

Structural investigation of Sb-based phase-change materials

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ABSTRACT

Sb-based phase-change materials, $\text{Ge}_{15}\text{Sb}_{70}\text{Te}_{15}$ and $\text{Ge}_{10}\text{Sb}_{80}\text{Te}_{10}$, were scrutinized by using an X-ray diffraction method. The sputtered films of these materials crystallize into A7-type single phases by instantaneous laser annealing; however, Ge atoms incorporated into the Sb matrix readily precipitate out of the matrix to cohere into the diamond-type Ge crystallites, and then, these Ge crystallites combine with Te in the matrix to form eventually NaCl-type GeTe crystallites. This decomposition was found occurred at relatively low temperatures. On the contrary to these GeTe-Sb materials, Sb-Te binary compounds keep their single phase structures up to near their melting temperatures; and besides, just after the transformations from the amorphous to crystalline phases, the structures of these binary materials are expected to be A7-type structure irrespective of their compositions. It is therefore, presumed that the amorphous and crystalline structures and material properties of Sb-Te binary alloys are worth scrutinizing for us to develop future new phase-change materials.

1. INTRODUCTION

Phase change recording is now extensively used for high density non-volatile memories [1]. Since 1970s, various materials have been proposed, and today, we have obtained two kinds of superior materials, GeTe-Sb₂Te₃ (GST) pseudobinary and Sb-based multinary alloys such as AIST (Ag-In-Sb-Te quadruple compounds). Of the two, many investigations have been made on the GST pseudobinary compounds; however, it is supposed that investigations on the Sb-based materials are still insufficient. To develop more superior materials for future high-density phase change memories, the examinations for both materials will be indispensable. We accordingly investigated several kinds of Sb-based multinary compounds by means of x-ray diffraction method. These investigations revealed, however, that all these alloys eventually separated into two crystalline phases: dopants such as Ge, Sn, Ag or Indium in the Sb-based materials are easy to come out of the Sb matrices, forming other tellurides. It is generally expected that single-phase crystalline compounds that robustly hold their phases are suitable for us to use them stably as phase-change random-access-memory materials. In many Sb-based phase-change materials, however, (Sb₂Te₃)-Sb, (Bi₂Te₃)-Bi, and (Bi₂Se₃)-Bi etc. can continuously form single-phase crystals over a wide composition range on their binary lines. Our present investigation pointed out that these pseudobinary-like multinary compounds have to be examined further in the future.

2. EXPERIMENTAL

Thin films of Ge₁₅Sb₇₀Te₁₅ and Ge₁₀Sb₈₀Te₁₀ with a thickness of approximately 300 nm were formed by sputtering on glass disks 120 mm in diameter. Each film was crystallized by laser irradiation and then scraped off with a spatula to create first powder specimens. Besides these sputtered films, we prepared Ge₁₅Sb₇₀Te₁₅ and Sn₁₀Sb₈₀Te₁₀ ingots by melting stoichiometric mixtures of 99.999%-pure Ge, Sn, Sb, and Te in argon atmosphere and then quenching them in ice water. The second powder specimens were produced by crushing the completed ingots. To prepare the two kinds of experimental specimens for X-ray diffraction, these powders were packed into quartz capillary tubes with an internal diameter of 0.3 mm. The openings of the capillaries were sealed by using an oxyacetylene flame to insulate them against the atmosphere. The diffraction experiments were carried out using the large-diameter Debye-Scherrer camera with an imaging plate on the BL02B2 beam line at SPring-8 [2]. In order to confirm the radiation beam energy used, diffraction pattern of powdered CeO₂ ($a = 5.4111$ Å) was taken under the same condition. The experiments at low and high temperatures were carried out while blowing nitrogen gas set at the specified temperatures onto the capillary tube. The crystal structures were examined and refined using the Rietveld method [3]. The program JANA2000 [4] was used for this purpose; intensity data in increments of 0.01° were obtained by reading the imaging plate for a pixel area of 50 μm².

