

## Sb K-edge absorption fine structure of $\text{Sb}_2\text{Te}_3$

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In order to study the local structure of some antimony compounds, Sb K-edge XAFS spectra were measured for  $\text{Sb}_2\text{Te}_3$  and InSb. The measurements were performed in the transmission mode at BL-01 of SPring-8. Though crystal structure of antimony telluride  $\text{Sb}_2\text{Te}_3$  is known by X-ray diffraction analysis, the EXAFS analyses give controversial result on the Sb-Te distance and the coordination number of  $\text{Sb}_2\text{Te}_3$ . Comparing the observed XANES spectra for  $\text{Sb}_2\text{Te}_3$  with FEFF8 calculation, we can explain the controversial results which are also supported by the observed X-ray powder diffraction.

**Keywords:** phase change material; telluride antimony; Sb K-Edge XAFS.

### 1. Introduction

Recently, reversible phase-change materials have been used as recording layer of optical storage media. One type of recording uses the difference in the refractive index between amorphous state and crystal, namely amorphous phase being associated with recorded state and crystalline phase with the erased state of the recording layer. Such phase changes depend on heating time and temperature. There are lots of materials that possess the above functionality.

Antimony compounds were considered as reversible phase change material (Tanabe et al., 1986). Because Sb is quite heavy atom, Sb K-Edge XAFS spectra for these compounds has not yet been measured. The high-energy beam-line BL01B1 in SPring-8 makes such measurements possible.

As the crystal structures of  $\text{Sb}_2\text{Te}_3$  and InSb are well-established (Donges, 1951, Giesecke and Pfister, 1958), we can use them as suitable reference samples to investigate the phase change materials. Since the EXAFS analyses of  $\text{Sb}_2\text{Te}_3$  gave inconsistent results in comparison with the X-ray diffraction result, we tried to identify the reason of this inconsistency by using the program FEFF8 (Ankudinov et al., 1998). We can give a reasonable explanation by XANES analyses and X-ray powder diffraction.

### 2. Experimental

The samples obtained from *Kojundo* Chemical Laboratory Co. Ltd., were 1–5mm grain and the purity of the constitution ratio is 99.999%. The samples for XAFS measurement are prepared by the following method. They are powdered in an agate mortar and mixed with powdered boron nitride (obtained from Aldrich Chemical Co. Ltd. 1µm grain). The mixed powder is hardened into small disk by applying pressure. The Sb K-edge X-ray absorption spectra were measured in the transmission mode at BL01B1 of SPring-8 using a Si (311) double crystal-monochromator. The electron storage ring current was 76–86 mA during measurement. The beam was cut by a 8×2 mm slit located before the sample. The second mirror angle was set to 1.3mrad to focus the beam at the sample and to reduce the level of higher harmonics. The counting time for each data point was 3s. The incident and transmitted photons were measured using

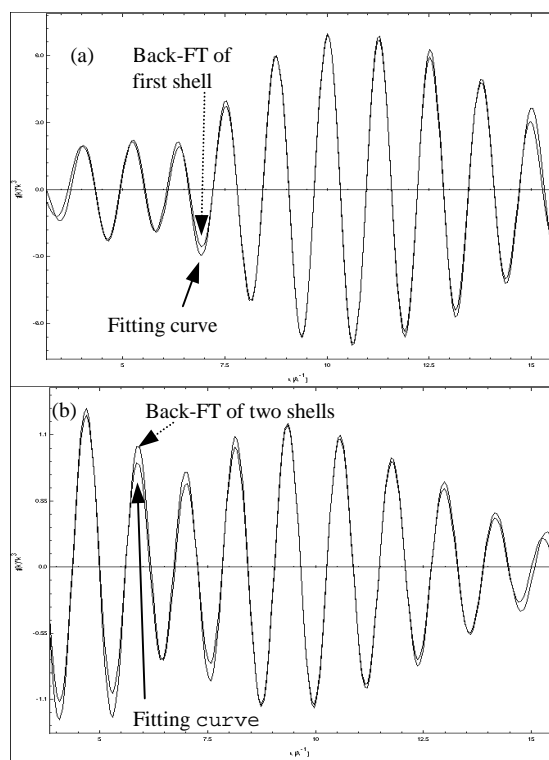
ionization chambers with Ar + 15% Kr and Kr, respectively. The sample was held in air between the ionization chambers.

After the XAFS measurement, X-ray Diffraction measurements on  $\text{Sb}_2\text{Te}_3$  were performed. The samples for X-ray Diffraction were prepared by the following method. After powdered in an agate mortar, the sample was pressed into a standard glass holder and mounted on an X-ray diffractometer (Mac-Science) which is equipped with a monochromator before detector. Continuously scanned data up to  $2\theta = 100^\circ$  with  $0.03^\circ$  sampling width and 2deg/min scanning speed were collected using Cu-K $\alpha$  radiation. The X-ray tube was operated at the accelerating voltage 40kV and tube current of 40mA.

