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Oscillatory diffuse X-ray scattering from lead chalcogenides

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Abstract Diffuse X-ray scattering from lead chalcogenides (PbS, PbSe, and PbTe) was measured at 15 and 294 K. The increase of the diffuse scattering intensities with the temperature was explained by the thermal correlation effects among thermal displacements of second nearest neighboring Pb–Pb atoms. The contribution from the second nearest neighboring atoms to the diffuse scattering was clearly confirmed.

Keywords Correlation effects · Diffuse scattering · Thermal vibration · X-ray diffraction

Introduction

Diffuse scattering is one of the tools for analyzing structural disorder in solids. It is well known that diffuse scattering contains information about a short-range order in a disordered arrangement (static disorder) and thermal vibration of atoms (thermal disorder) in crystals [1]. Anomalously strong and oscillatory diffuse scattering from α-AgI type solid electrolyte [2, 3] has been studied in X-ray and neutron scattering experiments. The first peak of the oscillatory diffuse scattering was due to static and thermal disorders. The oscillatory forms were also observed even from ordered crystals [4, 5]. The correlation effects between first nearest neighboring atoms were taken in and the profile of the diffuse scattering of ionic crystals had been analyzed. The presence of the correlation effects between second nearest neighboring atoms was pointed out from the analysis of diffuse scattering of copper halides [6]. The relationship between inter-atomic distance and the values of thermal correlations has been investigated by the computer simulation [7].

Lead oxides and chalcogenides are known as semiconductor materials that can be applied in optical fiber transmission and pollution monitoring in injection lasers [8]. Recently, these materials have been used to develop mixed conducting polymer, known as “semiconductor-dispersed polymer electrolyte” [9]. Many studies have been performed on thermal properties, electronic structures, and bonds of atoms in these compounds [10–12].

In order to inspect the correlation effects among thermal displacements of second nearest neighboring atoms to the diffuse scattering profile, the use of lead chalcogenides PbX (X = S, Se, Te) is important since the atomic scattering amplitude of Pb is much greater than that of chalcogen. The diffuse scattering has been investigated for powder PbS, PbSe, and PbTe at 15 and 294 K by X-ray diffraction measurement.

Experimental

The powder samples of PbS, PbSe, and PbTe (purity 99.9%) were obtained from High Purity Chemicals Co.

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X-ray diffraction measurements were carried out for powder lead chalcogenides in a cryostat by using CuKα radiation at 15 and 294 K. The experiments were performed using RIGAKU RINT2000 X-ray diffractometer. X-ray diffraction data were collected for 4 s per step at 0.05° intervals over the 2θ range from 10° to 90° by a step-scan mode. The reflection from (002) plane of a pyrolytic graphite crystal monochrometer was used.

Results and discussions

Figure 1 shows the observed diffuse X-ray scattering intensities of PbS, PbSe, and PbTe. Some peaks of oscillatory diffuse scattering of PbS were observed around $2\theta \sim 28°$, 52° and 72°. The diffuse scattering peaks were observed around $2\theta \sim 28°$, 50° and 70° for PbSe and around $2\theta \sim 27°$, 47° and 67° for PbTe. The temperature dependence on the diffuse scattering intensities of powder lead chalcogenides was obtained. The intensity of diffuse scattering at 15 K for each sample is smaller than that of 294 K.