3. RESULTS & DISCUSSION

3-1. X-ray-diffraction-experiment results for several Ge(Sn)Te-Sb alloys

Sputtered Ge₁₅Sb₇₀Te₁₅ film

The diffraction patterns obtained for the sputtered Ge₁₅Sb₇₀Te₁₅ film are shown in Fig.1. The result of a search-match analysis revealed the diffraction patterns taken at low temperatures in the figure to be almost identical to that of As, Sb or Bi crystal with an A7-type structure [5]. This phase belongs to the space group $R\bar{3}m$ [6]. The three constituent elements, Ge, Sb, and Te, randomly occupy 6(c) site. The changes in diffraction lines with increasing temperature show that the single-phase A7-type structure is kept up to 600 K; however the peaks for diamond-type Ge ($Fd\bar{3}m$ [6], $a = 5.65735 \text{ \AA}$ at 20 °C [7]) appear at 651 K along with the peaks indicating an A7-type structure. The Rietveld analyses performed with these diffraction patterns provided temperature dependence of the structural parameters of this material as shown in Fig.2. As seen in this figure, the cell dimensions almost linearly vary with temperature up to 360 K. However, above this temperature up to 600 K, a , c , and B irregularly vary with temperature. This curious behaviour of these parameters between 360 K and 600 K strongly implies that precipitation of Ge atoms begins to take place at around 360 K.

Sputtered Ge₁₀Sb₈₀Te₁₀ film

For sputtered Ge₁₀Sb₈₀Te₁₀ film, we have confirmed that it was crystallized into an A7-type single phase just after laser initialization as well as the sputtered Ge₁₅Sb₇₀Te₁₅ film. However, we found that, after keeping it at room temperature for half a year, diamond-type Ge was extracted out of the matrix even at that low temperature.

Melt-quench Ge₁₅Sb₇₀Te₁₅ alloy

Figure 3 shows the diffraction patterns obtained for Ge₁₅Sb₇₀Te₁₅ prepared by the melt-quench method. As seen in the figure, this specimen showed two-phase coexistence of A7-type Sb and NaCl-type GeTe phases irrespective of measurement temperature. This clearly shows that the cooling rate produced by the melt quenching method was insufficient to obtain an alloy crystallized into an A7-type single phase. The lattice constant of this GeTe phase is 5.990 Å at room temperature, which corresponds to that of (GeTe)_{0.90}(Sb₂Te₃)_{0.10} metastable cubic phase [8] (Here, we assume that the NaCl-type structures can be present only on the GeTe-Sb₂Te₃ pseudo-binary line in the Ge-Sb-Te ternary system). On the other hand, those of the remaining phase are $4.251 \times 11.297 \text{ \AA}$, which are slightly smaller than those of pure Sb, $4.307 \times 11.312 \text{ \AA}$ (from our measurement result). This means that the remaining phase is not a pure Sb material but contains a small number of Ge or Te atoms. The molar ratios analyzed by the Rietveld method are shown in the same figure, which shows that a few Sn

and Te atoms still remain in the Sb matrix.

Melt-quench $\text{Sn}_{10}\text{Sb}_{80}\text{Te}_{10}$ alloy

Figure 4 shows the diffraction patterns obtained for $\text{Sn}_{10}\text{Sb}_{80}\text{Te}_{10}$ prepared by the melt-quench method. As seen in the figure, this specimen showed two-phase coexistence of A7-type Sb and NaCl-type SnTe phases irrespective of measurement temperature. The molar ratios analyzed by the Rietveld method are shown in the same figure, which shows that Sb can dissolve little SnTe.

3-2. Reaction products

Our investigation on sputtered GeTe-Sb films revealed that Ge atoms incorporated into the Sb matrix precipitate out of the matrix to cohere into the diamond-type Ge crystallites first, and next, these Ge crystallites combines with Te in the matrix to form NaCl-type GeTe crystallites. These GeTe-Sb have semi-metallic features. GeTe-Sb₂Te₃ pseudo-binary compounds are semiconductors with very narrow band gaps. Semiconducting or semi-metallic feature gives a material low thermal conductivity, which is convenient for rapid ascending heat to cause an instantaneous phase change. For the Sb-based phase change materials, it is essential to add some other elements to pure Sb in order to ensure the amorphous stability, namely the long-term data retention. This investigation strongly suggests that, to make these Sb-based materials more superior phase-change materials, in other words, to give them higher cyclabilities, we have to carefully examine and adopt the precipitates in the Sb matrix. X-ray diffraction analyses for various future candidates will give us convincing clues to develop new material with better performance.

