JOURNAL OF SOLID STATE CHEMISTRY 76, 102–108 (1988)

Electron Microscopic Study of the Homologous Series of Mixed Layer Compounds $R_2Te_3(GeTe)_n$ (R = Sb, Bi)

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Received December 8, 1987

Through the use of electron diffraction and high-resolution electron microscopy, it is found that substitution of As by Sb or Bi in the homologous series of mixed layer compounds $As_2Te_3(GeTe)_n$ gives rise to a new, structurally identical, homologous series of mixed layer compounds $Sb_2Te_3(GeTe)_n$ and $Bi_2Te_3(GeTe)_n$. © 1988 Academic Press, Inc.

1. Introduction

The structures of several members of the series of mixed layer compounds $As_2Ge_nTe_{3+n}$ were determined by Han Wan Shu *et al.* (*1*) using X-ray diffraction. The compounds were found to form a homologous series. A study using electron diffraction and high-resolution electron microscopy was of interest, especially for the compounds with higher n values (*2*). It was found that no members of the homologous series with n values >9 were present. Instead the structure consisted of a GeTe matrix randomly interrupted by what are most likely As_2Te_3 slabs (*2*). In the present paper it will be shown however that by adapting the heat treatment more regular structures can be obtained. Furthermore the substitution of As in the $As_2Te_3(GeTe)_n$ compounds by elements figuring in the same row of the periodic system (Sb and Bi) leads to a new, structurally identical, homologous series of mixed layer compounds, as we will show. As yet attempts to prepare other mixed layer compounds by the substitution of Ge and/or Te have not been successful.

2. $GeBi_2Te_4$ and $GeSb_2Te_4$

We were led to the preparation of the Sb and Bi series for two reasons. First there was the obvious idea of substituting for As in the $As_2Ge_nTe_{3+n}$ series with an element figuring in the same row of the periodic system; second there was the early work by Agaev and Semiletov (*3, 4*). They reported on the structure determination of $GeBi_2Te_4$ and $GeSb_2Te_4$ by electron diffraction from thin films. Both compounds have rhombohedral structures and consist of GeTe layers and slabs of R_2Te_3 (R = Sb, Bi) periodically alternating along the c-axis in the hexagonal description. The stacking sequence for $GeBi_2Te_4$ is

$$A\gamma BaCBa/C\beta AcBAc/B\alpha CbACb/A\ .\ .\ .\ ,$$

0022-4596/88 $3.00

where the capital letters represent Te layers, the small letters Bi layers, and the Greek letters Ge layers.

This stacking sequence is identical to that of the first member ($n = 1$) of the homologous $As_2Te_3(GeTe)_n$ series with As replaced by Bi. For some reason the stacking found in the Sb_2Te_3 slab of $GeSb_2Te_4$ differs from that in the Bi_2Te_3 slab of $GeBi_2Te_4$ (*3*, *4*). This however is not confirmed by our observations where the stacking sequences observed for the As, Sb, and Bi series are identical.

3. $As_2Ge_nTe_{3+n}$

All members of the homologous series of mixed layer compounds $As_2Te_3(GeTe)_n$ consist of slabs of n (GeTe) layers and slabs of As_2Te_3 alternating along the hexagonal c-axis. The thickness of a GeTe layer and an As_2Te_3 slab are 0.349 and 1.011 nm, respectively, thus giving rise to a c parameter of

$$c = (n \times 0.349 + 1.011)\ \text{nm}.$$

The stacking of the Te layers in the GeTe slab is rhombohedral whereas in the As_2Te_3 slab it is hexagonal. Depending on the n value three structural types can be distinguished: (a) hexagonal [n = (threefold) − 1]; (b) rhombohedral I [n = (threefold)]; (c) rhombohedral II [n = (threefold) + 1]. A projection along $[11\bar{2}0]$ of the structure model proposed in (*1*) exhibits a characteristic feature: along a particular direction the rows of Te atoms are shifted on crossing the As_2Te_3 slab; this is due to the local hexagonal stacking (Fig. 1).

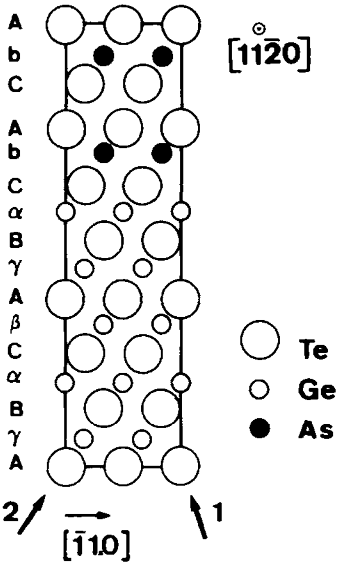

FIG. 1. Projection along $[11\bar{2}0]$ of the structure model proposed in (*1*) for a representative member ($n = 5$) of the $As_2Te_3(GeTe)_n$ homologous series. Along direction 1 the rows of Te atoms are shifted on crossing the As_2Te_3 slab.

