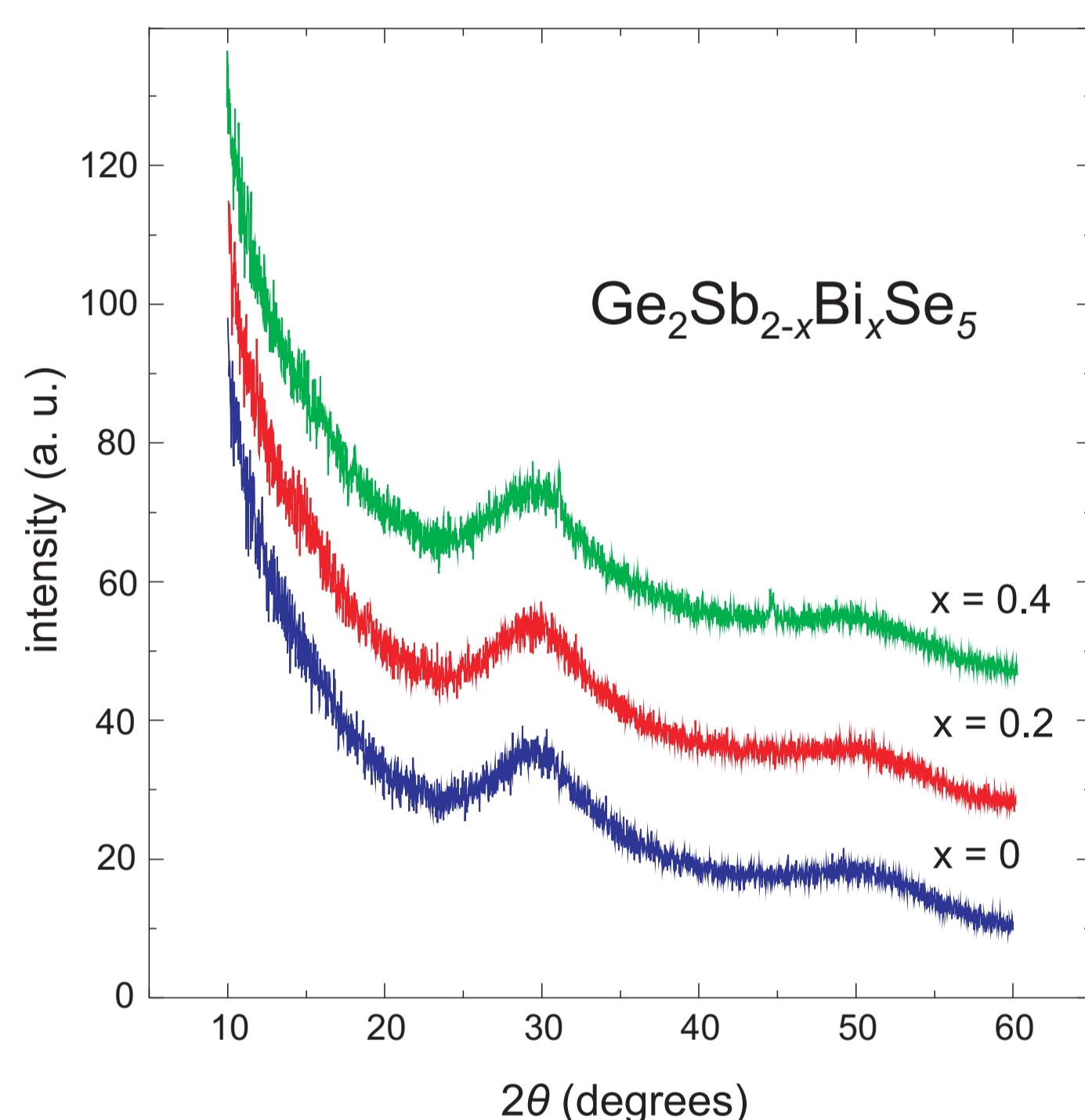


Fig. 1. Powder XRD patterns of $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ samples with various Bi content.

As follows from the XRD studies, all $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ alloys (x from 0 to 0.4) prepared both in the SQ and RQ modes, exhibit amorphous structure, i.e. without any signs of the presence of crystalline inclusions in the alloys (Fig. 1). Based on the DTA data, we carried out kinetic analysis of nonisothermal crystallisation of the synthesized $\text{Ge}_2\text{Sb}_2\text{Se}_5\text{xTex}$ glasses (x from 0 to 0.4). These measurements were performed at different heating rates from 3 to 15 K/min. The DTA traces enabled us to determine the exothermic crystallisation peak temperature T_p . The thermally stimulated crystallization occurs by a single-stage mechanism for all studied samples. Crystallisation of $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ glasses is a nucleation-dominated single-stage phase transformation of a metastable alloy into a stable crystalline phase. This fact correlates with the relatively low values of the activation energy E_a , determined from the DTA curves using the Kissinger method.

