

## Multiple scattering approach to K-edge XANES of Sb–Te systems

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The Sb–Te systems are important for optical memories. The local structures of these Sb–Te systems are crucial to understand the properties. Here we study three different Sb–Te systems, Sb<sub>2</sub>Te<sub>3</sub>, c- and a-SbTe (c; crystalline, a; amorphous) by use of XANES analyses. The present calculations for Sb<sub>2</sub>Te<sub>3</sub> system show quite good agreement with the observed spectra. In contrast to Sb<sub>2</sub>Te<sub>3</sub> system, both c- and a-SbTe systems, in which a ratio of Sb to Te is 3, are metastable; both of the structures have not been known yet. We thus investigate these local structures by use of the multiple scattering approach, and propose a possible model for each of c- and a-SbTe.

**Keywords:** Sb–Te systems; disordered systems; XANES analyses; multiple scattering approach.

### 1. Introduction

Since 1968 (Ovshinsky, 1968), amorphous chalcogenide semiconductors have been applied to the optical disks using reversible transition between amorphous and crystalline phases.

Antimony and tellurium systems have often been used as optical disks, and they are considered as important materials. So far we have had small amount of structural information on two metastable states, crystalline (c) and amorphous (a) states. We measure XAFS spectra for three different Sb–Te system, Sb<sub>2</sub>Te<sub>3</sub>, crystalline and amorphous SbTe to study the local structures. In particular Sb and Te K-edge XANES spectra are analyzed by use of the full multiple scattering calculation for that purpose.

### 2. Experiment

Samples are 200nm thick film of binary alloy Sb–Te deposited by sputtering on polycarbonate substrates with 0.6mm thickness. The films are sandwiched by SiO<sub>2</sub>/ZnS 55nm dielectric layers. Films as deposited are amorphous and films which are heated by laser under melting point are in crystalline phase. Each sample disk is diced into 4mm × 12mm chips.

XAFS spectra were recorded in transmission mode with a pile of 200 sheets of these chips. Measurement was carried out using Si (311) double-crystal monochromator at BL01B1 in Spring-8 whose energy resolution is about 1.8eV.

### 3. Method of Calculation

The XANES theory used in this paper is based on the short-range-order full multiple scattering theory proposed by Fujikawa *et al.* (1983). Here, we summarize the theoretical methods for later discussion.

The X-ray absorption intensity  $\sigma$  from the core orbital  $\phi_c(\mathbf{r}) = R_{l_c}(r)Y_{l_c}(\hat{\mathbf{r}})$ ,  $L_c = (l_c, m_c)$  at site A (X-ray absorbing atom) is given by eq. (1) for photoelectron kinetic energy  $\varepsilon_k = k^2/2$ . We assume

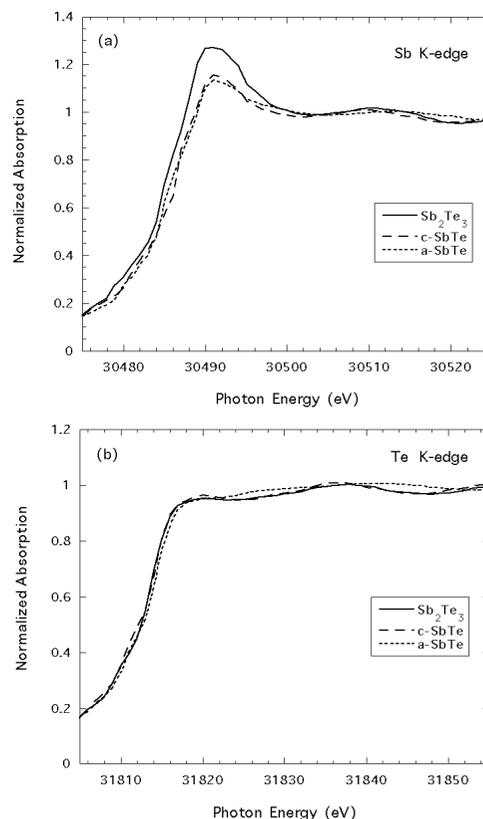
excitation by a linearly polarized X-ray in the  $z$ -direction (Fujikawa *et al.*, 1983; Fujikawa, 1993)

$$\sigma = -\frac{8}{3} \text{Im} \left\{ \sum_{m_c, L, L'} t^{l-l'} \exp \{ i(\delta_l^A + \delta_{l'}^A) \} \rho_c(l) \rho_c(l') \right. \\ \left. \times G(L_c 10 | L) G(L_c 10 | L') (t^{-1})_{LL}^{AA} [(1-X)^{-1}]_{LL}^{AA} \right\}, \quad (1)$$

