



ELSEVIER

Contents lists available at ScienceDirect

## Journal of Solid State Chemistry

journal homepage: [www.elsevier.com/locate/jssc](http://www.elsevier.com/locate/jssc)

# Pb<sub>5</sub>Bi<sub>24</sub>Se<sub>41</sub>: A new member of the homologous series forming topological insulator heterostructures

Kouji Segawa, A.A. Taskin, Yoichi Ando\*

Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan



## ARTICLE INFO

## Article history:

Received 13 June 2014

Received in revised form

21 August 2014

Accepted 29 September 2014

Available online 13 October 2014

## Keywords:

Topological insulator

Bismuth selenide

Crystal growth

Quasi-two-dimensional transport

## ABSTRACT

We have synthesized Pb<sub>5</sub>Bi<sub>24</sub>Se<sub>41</sub>, which is a new member of the (PbSe)<sub>5</sub>(Bi<sub>2</sub>Se<sub>3</sub>)<sub>3m</sub> homologous series with  $m=4$ . This series of compounds consist of alternating layers of the topological insulator Bi<sub>2</sub>Se<sub>3</sub> and the ordinary insulator PbSe. Such a naturally-formed heterostructure has recently been elucidated to give rise to peculiar quasi-two-dimensional topological states throughout the bulk, and the discovery of Pb<sub>5</sub>Bi<sub>24</sub>Se<sub>41</sub> expands the tunability of the topological states in this interesting homologous series. The trend in the resistivity anisotropy in this homologous series suggests an important role of hybridization of the topological states in the out-of-plane transport.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

Topological insulators (TIs) are a new class of materials characterized by a nontrivial topology of the Hilbert space spanned by the wave functions of the occupied electronic states [1–3]. They are expected to be useful for various applications including high-frequency electronics, transparent electrodes, spintronics, and quantum computations [4–6]. Already a number of bulk materials have been found to be three-dimensional (3D) TIs [3], and they are all narrow-gap semiconductors composed of heavy elements which cause band inversions [3,6]. When the band inversion occurs at an odd number of the high-symmetry points in the Brillouin zone, the topological principle [3] dictates that charge-conducting gapless states show up on the surface. Hence, 3D TIs are peculiar in that they consist of gapped bulk states accompanied by gapless surface states of topological origin. Syntheses of new 3D TI materials are of great current interest for expanding our knowledge about the relationship between chemistry and quantum-mechanical functionalities [6].

In this context, there is an intriguing class of materials whose crystal structures realize a naturally-formed heterostructure consisting of alternating layers of topological insulators and ordinary insulators [3]; due to their constructions, such materials can be considered to lie at the boundary between topologically trivial and nontrivial materials. Specifically, in the homologous series of Pb–Bi–Se ternary compounds expressed in the formula (PbSe)<sub>5</sub>(Bi<sub>2</sub>Se<sub>3</sub>)<sub>3m</sub> [7–9], which we call PSBS here, layers of PbSe (which is an

ordinary insulator) alternate with layers of Bi<sub>2</sub>Se<sub>3</sub> (which is a prototypical topological insulator [10]). In these series of compounds, it was inferred from the band structure data obtained from angle-resolved photoemission spectroscopy (ARPES) that each internal interface between PbSe and Bi<sub>2</sub>Se<sub>3</sub> layers harbor topological interface states, leading to the situation that the whole bulk is filled with quasi-two-dimensional states of topological origin [11].

Interestingly, since the topological interface states appear on both sides of each Bi<sub>2</sub>Se<sub>3</sub> layer sandwiched by PbSe layers, the two topological states at the top and bottom interfaces can hybridize within each Bi<sub>2</sub>Se<sub>3</sub> layer, leading to the opening of a gap in the topological states [11]. The size of this hybridization gap becomes smaller as the Bi<sub>2</sub>Se<sub>3</sub> layer becomes thicker and the hybridization becomes weaker. Based on the electronic structure data obtained from ultrathin films of Bi<sub>2</sub>Se<sub>3</sub> [12], it is expected that the hybridization is gone when the Bi<sub>2</sub>Se<sub>3</sub> layer becomes thicker than 5 nm. Note that the crystal structure of Bi<sub>2</sub>Se<sub>3</sub> consists of covalently-bonded Se–Bi–Se–Bi–Se quintuple layers (QLs) that are interconnected by weak van der Waals force [3]. The thickness of each QL is 0.9545 nm. Thus, the hybridization of topological states in PSBS would disappear when each Bi<sub>2</sub>Se<sub>3</sub> layer contains more than 5 QLs.

