Single Crystal Growth and Magnetic Properties of Mn-doped Bi₂Se₃ and Sb₂Se₃

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We have grown Mn-doped Bi₂Se₃ and Sb₂Se₃ single crystals using the temperature gradient solidification method. We report on the structural and magnetic properties of Mn-doped Bi₂Se₃ and Sb₂Se₃ compound semiconductors. The lattice constants of several percent Mn-doped Bi₂Se₃ and Sb₂Se₃ were slightly smaller than those of the un-doped samples due to the smaller Mn atomic radius (1.40 Å) than those of Bi (1.60 Å) and Sb (1.45 Å). Mn-doped Bi₂Se₃ and Sb₂Se₃ showed spin glass and paramagnetic properties, respectively.

Key words: magnetic semiconductor, thermoelectric, Bi₂Se₃, Sb₂Se₃

1. Introduction

Group V₂-V₃ compounds are known as good materials for room-temperature thermoelectric and thermomagnetic refrigeration and power generation. Bi₂Se₃ are narrow-bandgap semiconductors with rhombohedral layered crystal structure; three Se-Bi-Se-Bi-Se sequences combine to make a unit cell [1]. They can be cleaved easily along planes perpendicular to the trigonal axis (i.e., along the basal planes) due to a weak van der waals bonding between Se atoms over a strong covalent bonding between Bi and Se layers. On the other hand, Sb₂Se₃ is a relatively wide-bandgap semiconductor (Eg = 1.3 eV) with orthorhombic crystal structure [2].

Currently diluted ferromagnetic semiconductors (DFS), which are prepared by substituting transition metals into nonmagnetic semiconductors, have attracted the worldwide scientific interests for the possible spintronic devices. Ferromagnetism was observed in various systems such as group II-VI [3-5], III-V [6-8], and IV [9, 10], II-IV-V₂ [11], etc. It was also reported that Fe-doped Bi₂Te₃ and V-doped Sb₂Te₃ had ferromagnetic (FM) ordering at 12 and 22 K, respectively [12, 13]. Also, we observed that Mn-doped Bi₂Te₃ and Sb₂Te₃ had ferromagnetic ordering at Tc = 10 and 17 K, respectively [14].

Here we report on the single crystal growth and magnetic properties of Mn-doped group Bi₂Se₃ and Sb₂Se₃ compound semiconductors.

2. Experiment

Single crystalline Mn-doped Bi₂Se₃ and Sb₂Se₃ were prepared from high-purity (99.999%) manganese (Mn), bismuth (Bi), antimony (Sb) and selenium (Se) powders with particle sizes < 200 meshes to maximize the surface area and thereby enhance the reaction kinetics. First, the powders were weighed and loaded into thick walled quartz ampoules. The ampoules were then evacuated (< 10⁻⁶ Torr) and sealed. After encapsulation, the sealed ampoules were mixed, loaded into a vertical furnace and heated slowly to form single phase. For single crystal growth, Bi₂₋ₓMnₓSe₃ and Sb₂₋ₓMnₓSe₃ were cooled from 800 °C to 600 °C at 1 °C/h and thereafter at 100 °C/h. This procedure resulted in single crystals approximately 8 mm in size. The compositions of Mn were determined using EPMA (Electron Probe Micro-Analyzer).

3. Results and Discussion

We have prepared Bi₁₋ₓMn₀·₀₃Se₃ and Sb₁₋ₓMn₀·₀₄Se₃ single crystals. In order to confirm the crystal structures of Bi₁₋ₓMn₀·₀₃Se₃ and Sb₁₋ₓMn₀·₀₄Se₃, we performed θ-2θ powder X-ray diffraction (XRD) studies as shown in Fig. 1. We have carefully searched for intermetallic secondary

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Fig. 1. Powder XRD patterns of (a) Bi$_{1.97}$Mn$_{0.03}$Se$_3$ and (b) Sb$_{1.96}$Mn$_{0.04}$Se$_3$ single crystals.

Fig. 2. The scanning electron microscopy (SEM) image of Sb$_{1.96}$Mn$_{0.04}$Se$_3$ single crystal.

Sb$_{1.96}$Mn$_{0.04}$Se$_3$ was $a = 11.565$ Å, $b = 11.773$ Å, $c = 3.971$ Å with orthorhombic crystal structure. All of them were slightly smaller than those of Bi$_2$Se$_3$ ($a = 4.1396$ Å, $c = 28.636$ Å), and Sb$_2$Se$_3$ ($a = 11.633$ Å, $b = 11.780$ Å, $c = 3.985$ Å) due to the smaller Mn atomic radius (1.40 Å) than those of Bi (1.60 Å) and Sb (1.45 Å). The variations of lattice constants with Mn addition indicate the substitution of Mn in Bi$_2$Se$_3$ and Sb$_2$Se$_3$ lattices. We observed rod-like micro-sized structures in Sb$_{1.96}$Mn$_{0.04}$Se$_3$ as shown in Fig. 2 [15].

We have investigated the magnetic properties of Mn-doped Bi$_{1.97}$Mn$_{0.03}$Se$_3$ and Sb$_{1.96}$Mn$_{0.04}$Se$_3$ single crystals using physical and magnetic property measurement systems (PPMS and MPMS, Quantum Design). Figure 3(a) shows the temperature dependent field-cooled and zero-field-cooled magnetization (M) of Bi$_{1.97}$Mn$_{0.03}$Se$_3$ single crystal in a 100 Oe magnetic field. The reciprocal temperature dependent M (the inset of Fig. 3(a)) and M-H curve (Fig. 3(b)) indicate that Bi$_{1.97}$Mn$_{0.03}$Se$_3$ shows spin glass. Figure 4 shows temperature dependent zero-field
Fig. 4. (a) Temperature dependent magnetization and (b) M-H curves of of Sb$_{0.96}$Mn$_{0.04}$Se$_3$ single crystal. A reciprocal magnetization ($1/M$) is shown in the inset of Fig. 4 (a).

cooled magnetizations (Fig. 4(a)) and M-H curves (Fig. 4(b)) of Sb$_{0.96}$Mn$_{0.04}$Se$_3$ single crystal. It is observed that Sb$_{0.96}$Mn$_{0.04}$Se$_3$ shows a typical paramagnetic behavior.

We now address the effects of some possible magnetic clusters such as MnTe, MnTe$_2$, MnBi and MnSb on the observed magnetic properties. MnTe [16] and MnTe$_2$ [17] are antiferromagnetic materials with a Néel temperature of 320 and 86.55 K, respectively. The intermetallic MnBi [18] and MnSb [19] have FM ordering at 630 and 587 K, respectively. Thus, the observed spin glass property in Bi$_2$Se$_3$ crystal may exclude effects from some possible clusters.

4. Conclusion

We have grown Mn-doped Bi$_2$Se$_3$ and Sb$_2$Se$_3$ bulk single crystals using vertical gradient solidification method. Both compounds had smaller lattice constants because of the smaller atomic radius of Mn than those of Bi (Sb). Mn-doped Bi$_2$Se$_3$ and Sb$_2$Se$_3$ have spin glass and paramagnetic properties, respectively.

References