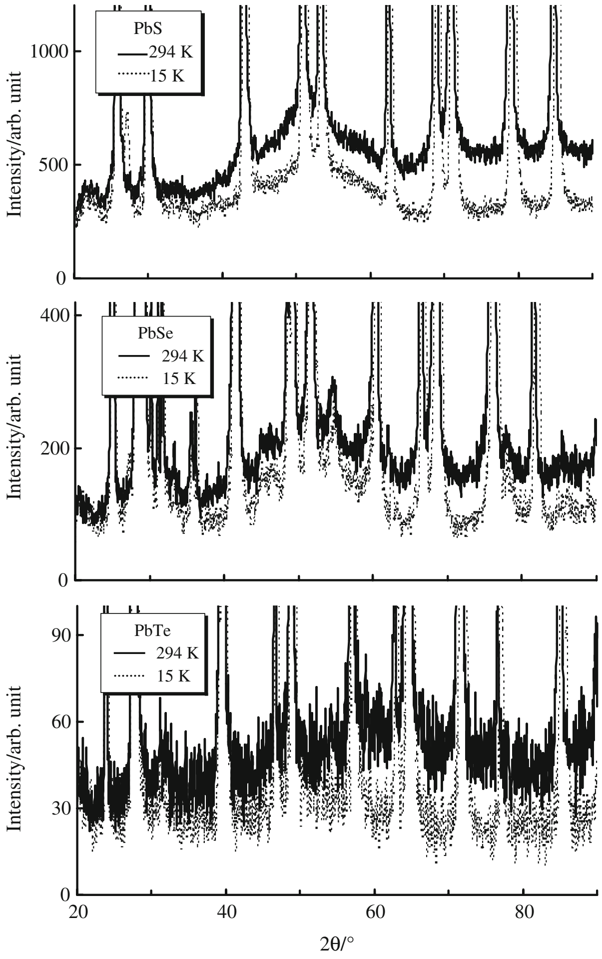

Fig. 1 Diffuse X-ray scattering intensities of lead chalcogenides at 15 K (*dotted line*) and 294 K (*solid line*)

In the analysis of diffuse X-ray scattering, the intensity of diffuse background I_B including the correlation effects among thermal displacements of atoms is expressed as follows [6];

$$\begin{aligned} I_{\mathrm{B}} =& I_{\mathrm{o}} K N_{\mathrm{o}} \sum_{s} n_i f_{s(i)} f^{*}_{s(i)} \left[1 - \exp\left(-2M_{s(i)}\right)\right] \\ &+ I_{\mathrm{o}} K N_{\mathrm{o}} \sum_{s} \sum_{s'} n_i f_{s(i)} f^{*}_{s'(j)} \\ &\left[\exp\left\{-\left(M_{s(i)} + M_{s'(j)}\right)\left(1 - \mu_{rs(i)s'(j)}\right)\right\}. \right. \\ &\left. - \exp\left\{-\left(M_{s(i)} + M_{s'(j)}\right)\right\}\right] Z_{s(i)s'(j)} \frac{\sin(Qr)}{Qr} \\ &+ I_{\mathrm{o}} K N_{\mathrm{o}} \sum_{s} n_i \sigma_{\mathrm{inc}} + C, \end{aligned} \qquad (1)$$

where $f_{s(i)}$ is the atomic scattering factor for atom in site $s(i)$, I_o a scale factor, K a function depending on the polarization factor, N_o the number of the unit cell in unit volume, and Z the number of sites belonging to the sth j-type neighbor around an sth i-type site. n_i corresponds to the number of i atoms per unit cell. f^* means the complex conjugate of f. Two sites $s(i)$ and $s'(j)$ are apart by the distance r. $\exp(-M_i)$ $(=\exp\{-B_i(\sin\theta/\lambda)^2\})$ is Debye–Waller factor of the i atom. σ_{inc} is incoherent scattering cross section of atoms. The constant C is added for the corrections of background noise. The oscillatory form is expressed as $\sin(Qr)/Qr$, where Q is equal to $4\pi\sin\theta/\lambda$. The correlation effects among the thermal displacements of atoms μ are written as follows;

$$\mu_{r_{s(i)s'(j)}} = \frac{2\left\langle \Delta\mathbf{r}_{s(i)} \cdot \Delta\mathbf{r}_{s'(j)} \right\rangle}{\left\langle \Delta\mathbf{r}^2_{s(i)} \right\rangle + \left\langle \Delta\mathbf{r}^2_{s'(j)} \right\rangle}. \qquad (2)$$

The values of the correlation effects among the thermal displacements of $s(i)$ and $s'(j)$ atoms is 0 in the case of no correlation among thermal displacements, and in the case of perfect correlation μ is $2\sqrt{B_{s(i)}B_{s'(j)}}/\left(B_{s(i)} + B_{s'(j)}\right)$.

Rietveld analysis has been performed on the X-ray intensities of lead chalcogenides using RIETAN-2000 [13]. The crystals of lead chalcogenides are assumed to belong to NaCl type structure with the space group *Fm3m*, where lead and chalcogen atoms occupy 4(a) and 4(b) sites, respectively [8]. The Debye–Waller temperature parameters were obtained from the analysis of the intensities of Bragg lines. The obtained final results of the structural parameters (a: lattice constant, B: Debye–Waller temperature parameter) and the reliability factors R at 15 and 294 K are shown in Table 1. The number of neighboring atoms Z and inter-atomic distances r in the crystals of lead chalcogenides are shown in Table 2.