4. Electron Microscopy

4.1. Sample Preparation

Several members of the series of compounds $Sb_2Ge_nTe_{3+n}$ and $Bi_2Ge_nTe_{3+n}$ were prepared by mixing the constituent elements and heating in evacuated quartz tubes first at 800°C for a few hours and subsequently at 350°C for 2 weeks. For higher n values (n = 11, 12, 15, 18) of the As, Sb, and Bi series and for a particular low n value of the Sb series ($n = 4$) the second part of the heat treatment was extended to 3 weeks at 300°C to increase the possibility of forming members of the homologous series corresponding with higher n values and of obtaining more regular structures.

It has to be mentioned that a compound prepared in the way described above always contains several members of the homologous series, with n values varying around that corresponding with the overall composition. This is presumably due to residual variations in local composition. Specimens suitable for electron microscopic investigation were obtained by depositing crushed material on copper grids previously dipped in an adhesive solution.

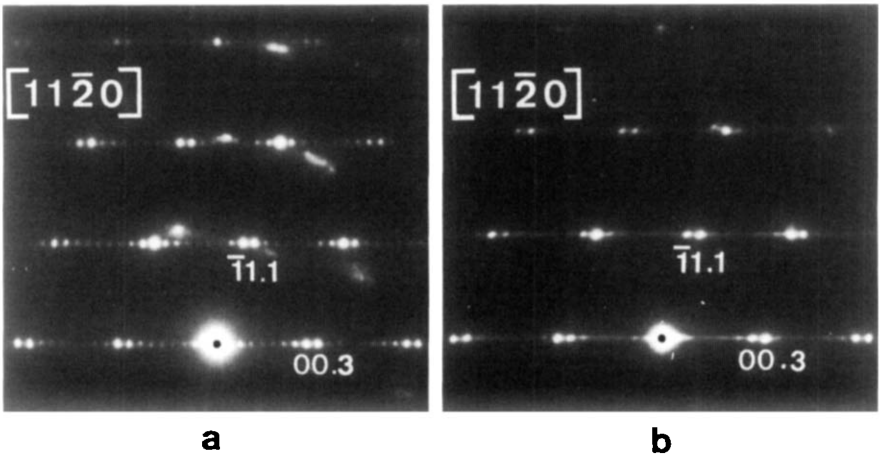

FIG. 2. Electron diffraction patterns along the [11$\bar{2}$0] zone of (a) $Bi_2Te_3(GeTe)_6$ and (b) an Sb compound; the discrete superstructure spots of (a) are replaced by weak elongated maxima.

4.2. Electron Diffraction Patterns

The most representative electron diffraction patterns for the mixed layer compounds under study are the [hk.0] zone patterns. In these patterns apart from more intense spots that can roughly be indexed on a rhombohedral lattice, superstructure spots are observed along [00.1]* (*2*). The geometry and the intensity variations in the diffraction patterns are typical for mixed layer compounds and can be fully accounted for (*5*, *6*).

If an arrangement of $R_2Te_3(GeTe)_n$ blocks with the same n value occurs over a large enough area the distance between two successive basic spots along [00.1]* is divided into N (= n + 3) equal parts by sharp superstructure spots; the distance between two such spots is inversely proportional to the c parameter of the $R_2Te_3(GeTe)_n$ unit cell. However when there is a (quasi-) random mixture of $R_2Te_3(GeTe)_n$ blocks of different n value no sharp superstructure spots occur, but streaks containing weak elongated maxima are observed.

In Fig. 2 a comparison is made between a [1120] electron diffraction pattern observed in a Bi-containing compound and in an Sb-containing compound with the same nominal n value and after the same heat treatment.

From the pattern in Fig. 2a it is expected through analogy with $As_2Ge_nTe_{3+n}$ (*2*) that the structure under observation has a nine-layer unit cell, probably consisting of six layers of GeTe and one slab of Bi_2Te_3 as will be verified by high-resolution electron microscopy.