3-3. Similarity in crystal structure between GeTe-Sb₂Te₃ pseudo-binary and Sb-Te binary systems

The $(\text{Sb}_2)_n(\text{Sb}_2\text{Te}_3)_m$, $(\text{Bi}_2)_n(\text{Bi}_2\text{Te}_3)_m$, $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$, and $(\text{GeTe})_n(\text{Bi}_2\text{Te}_3)_m$ homologous series are generally expected to have (stable) structures with the same stacking period in the thermal equilibrium when each series has the same values of n and m . In other words, all these homologous structures can be characterized as trigonal structures with $2n+5m$ cubic close-packed periodicity. The residual of $(2n+5m)/3 = 0$ and $\neq 0$ lead to the formation of crystals having structures with primitive (P) and rhombohedral (R) unit cells, respectively. In the former structures, a unit cell is identical to a basic structural unit specific to the homologous structures mentioned above; on the other hand, in the latter case, a unit cell comprises three cubic close-packed units [9]. The binary compounds can be obtained by replacing Ge and Te layers in the pseudobinary compounds with Sb or Bi layers, and vice versa, i. e., $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m \leftrightarrow (\text{Sb}_2)_n(\text{Sb}_2\text{Te}_3)_m$ or $(\text{GeTe})_n(\text{Bi}_2\text{Te}_3)_m \leftrightarrow (\text{Bi}_2)_n(\text{Bi}_2\text{Te}_3)_m$. On the other hand, the structure of the metastable phases of the GST materials is very similar to that of the A7 type structure of Sb or Bi. If Ge(/Sb) and Te randomly occupy the two kinds of the atomic sites, namely Cl and Na sites, the structure with the resultant atomic configuration corresponds to the latter structure. Thus GST

and Sb-Te compounds are very similar in structure with each other.

4. CONCLUSION

The crystalline and electronic structures of the GeTe-Sb materials are very similar to those of GST materials; i.e., the atoms are orthogonally connected by p - p bond in common with both materials [8]. It was found that the sputtered films of these GeTe-Sb compounds crystallize into single phases with the A7 structure of the same type as Sb by an instantaneous laser annealing; however, these compounds tend to readily separate into two phases. One is the diamond-type Ge (or NaCl-type GeTe) cubic phase and the other is the A7-type Sb(-Te) trigonal phase. Interestingly, the sputtered and laser crystallized $\text{Ge}_{15}\text{Sb}_{70}\text{Te}_{15}$ film showed a completely different thermal response to an ingot $\text{Ge}_{15}\text{Sb}_{70}\text{Te}_{15}$ made by a melt-quench method. The former showed phase separation at around 600K with increasing temperature, on the other hand, the latter had already shown a diffraction pattern of the two-phase coexistence as prepared. A $\text{Ge}_{10}\text{Sb}_{80}\text{Te}_{10}$ sputtered film, which had formed a single-phase A7-type crystalline phase just after laser initialization, gave the Bragg peaks of the diamond-Ge phase in the A7-type diffraction pattern a few months later by keeping it at room temperature. On the contrary to these GeTe-Sb materials, Sb-Te binary compounds keep their single phase structures up to near their melting temperatures; and besides, just after the transformations from the amorphous to crystalline phases, the structures of these binary materials are expected to be A7-type structure irrespective of their compositions. Thus Sb-Te compounds are very similar in structure with GST compounds; therefore, the amorphous and crystalline structures and material properties of Sb-Te binary alloys are worth scrutinizing for us to develop future new phase-change materials.