In the (PbSe)<sub>5</sub>(Bi<sub>2</sub>Se<sub>3</sub>)<sub>3m</sub> homologous series, the parameter  $m$  gives the number of QLs included in each Bi<sub>2</sub>Se<sub>3</sub> layer, and the topological states becomes more robust for larger  $m$ . So far, syntheses of compounds with  $m=1, 2$ , and 3 have been reported [7–9,13], and it is naively expected that, based on the phase diagram of the PbSe–Bi<sub>2</sub>Se<sub>3</sub> pseudo-binary system reported by Shelimova et al. [9], compounds with larger  $m$  would not be naturally synthesized because they are not thermodynamically

\* Corresponding author. Tel.: +81 6 6879 8440; fax: +81 6 6879 8444.

E-mail address: [y\\_ando@sanken.osa-u.ac.jp](mailto:y_ando@sanken.osa-u.ac.jp) (Y. Ando).

stable. Despite this naive expectation, we have successfully synthesized  $m=4$  compound based on a melt-growth strategy in which the composition of the melt changes continuously as the growth proceeds. The expansion of the available compounds in this interesting homologous series is useful, because one can tune the hybridization of the topological states by changing  $m$ , which is a unique tunability among topological materials. In this paper, we report the synthesis and analyses of the  $\text{Pb}_5\text{Bi}_{24}\text{Se}_{41}$  [ $=(\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_{12}$ , called PSBS  $m=4$ ] compound, as well as its anisotropic transport properties which support the quasi-two-dimensional nature of its electronic states.

## 2. Materials and methods

### 2.1. Experimental methods

The X-ray diffraction (XRD) analysis using  $2\theta$ – $\theta$  scan is performed with Rigaku Ultima-IV X-ray apparatus equipped with a 1D-detector. For single-crystal X-ray analysis, Rigaku Mercury CCD system with graphite-monochromated  $\text{MoK}\alpha$  radiation is used. The in-plane transport properties of PSBS single crystals are measured by standard AC six-probe method, which allows measurements of the in-plane resistivity  $\rho_{ab}$  and the Hall resistivity  $\rho_H$  at the same time. By sweeping the magnetic field up to  $\pm 2$  T, the linear slope of  $\rho_H$  vs.  $B$  is obtained, from which the Hall coefficient  $R_H$  is calculated. The out-of-plane resistivity  $\rho_{c^*}$  is measured by using a four-probe method, in which the current and voltage contacts are made near the edges of the top and bottom surfaces of a rectangular sample. In the present work,  $\rho_{ab}$  and  $\rho_{c^*}$  are measured on the same samples to avoid unnecessary complications, and the results from several samples are compared to assess the reproducibility of the anisotropy measurements.

### 2.2. Crystal growth

Single crystalline samples of PSBS with a series of  $m$  values are grown by a combination of modified Bridgman and self-flux methods. The growth process is complicated, because these compounds do not exhibit congruent melting [9]. To grow high-quality single crystals, the following steps are taken: High-purity raw material shots of Pb (99.998%), Bi (99.9999%), and Se (99.999%) are sealed in a quartz tube that was heat-treated beforehand. For removing oxidization layers formed in air on the raw shots of Pb and Bi, surface cleaning procedures are performed; Pb shots are annealed in hydrogen atmosphere, and Bi shots are washed with diluted  $\text{HNO}_3$ . Based on the phase diagram reported by Shelimova et al. [9], we choose the starting composition of  $\text{PbSe}:\text{Bi}_2\text{Se}_3=45:55$  in molar ratio. The raw materials are reacted and homogenized in a melt held at 1173 K for 6 h, and the crystal growth was fostered by slowly sweeping the temperature from 1023 K to 923 K at a rate of 2 K/h in a temperature gradient of roughly 1 K/cm. At the beginning of the growth,  $m=1$  crystals are formed at the low-temperature end of the melt, which causes the composition of the melt to become PbSe-poor. As the temperature is lowered and the crystals growth proceeds, the melt becomes more and more PbSe-poor and the composition of the grown crystals changes from  $m=1$  to higher  $m$  values.