Table 1. Activation energy E_a for crystallisation for $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ glasses prepared in SQ and RQ modes.

x , [$\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$]	E_a [kJ/mole], SQ mode	E_a [kJ/mole], RQ mode
0.0	142.8	76.2
0.1	108.1	118.2
0.2	96.6	143.9
0.3	98.5	158.4
0.4	117.2	200.9

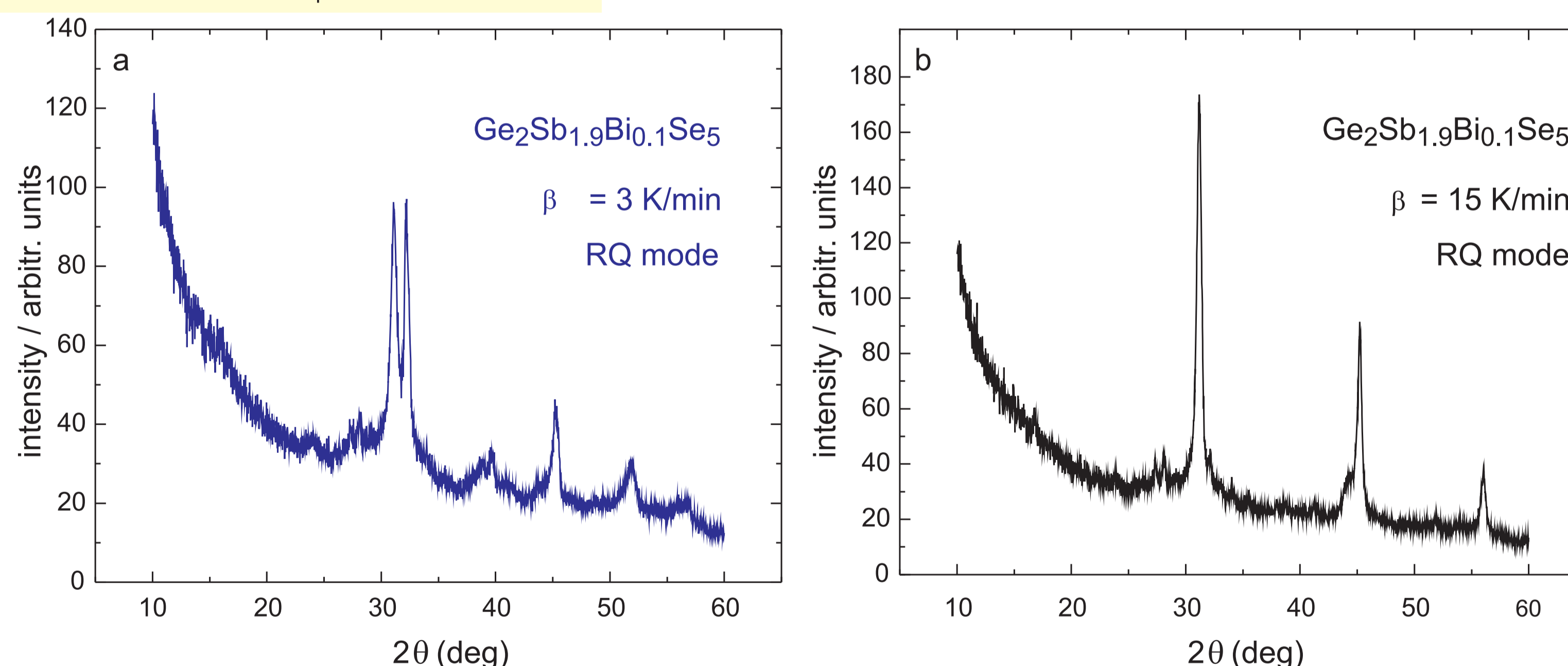


Fig. 2. XRD patterns of $\text{Ge}_2\text{Sb}_{1.9}\text{Bi}_{0.1}\text{Se}_5$ alloys after heat treatments with different heating rates.

As can be seen from Table 1, for the $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ alloys prepared in RQ modes the activation energy E_a for crystallization increases with increasing x . The dependence of $E_a(x)$ for alloys manufactured in the SQ mode does not seem so unambiguous. Moreover, for samples synthesized in the RQ mode, the parameter E_a is mostly higher than for samples prepared in the SQ mode. We explain this by the peculiarity of the structure of $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ glasses with $x \leq 0.4$ synthesized in the SQ mode, which is arranged in such a way that the contribution to the activation energy for crystallization from the primary nucleation process was smaller than for glasses prepared in the RQ mode. For samples after the non-isothermal heating procedure with high β , the formed crystalline phases were identified by comparison with known data. XRD measurements unambiguously confirmed the crystalline structure of the $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ samples formed after the DTA heating procedure performed at different rates β . Narrow reflections in the XRD pattern for $\text{Ge}_2\text{Sb}_2\text{Se}_5$ show a good agreement with the reference data for the orthorhombic (Pnma) structure of this compound. The process of formation of crystalline inclusions in the amorphous matrix of alloys with $x \leq 0.10$ was influenced by the heating rate (see Fig. 2), i.e. the result of crystallization was temperature-dependent.

CONCLUSIONS

§ XRD measurements for as-prepared $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ glass samples ($x = 0.0-0.4$) clearly demonstrate the absence of reflexes that could provide evidence for the existence of any crystallites in the samples.

§ Based on the analysis of the experimental DTA curves in the framework of the original Kissinger method, it is shown that non-isothermal crystallization of $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ samples upon heating is a single-stage process. The activation energy of which depends on the preparation mode, being noticeably higher for slow quenching compared to the rapid quenching mode.

§ For the $\text{Ge}_2\text{Sb}_{2-x}\text{Bi}_x\text{Se}_5$ alloys prepared in RQ modes the activation energy E_a for crystallization increases with increasing x . The dependence of $E_a(x)$ for alloys manufactured in the SQ mode does not seem so unambiguous.

$\text{Ge}_2\text{Sb}_2\text{Se}_5$ glass crystallizes upon heating in the orthorhombic structure (Pnma space group). For the Bi-containing samples at a low heating rate the formation of several crystalline phases is possible.