### 3. Results and Discussion

According to previous papers (Donges, 1951, Giesecke and Pfister, 1958), the structure of  $\text{Sb}_2\text{Te}_3$  is hexagonal with space group number 166 and lattice constants  $a=4.25\text{\AA}$   $c=30.4\text{\AA}$ , and the structure of InSb is cubic with space group number 216 and lattice constant  $a=6.48\text{\AA}$ . In crystalline  $\text{Sb}_2\text{Te}_3$ , each Sb atom is surrounded by six Te atoms, three of them with the distance 2.98Å and other atoms with 3.18Å. In crystalline InSb, Sb atom is surrounded four In atoms with Sb-In distance 2.80Å.

Figure 1 (a), (b) shows the Back Fourier Transform and corresponding fits for these compounds. The Fig.(a) is the curve of InSb and Fig.(b) is the one of  $\text{Sb}_2\text{Te}_3$ . Using theoretical parameter calculated with the FEFF8 program (Ankudinov et al., 1998), the EXAFS analyses were refined using the program of Ressler (Ressler, 1997). For the EXAFS analysis of  $\text{Sb}_2\text{Te}_3$ , we used a two-distance model where the EXAFS oscillation is given by the superposition of two EXAFS function, one is for the short Sb-Te distance ( $\sim 2.98\text{\AA}$ ) and the other for the long Sb-Te distance ( $\sim 3.18\text{\AA}$ ). From the fitting results, the distance and the coordination number of InSb agree well



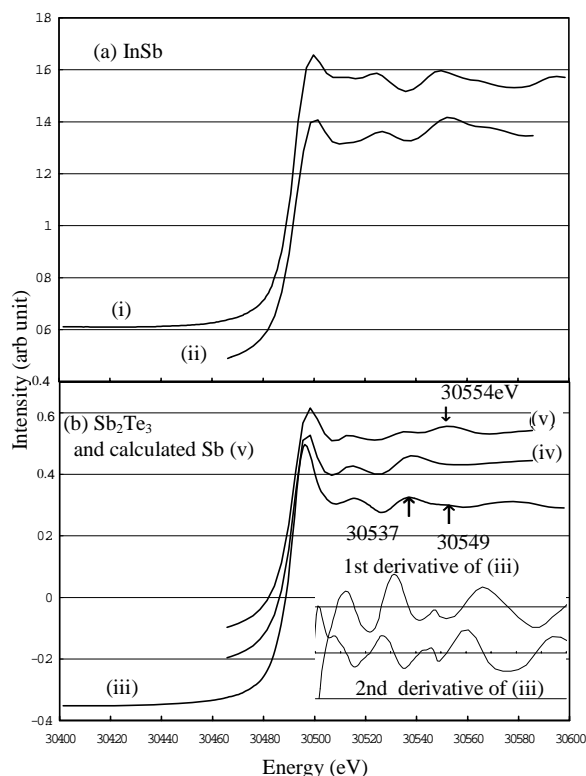
**Figure 1**

The Back Fourier Transform and corresponding fits for  $\text{Sb}_2\text{Te}_3$  and InSb.

with the data ( $N=4.1$ ,  $r=2.800$  (Å),  $\sigma^2=0.005$  (Å<sup>2</sup>)) by X-ray diffraction, but these of  $\text{Sb}_2\text{Te}_3$  do not agree with the data by diffraction.

Figure 2 (a) and (b) show the experimental and calculated spectra for Sb-K Edge XANES spectra. The lines (i) and (iii) are the experimental spectra for  $\text{Sb}_2\text{Te}_3$  and InSb, the lines (ii), (iv) and (v) are the calculated spectra by FEFF8 for InSb,  $\text{Sb}_2\text{Te}_3$  and Sb crystals. Good convergence is obtained for a cluster size up to 7.0Å including about 30 atoms.

We use the geometrical parameters of crystal Sb determined by James et al. (1921) for the present calculations. The crystal Sb and  $\text{Sb}_2\text{Te}_3$  belong to the same space group. In crystal Sb, each Sb atom is surrounded by six Sb atoms, three of them have the Sb-Sb distance with 2.90 Å, and three have 3.36 Å. Thus the local structure around Sb atom is very similar to the structure in  $\text{Sb}_2\text{Te}_3$ . Figure 2(a) compares the experimental and calculated XANES spectra of InSb, and shows good agreement. On the other hand, the calculated result for  $\text{Sb}_2\text{Te}_3$  also show a good agreement with the experimental one, however we find a small peak at 30549eV in the experimental spectrum of  $\text{Sb}_2\text{Te}_3$  (iii). The first and the second derivative