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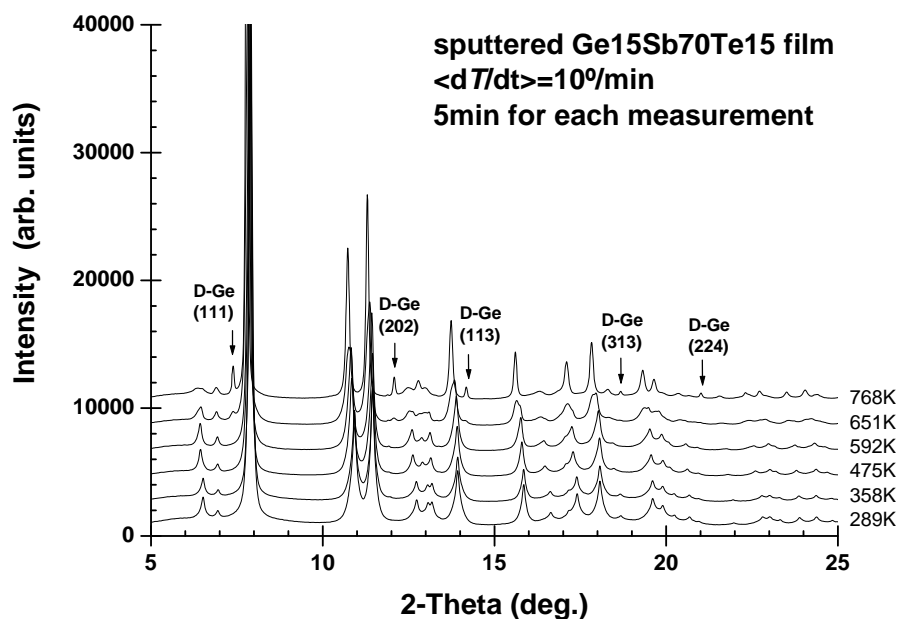


Figure 1. X-ray diffraction patterns for the sputtered $\text{Ge}_{15}\text{Sb}_{70}\text{Te}_{15}$ crystalline film. No Bragg peaks are detected at lower angles than $2\theta=5^\circ$ (not shown).

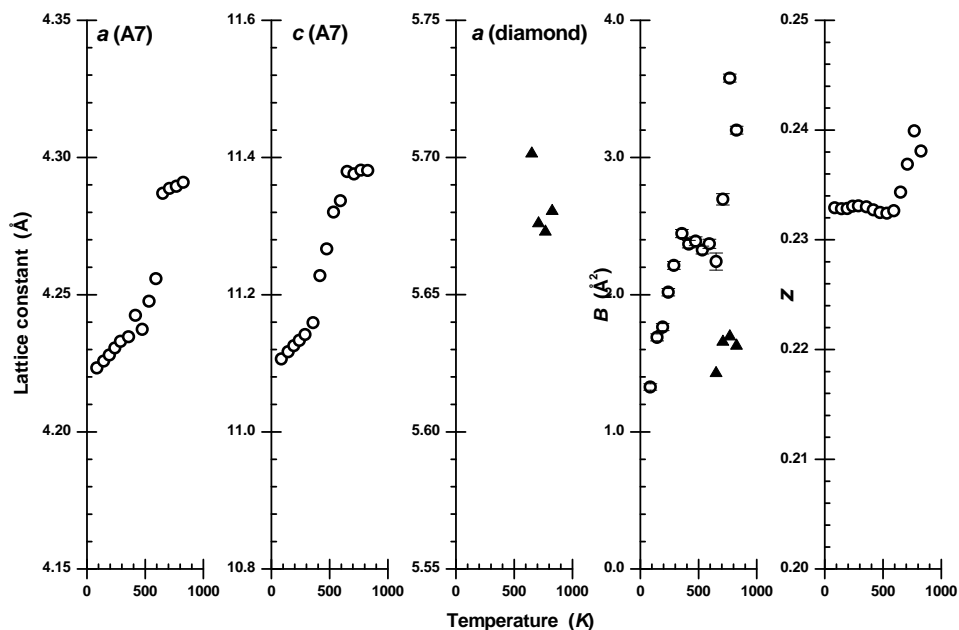


Figure 2. Temperature dependences of the structural parameters and the atomic displacement parameters (isotropic temperature factors) B . In the structural parameters, a and c , show the unit cell edge lengths and z represents the atomic position. The marks, \circ and \blacktriangle , in these figures represent those for A7-type SbTe, and diamond-type Ge, respectively. Error bars are omitted for data with errors smaller than the marks.