From the pattern in Fig. 2b, considering the overall geometry and the intensity variations, it can be estimated that the structure consists of the same building blocks as the $Bi_2Te_3(GeTe)_n$ and $As_2Te_3(GeTe)_n$ structures. The replacement of discrete superstructure spots by diffuse elongated maxima is indicative for a mixture of $Sb_2Te_3(GeTe)_n$ blocks with different widths. From the separation of two adjacent more intense spots an average block thickness of about 2.8 nm can be deduced, corresponding with an n value of 5. Details about the arrangement in, and the variation in width of, the blocks can be obtained by high-resolution electron microscopy.

4.3. High-Resolution Electron Microscopy

The most interesting high-resolution images for different members of the series

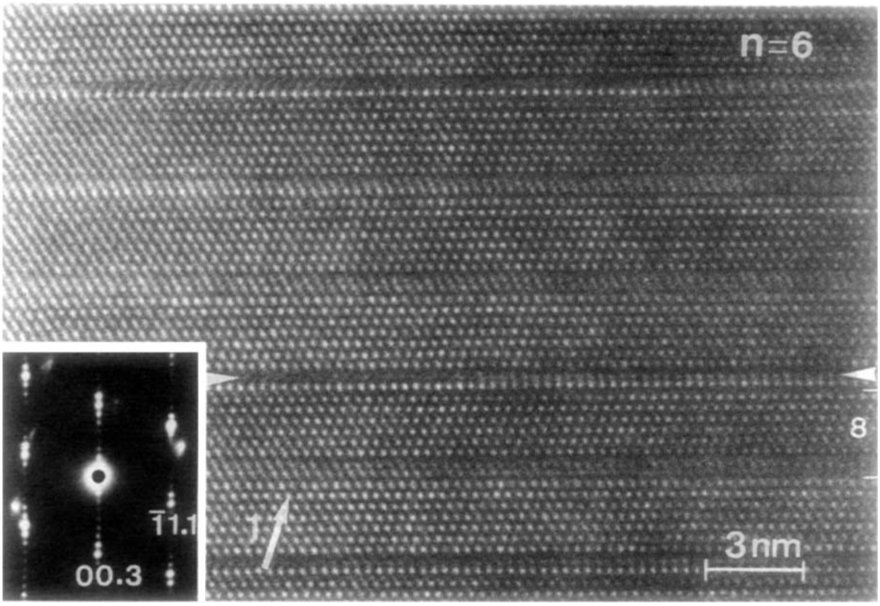

FIG. 3. High-resolution image along [11$\bar{2}$0] of $Bi_2Te_3(GeTe)_6$. Along direction 1 the rows of bright dots are shifted on crossing the Bi_2Te_3 slabs. In the Bi_2Te_3 slab, indicated by white arrows, a deviation from normal image contrast is observed. As indicated one of the blocks contains only eight instead of nine Te layers.

were obtained along the [11$\bar{2}$0] zone, where the structure is viewed along the close-packed rows of Te atoms. The interpretation of these images by comparison with the projection along [11$\bar{2}$0] of the structure model in Fig. 1 is obvious [cf. Fig. 6 in (*2*)]: the two distinct configurations of bright dots in the images correspond with the rhombohedral stacking in the GeTe slab and the hexagonal stacking in the narrow As_2Te_3 slab, respectively; along a particular direction (1 in Fig. 1) the rows of bright dots are shifted on crossing the As_2Te_3 lamellae. From image simulations it was deduced that the bright dots represent Te columns under the adequate imaging conditions (*2*). All the characteristic features present in the high-resolution images of members of the $As_2Te_3(GeTe)_n$ series are also found in the corresponding images of the Bi- and Sb-containing compounds.

Figure 3 is a high-resolution image obtained along [11$\bar{2}$0] of $Bi_2Te_3(GeTe)_6$. Apart from the characteristic configurations of dots in the GeTe and Bi_2Te_3 slabs and the lateral shift of the rows of bright dots when crossing the Bi_2Te_3 layer in the indicated direction, two other features are to be noted:

—One of the blocks contains only eight Te layers instead of nine, which is the number derived from the corresponding diffraction pattern; this small deviation clearly does not influence noticeably the diffraction pattern shown as an inset.