**Figure 2**  
The experimental and calculated Sb K-edge XANES for  $\text{Sb}_2\text{Te}_3$ , InSb

spectrum of (iii) are also shown in Figure 2. These derivative spectra clearly show a small peak at 30549eV. The comparison between the calculated spectra of  $\text{Sb}_2\text{Te}_3$  (iv) and Sb (v) shows a significant difference at  $\sim 30554$ eV. Therefore if the spectrum of Sb is superposed on the  $\text{Sb}_2\text{Te}_3$  spectrum, the shoulder peak would appear at  $\sim 30554$ eV. The overall experimental XANES could be explained by the superposition of the spectrum of  $\text{Sb}_2\text{Te}_3$  and Sb.

Figure 3 (a), (b) shows the observed X-ray powder diffraction pattern of the same  $\text{Sb}_2\text{Te}_3$  sample except for the crystallized grain size, the Fig (a) being for the 1–5mm grain sample measured by this

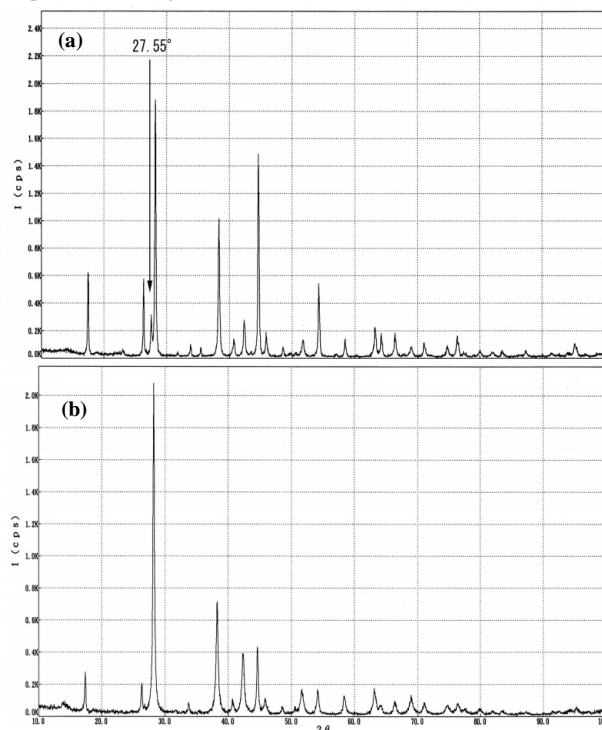
XAFS measurement and Fig (b) for the about 70 $\mu\text{m}$  grain sample. Most of peaks are assigned to  $\text{Sb}_2\text{Te}_3$ , and the peak at  $2\theta=27.55^\circ$  in Figure 3 (a) is not assigned. The crystal structure of Te (Slattery, 1923) shows the maximum intensity at  $2\theta=27.55^\circ$ ; we can expect that there is crystallized Te in this  $\text{Sb}_2\text{Te}_3$  sample. The maximum intensity peak of crystal Sb is not separated out in this measurement because the maximum intensity peak of crystal Sb appears at nearly same angle of  $\text{Sb}_2\text{Te}_3$ .

Though the Sb/Te ratio in  $\text{Sb}_2\text{Te}_3$  is fixed, crystalline  $\text{Sb}_2\text{Te}_3$  can mix with crystallized Sb and Te. Because this ratio is not eutectic point (Abrikosov et al., 1959), the delicate condition of homogeneity and crystallization led to the crystal growth of Sb and Te in this sample. To crystallize antimony telluride for the recording materials, we have to pay attention not only to the atomic ratio but also to the crystallized condition to avoid the coexistence of Sb and Te crystals.

#### 4. Conclusion

Sb K-edge X-ray absorption fine structure of  $\text{Sb}_2\text{Te}_3$  and InSb were measured at BL01B1 of SPring-8. The EXAFS analyses for InSb yield the consistent results, whereas the  $\text{Sb}_2\text{Te}_3$  sample yielded results which inconsistent with the crystal structure. The peak around 30549eV, which is not predicted by a XANES calculation, indicates the coexistence of Sb and  $\text{Sb}_2\text{Te}_3$  crystals. The observed X-ray powder diffraction pattern of  $\text{Sb}_2\text{Te}_3$  supported the coexistence of Te and  $\text{Sb}_2\text{Te}_3$  crystals because we observe a strong peak characteristic for crystallized Te. Depending on the crystallized condition,  $\text{Sb}_2\text{Te}_3$  sample can involve Sb and Te crystals.

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**Figure 3**  
The X-ray diffraction spectra of  $\text{Sb}_2\text{Te}_3$  measured by this Sb-K Edge XAFS for (a) and of the other  $\text{Sb}_2\text{Te}_3$  sample for (b).

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