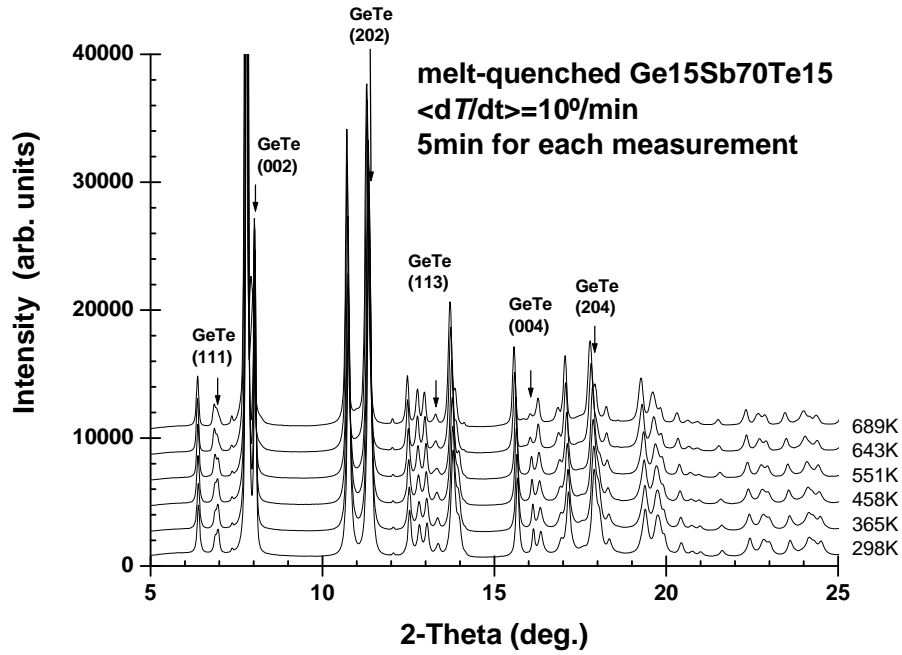


Figure 3. X-ray diffraction patterns for Ge₁₅Sb₇₀Te₁₅ prepared by the melt-quench method. No Bragg peaks are detected at lower angles than $2\theta=5^\circ$ (not shown).

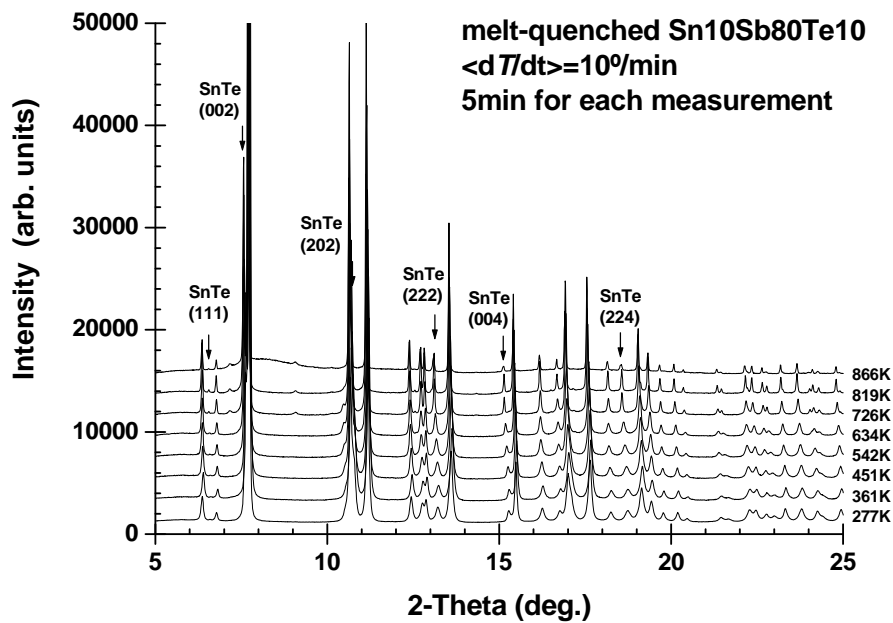


Figure 4. X-ray diffraction patterns for Sn₁₀Sb₈₀Te₁₀ prepared by the melt-quench method. No Bragg peaks are detected at lower angles than $2\theta=5^\circ$ (not shown).