—Irregularities occur at some of the Bi_2Te_3 slabs (e.g., at the one indicated by arrows in Fig. 3). A possible explanation is that at the right side an extra Bi layer pushes Te atoms of neighboring layers out of their normal positions; near the middle of the figure the extra layer ends, part of it being incorporated in a Te layer of the Bi_2

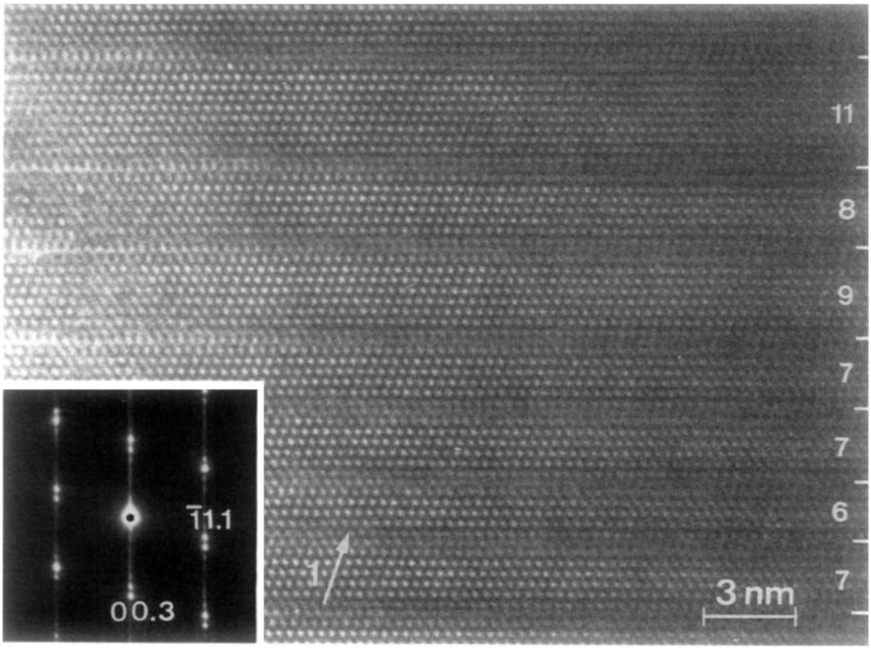

FIG. 4. High-resolution image along [11$\bar{2}$0] in the $Sb_2Ge_4Te_7$ compound. To the right the number of Te layers N (= $n + 3$) in each block is indicated.

Te_3 lamella. This could be responsible for the local deviation in brightness of the image dots.

Figure 4 is an image again produced along [11$\bar{2}$0]. It is part of the area selected for the diffraction pattern shown in Fig. 2b. As can be seen all aspects of the $R_2Te_3(GeTe)_n$ structures are again present. There is however a large variation in block thickness as was expected from the diffraction pattern; blocks with n values between 4 and 8 occur in a random sequence. The average width over the area corresponds with $n = 5$, as was also deduced from the corresponding electron diffraction pattern. In other areas in the same compound ($Sb_2Ge_4Te_7$) the variation in block width is often somewhat smaller (n = 2 to 4; n = 4 to 6).

4.4. Higher Members of the Series

It is clear from earlier observations in the $As_2Ge_nTe_{3+n}$ compounds (*2*) that to obtain members of the homologous series with large n values ($n > 9$) a prolonged heat treatment at somewhat lower temperature will be necessary. For the Sb-containing materials even longer heat treatments will be required, since in this case a treatment of 2 weeks was not even sufficient to obtain regular block arrangements in the $Sb_2Ge_4Te_7$ compound.

Figure 5 is a high-resolution image taken along [11$\bar{2}$0] in an As compound with overall composition $As_2Ge_{15}Te_{18}$ after a heat treatment of 3 weeks at 300°C. $As_2Te_3(GeTe)_n$ blocks corresponding with n values of 13 and 14 are present. Increasing the n value without adapting the preparation time leads of course to observations as those previously reported for $As_2Ge_{16}Te_{19}$ heat treated for 2 weeks at 350°C (*2*). We illustrate this in Fig. 6. In this high-resolution image taken in a compound with overall composition $Bi_2Ge_{18}Te_{21}$, heat treated for 3 weeks at 300°C, the distribution of Bi_2Te_3