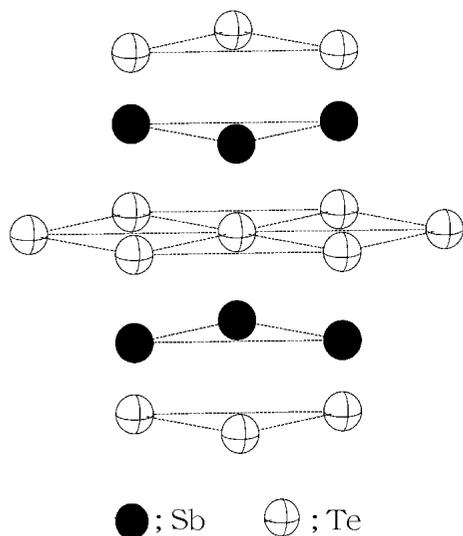
where  $G(LL' | L'')$  is Gaunt's integral and  $\rho_c(l)$  is the radial dipole integral between the radial part of  $\phi_c(\mathbf{r})$  and the  $l$ th partial wave of photoelectrons  $R_l(r)$  at site A. The phase shift of the  $l$ th partial wave at site A is represented by  $\delta_l^A$ . We introduce the matrix  $X$  specified with site index  $\alpha$  and angular momentum  $L$  and so on; it is defined as

$$X_{LL'}^{\alpha\beta} = t_l^\alpha G_{LL'}(\mathbf{R}_\alpha - \mathbf{R}_\beta) (1 - \delta_{\alpha\beta}), \quad (2)$$

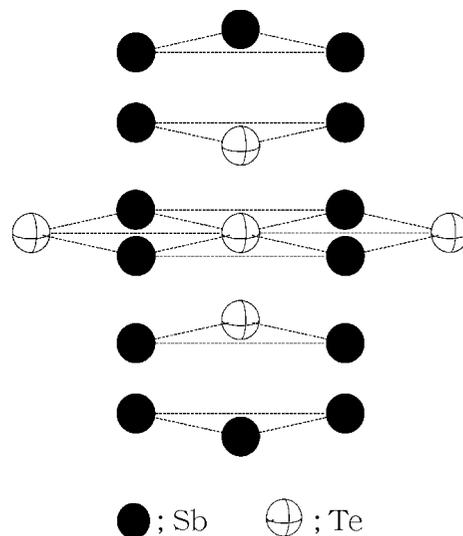
where  $t_l^\alpha$  and  $G_{LL'}$  represent the  $t$ -matrix at site  $\alpha$  and the Green's function in an angular momentum representation. The inverse matrix  $(1-X)^{-1}$  includes an infinite order of the full multiple scattering inside the cluster we are considering. The phase shifts in  $t_l$  ( $= -[\exp(2i\delta_l) - 1]/2ik$ ) are one of the most important features and reflect the electronic structure of the surrounding atoms, whose potentials are constructed within muffin-tin approximation. The Green's function  $G_{LL'}$  reflects the geometrical structure.



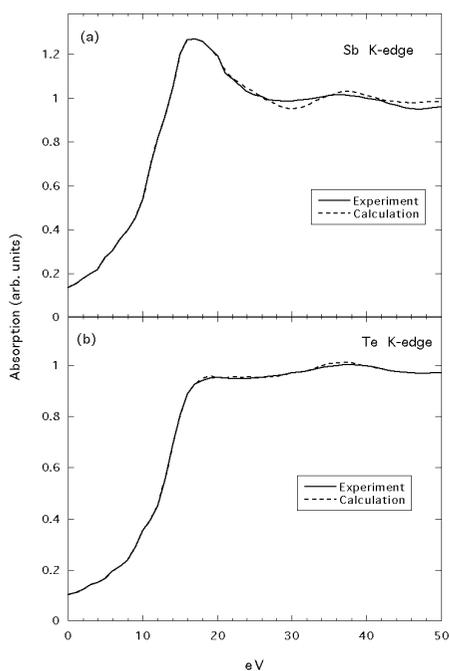
**Figure 1**  
Measured (a) Sb and (b) Te K-edge XANES spectra of Sb<sub>2</sub>Te<sub>3</sub>, c- and a-SbTe.



**Figure 2**  
The unit cell of  $\text{Sb}_2\text{Te}_3$  in hexagonal structure has -Te-Sb-Te-Sb-Te-arrangement.



**Figure 4**  
The unit cell of c-SbTe with hexagonal structure, which is similar to the local structure of  $\text{Sb}_2\text{Te}_3$ .