In Fig. 1, a large diffuse scattering peak of PbS, PbSe, and PbTe was observed at $2\theta \sim 50°$ at 15 K. The similar diffuse scattering peak existed also at 294 K. This peak

Table 1 Structure parameters (*a*: lattice constant, *B*: Debye–Waller temperature parameter) and *R* factors obtained by Rietveld refinement analysis of lead chalcogenides

	PbS		PbSe		PbTe	
	15 K	294 K	15 K	294 K	15 K	294 K
a/nm	0.5919	0.5931	0.6123	0.6194	0.6462	0.6519
B_{Pb}/nm^2	0.00041	0.00223	0.00025	0.00367	0.00035	0.00393
B_X/nm^2	0.00097	0.00720	0.00054	0.00598	0.00031	0.00356
R_{wp}/%	15.52	10.10	15.59	13.67	16.20	15.61
R_I/%	6.34	4.51	6.18	5.50	8.04	1.95
R_F/%	4.32	3.00	4.56	3.30	5.75	2.08
S	2.14	2.01	2.350	2.09	1.79	1.76

Table 2 Number of neighboring atoms *Z*, inter-atomic distances *r*, and the value of correlation effects between thermal displacements of atoms μ in the crystal PbS, PbSe, and PbTe

	Z	$r_{15\ K}$/nm	$r_{294\ K}$/nm	μ
Pb–S	6	0.2959 (5)	0.2965 (6)	0.60
Pb–Pb	12	0.4185 (2)	0.4193 (4)	0.45
Pb–S	8	0.5126 (4)	0.5136 (4)	0
Pb–Pb	6	0.5919 (6)	0.5931 (2)	0
S–Pb	6	0.2959 (5)	0.2965 (6)	0.60
S–S	12	0.4185(2)	0.4193 (4)	0.45
S–Pb	8	0.5126 (4)	0.5136 (4)	0
S–S	6	0.5919 (6)	0.5931 (2)	0
Pb–Se	6	0.3061 (9)	0.3097 (2)	0.60
Pb–Pb	12	0.4329 (6)	0.4379 (4)	0.45
Pb–Se	8	0.5303 (3)	0.5364 (2)	0
Pb–Pb	6	0.6123 (9)	0.6194 (3)	0
Se–Pb	6	0.3061 (9)	0.3097 (2)	0.60
Se–Se	12	0.4329 (6)	0.4379 (4)	0.45
Se–Pb	8	0.5303 (3)	0.5364 (2)	0
Se–Se	6	0.6123 (9)	0.6194 (3)	0
Pb–Te	6	0.3231 (4)	0.3259 (9)	0.60
Pb–Pb	12	0.4569 (1)	0.4609 (4)	0.45
Pb–Te	8	0.5596 (7)	0.5646 (1)	0
Pb–Pb	6	0.6462 (7)	0.6519 (7)	0
Te–Pb	6	0.3231 (4)	0.3259 (9)	0.60
Te–Te	12	0.4569 (1)	0.4609 (4)	0.45
Te–Pb	8	0.5596 (7)	0.5646 (1)	0
Te–Te	6	0.6462 (7)	0.6519 (7)	0

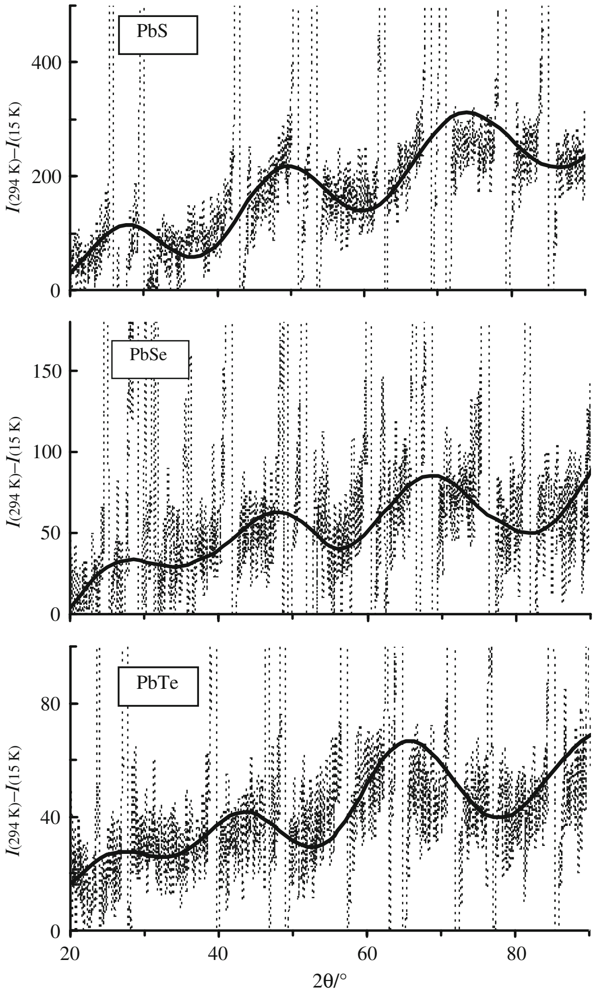

Fig. 2 The difference between diffuse X-ray scattering intensities at 294 K and 15 K for lead chalcogenides. The *dotted line* and *solid line* show the observed and calculated intensities, respectively

might be related to a static disorder that would be occurred because of the grinding process in the X-ray sample preparation. In order to analyze the temperature influence of the diffuse scattering intensities, the differences between the intensities at 294 and 15 K have been investigated. The dotted lines in Fig. 2 show the difference between the observed intensities at 294 and 15 K of lead chalcogenides. The oscillatory profile of the difference between the diffuse scattering intensities at 294 and 15 K was clearly obtained.