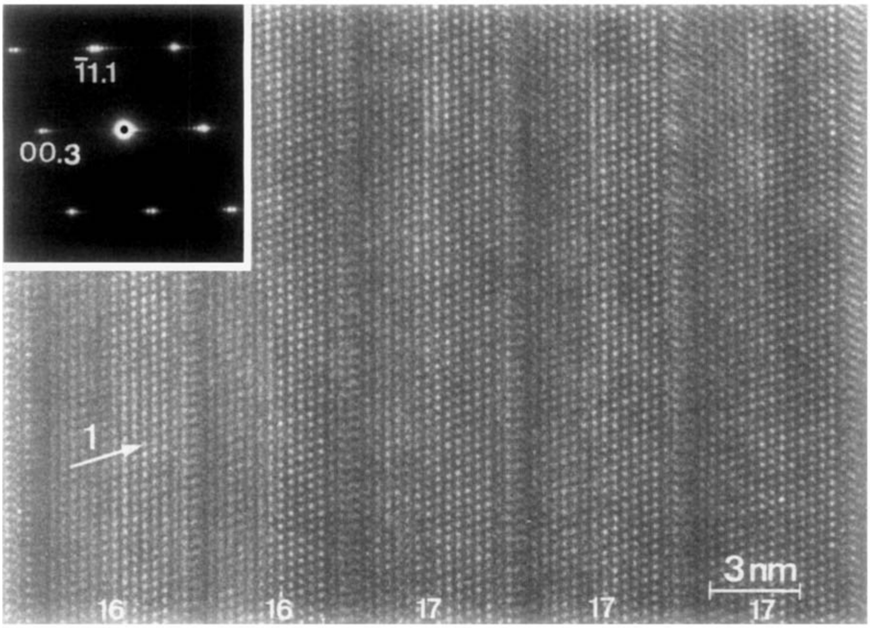

FIG. 5. High-resolution image along $[11\bar{2}0]$ in $As_2Ge_{15}Te_{18}$. $As_2Te_3(GeTe)_n$ blocks corresponding with n = 13 and n = 14 are present.

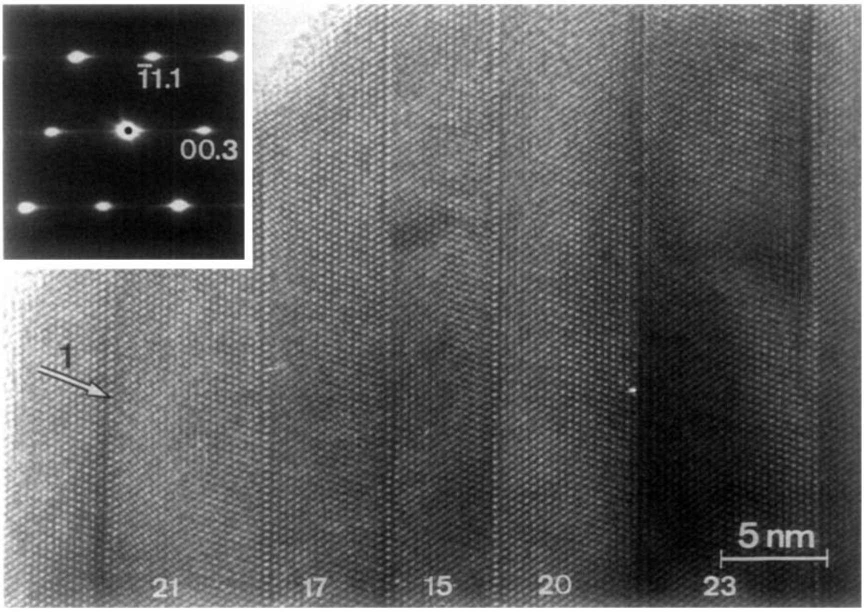

FIG. 6. High-resolution image along $[11\bar{2}0]$ in $Bi_2Ge_{18}Te_{21}$. $Bi_2Te_3(GeTe)_n$ blocks of strongly varying width (i.e., with different n values) occur in random order.

layers in the GeTe matrix can indeed be described as random; the variation in n value over the whole area is as large as 16. Both due to this large variation and the large "average width" of the blocks the arrays of superstructure spots in the electron diffraction pattern are replaced by streaks as can be seen in the inset of Fig. 6.

5. Discussion

By means of electron diffraction and high-resolution electron microscopy we have shown that substitution of As in the homologous series of mixed layer compounds $As_2Te_3(GeTe)_n$ by Sb or Bi gives rise to a new, structurally identical, series of mixed layer compounds $Sb_2Te_3(GeTe)_n$ and $Bi_2Te_3(GeTe)_n$. The duration of the heat treatment required to obtain regular structures increases with n and depends on the substituted element.

The compounds of the type discussed here may be of interest for their electronic properties. The compounds Sb_2Te_3, Bi_2Te_3, and As_2Te_3 as well as GeTe when considered separately are semiconductors with different band structures and different energy gaps. It could be of interest to investigate whether the mixed layer compounds under study have peculiar electronic properties similar to those found in GaAs and (Ga,Al)As artificial layer structures.

Replacement of Ge by Sn or Pb and/or replacement of Te by S or Se in the $R_2Ge_nTe_{3+n}$ compounds does not lead to isomorphous substitution. The reason for this is presumably to be found in the fact that the compounds that would take over the role of GeTe have the cubic NaCl-type structure or a structure different from the trigonal structure of α-GeTe. In a NaCl-type structure there is no preference for a particular close-packed plane and it is therefore unlikely that a highly anisotropic mixed layer structure would form.

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