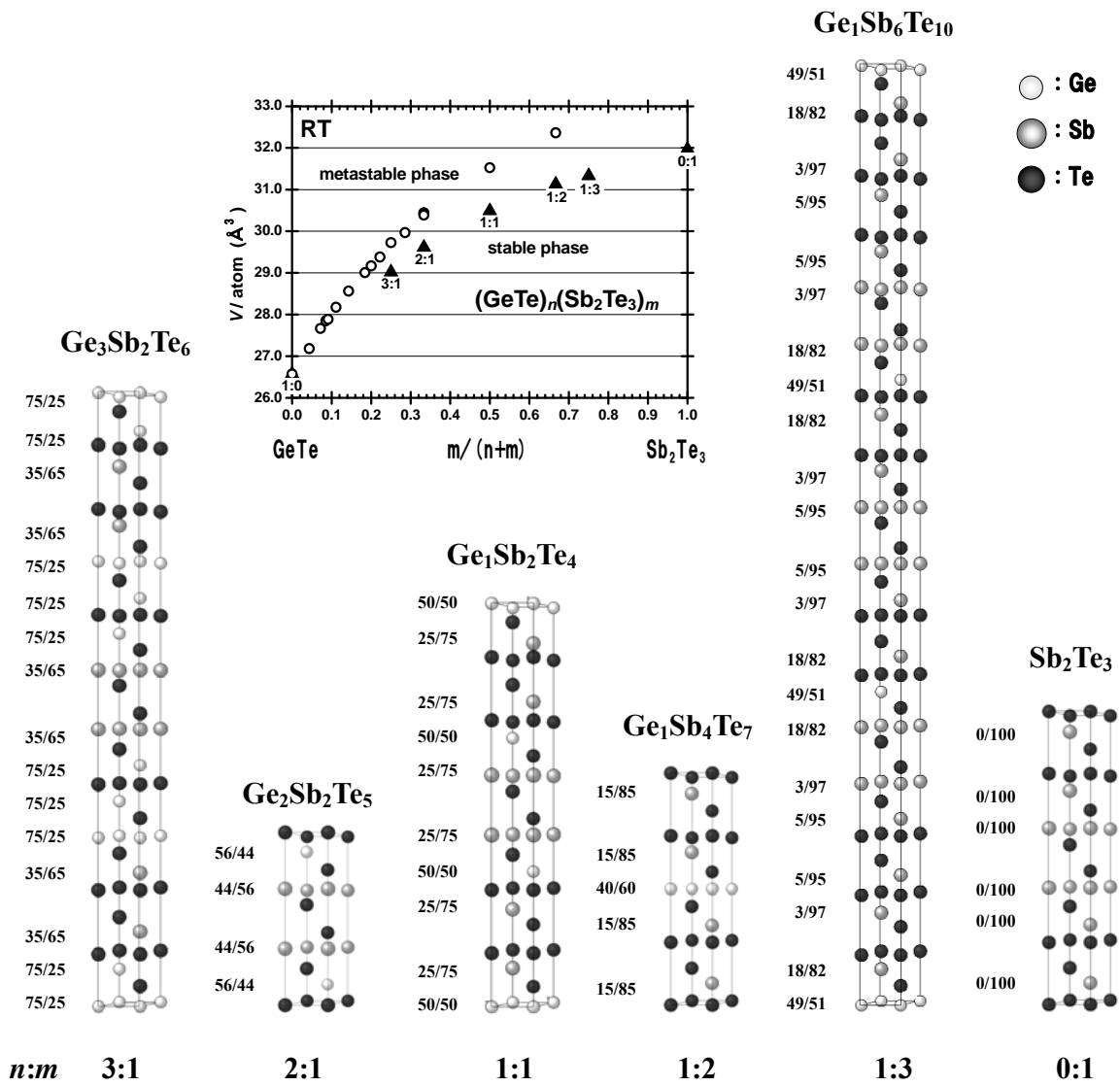


Figure 5. Crystal structures of the GeTe-Sb₂Te₃ stable (homologous) phases. The inserted graph shows composition dependence of the cubic root unit cell volume ($V^{1/3}$) for the metastable and stable structures. In these structures, by appropriately replacing Ge and Te with 2xSb, we can obtain (Sb₂)_n(Sb₂Te₃)_m homologous structures instead.