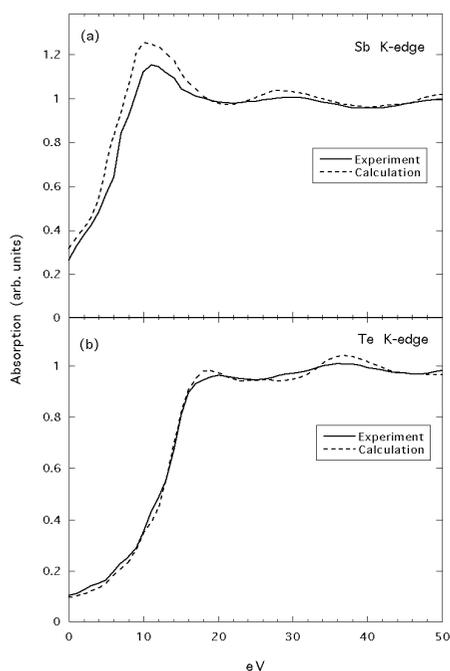
**Figure 3**  
Calculated (a) Sb and (b) Te K-edge XANES spectra for  $\text{Sb}_2\text{Te}_3$  are compared with the experimental spectra.

#### 4. XANES Analyses

Figure 1 shows the measured Sb (a) and Te (b) K-edge XANES spectra for  $\text{Sb}_2\text{Te}_3$ , c- and a-  $\text{SbTe}$ . In the Sb spectra, the three systems show slightly different position at the second peak (for  $\text{Sb}_2\text{Te}_3$  30510eV, for c-SbTe 30508eV, for a-SbTe 30514eV). In the Te K-edge spectra,  $\text{Sb}_2\text{Te}_3$  and c-SbTe also give rise to the shift at the second peak as observed in the Sb K-edge spectra in Fig. 1 (a) (for  $\text{Sb}_2\text{Te}_3$  31838eV, for c-SbTe 31836eV). Though L-edge spectra can be measured in high resolution, however Sb and Te L-edge are too close to measure each of XANES spectrum. In both of Sb and Te K-edge spectra, a-SbTe gives structureless XANES, which are typically observed for amorphous systems (Yanagisawa *et al*, 1998).

From now on, energy 0 is set to be the onset of the Sb and Te K absorption edge. First we apply the full multiple scattering approach to the analyses of  $\text{Sb}_2\text{Te}_3$  XANES. In our calculations, we considered all atoms within about 8 Å around an X-ray absorbing atom including 75 atoms. The structure of  $\text{Sb}_2\text{Te}_3$  is hexagonal with -Te-Sb-Te-Sb-Te- arrangement as shown in Fig. 2 (Richter *et al*, 1977). The calculated result is shown in Fig. 3 compared with the observed spectra for both (a) Sb and (b) Te K-edge spectra, which show good agreement. Here we chose the  $E_0$  value as a fitting parameter so as to obtain the best agreement with the observed spectra. The white line height is the standard to be normalized. For the phase shift calculation we refer to the electronic structure of Sb and Te calculated by FEFF8 program (Ankudinov *et al*, 1998). The calculated XANES spectra show nearly the same result even if we use slightly different electronic structures; for example,  $5p^3$ ,  $5p^25d^1$  and  $5p^{2.97}5d^{0.03}$  (FEFF8) electronic configurations of Sb give nearly the same calculated spectra. From this result, we found that the electronic structure has small influence on the calculated spectra for these systems.

Next, we have calculated the XANES spectra for c-SbTe, in which the ratio of Sb to Te is 3. Though the X-ray diffraction gives the information on the unit cell, whereas Sb and Te are near neighbours in the periodic table and it is difficult to distinguish them by use of this technique. Both Te and  $\text{Sb}_2\text{Te}_3$  crystals have hexagonal structure, and the observed XANES spectra are quite similar (see



**Figure 5**  
Calculated (a) Sb and (b) Te K-edge XANES spectra for the c-SbTe model shown in Fig. 4 compared with the experimental spectra.

Fig. 1). The X-ray diffraction patterns for  $\text{Sb}_2\text{Te}_3$  and c-SbTe are nearly the same. These results suggest a plausible model shown below. Rearrangement of hexagonal structure shown in Figure 2

leads to a possible model for this system shown in Fig. 4. This model satisfies the conditions Sb/Te ratio = 3 and the coordination number = 6. This model has five layers whose outer two layers are Sb layers and inner three layers include both Sb and Te atoms. The calculated result is shown in Fig. 5 compared with the experimental one. The calculated spectra give strong structures, whereas the peak position are well predicted. Those strong structures could be suppressed by considering large Debye-Waller factors, since c-SbTe is very soft matter in metastable state. We have also studied other possible models, such as fcc models and loosely packed models, which gave rise to poor agreement.

We also investigate the XANES spectra of a-SbTe. Though the result is not shown in this paper, possible models including the angular fluctuation give a comparable result for a-SbTe spectra.

## 5. Concluding Remarks

The observed Sb and Te K-edge XANES spectra of three systems ( $\text{Sb}_2\text{Te}_3$ , c- and a-SbTe) are studied by use of the full multiple scattering calculations. The calculated spectra are not sensitive to the electronic structures. We thus extract the geometric information of the latter two systems. For  $\text{Sb}_2\text{Te}_3$  a good agreement is obtained. On the other hand for c-SbTe the calculated spectra show strong structures, though the peak positions are well predicted. Further study is necessary to obtain a better agreement.

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