## 3. Results: grown crystals

After cutting the grown boule (Fig. 1a) with a wire saw, cleavable single crystals can be separated. The phase of each piece is determined by the  $2\theta$ – $\theta$  XRD analysis on a cleaved surface. Even when the appearance of the surface is clean and shiny, the XRD

profile can sometimes contain peaks from multiple phases; we discard such multi-phase crystals and only use those crystals that show single-phase peaks on both top and bottom surfaces for further characterizations. The largest size of the single-phase crystal we obtained was roughly  $2 \times 1 \times 0.2 \text{ mm}^3$ . The XRD pattern confirmed that the cleavage plane is along the  $ab$ -plane. Note that, because the crystal structures of the PSBS homologous series are monoclinic [13], the  $c$ -axis is *not* perpendicular to the  $ab$ -plane, and hence the direction normal to the  $ab$  plane is called  $c^*$ -axis. This means that the  $2\theta$ – $\theta$  XRD profile on a cleaved surface of a PSBS single crystal reflects the periodicity along the  $c^*$ -axis, which corresponds to  $c \sin \beta$  with  $c$  and  $\beta$  the  $c$ -axis lattice constant and the angle between the  $c$ -axis and the  $ab$ -plane, respectively. The periodicities (i.e. the  $c \sin \beta$  values) for  $m=1, 2$ , and  $3$  are obtained in the present experiments to be 1.5795(19), 2.5287(11), and 3.4753(15) nm, respectively [Fig. 1b–d and Table 1] [14]; these results are consistent with those previously reported [9,13]. However, in addition to these three phases, we found a new phase of unknown XRD profile, as shown in Fig. 1e. The crystals of this new phase presents a shiny cleavage plane, and the appearance is indistinguishable from other PSBS phases nor the  $\text{Bi}_2\text{Se}_3$  compound. Nevertheless, from the XRD profile, the periodicity perpendicular to the cleavage plane is calculated to be 4.4274(15) nm, which is very long and is obviously different from any known phase in this Pb–Bi–Se ternary system. The detailed XRD data for all four phases are presented in the Supplementary Materials.

In the PSBS compound, an increase in  $m$  corresponds to an increase in the thickness of the  $\text{Bi}_2\text{Se}_3$  layer. In fact, when  $m$  increases by one from  $m=1$  to 2 and from  $m=2$  to 3, the  $c \sin \beta$  value increases by 0.9492 and 0.9466 nm, respectively; these values are close to 0.9545 nm, the thickness of the QL unit of bulk  $\text{Bi}_2\text{Se}_3$ . In this respect, the difference in  $c \sin \beta$  between the  $m=3$  phase and the new phase is 0.9521 nm, which is also close to the QL-unit thickness of  $\text{Bi}_2\text{Se}_3$ , suggesting that the new phase corresponds to the  $m=4$  phase of the homologous series. This systematic is graphically confirmed by plotting  $c \sin \beta$  vs.  $m$  (assuming that the new phase is  $m=4$ ), which clearly presents a linear relation (Fig. 1f). Fig. 1g shows a Laue picture taken on the  $ab$ -plane of a single crystal of the  $m=4$  phase. The same pattern is obtained from any spot on the surface, which confirms the single-crystal nature of the sample. The Laue picture clearly shows three-fold symmetry and is very similar to that of the  $m=2$  and 3 phases. We show schematic pictures of the crystal structures for  $m=3$  and 4 in Fig. 1h and i; these pictures are drawn by expanding the crystal structure data for  $m=2$  [13].

We have further analyzed the crystal structure of the new phase with single-crystal X-ray apparatus with CCD imaging. The space group is identified to be monoclinic P2 with the Laue class  $2/m$ . The lattice parameters are  $a = 2.167(3)$  nm,  $b = 0.4123(5)$  nm,  $c = 4.431(8)$  nm,  $\beta = 93.35(5)^\circ$ , and  $c \sin \beta = 4.424(9)$  nm. The values of  $a$  and  $b$  are close to those reported for  $m=1$  and 2 [13], and  $c \sin \beta$  is in good agreement with that obtained from the  $2\theta$ – $\theta$  analysis. It is useful to note that  $\beta$  is closer to  $90^\circ$  than that for smaller  $m$  [9], and this is naturally explained by the elongated  $c$  unit while keeping  $a$  and  $b$  units to be essentially unchanged. Further refinement was tried both for powder and single-crystal XRD data, but it was difficult because the crystals are relatively soft and easily deformed, and also because the PSBS system appears to be metastable and the  $m=4$  homologous phase disappears upon grinding. More detailed information on this X-ray analysis is presented in the Supplementary Materials.

To quantitatively determine the actual compositions of the grown crystals, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis is employed. The results for all the grown phases, including the new phase, are shown in Table 2, in which the Se contents are fixed to the stoichiometric values

Download English Version:

<https://daneshyari.com/en/article/1329623>

Download Persian Version:

<https://daneshyari.com/article/1329623>

[Daneshyari.com](https://daneshyari.com)