The diffuse scattering intensities at 294 and 15 K were calculated with the parameters in Tables 1 and 2. The values of correlation effects between the first and the second nearest neighboring atoms are 0.60 and 0.45, respectively. The other values of correlation effects are assumed to be 0, as shown in Table 2. The values of correlation effects decrease with the inter-atomic distances [6]. The calculated intensities are shown in Fig. 2 by solid lines. The calculated intensities could explain the characteristics of the observed diffuse scattering intensities in Fig. 2.

In order to estimate the contribution from first and second neighboring atoms to the intensity of diffuse scattering, the intensity I_{corr} of the second term in Eq. 1 is written with three components:

$$I_{\mathrm{corr}} = I_{\mathrm{c-a}} + I_{\mathrm{c-c}} + I_{\mathrm{a-a}}, \quad (3)$$

where $I_{\mathrm{c-a}}$, $I_{\mathrm{c-c}}$, and $I_{\mathrm{a-a}}$ are contribution from cation–anion (first nearest neighbor pairs; Pb–chalcogen), cation–cation (second nearest neighbor pairs; Pb–Pb), and anion–anion (second nearest neighbor pairs; chalcogen–chalcogen), respectively. The contribution from each component of Eq. 3 at 294 K is shown in Fig. 3. It is found that the oscillatory scheme in the diffuse scattering profile of lead chalcogenides (solid lines) is mainly from the contribution of Pb–Pb pair (open circle symbol) as shown in Fig. 3. Although the value of the correlation effects of Pb–Pb atoms is less than that of Pb–chalcogen, the strong contribution from lead–lead pair was caused by the large value of atomic scattering factor of Pb. Atomic scattering factor of Pb is much greater than that of chalcogen (S, Se, and Te). The contributions of anion–anion (chalcogen–chalcogen) pair in the crystal of lead chalcogenides are small in the whole scattering angle.

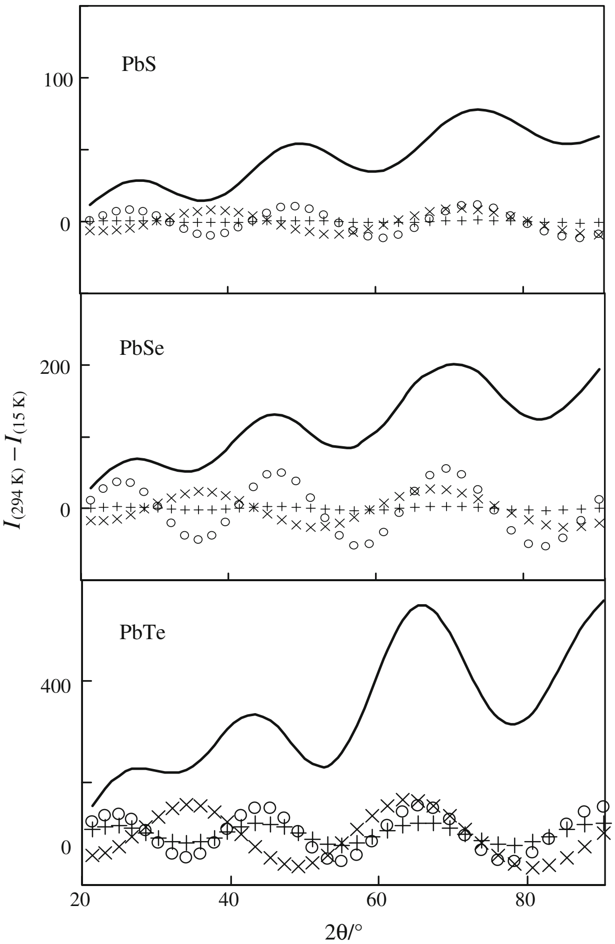

Fig. 3 The difference between calculated diffuse X-ray scattering intensities at 294 and 15 K of lead chalcogenides. The total intensity *I* is shown by *solid line*; contribution from cation–cation (Pb–Pb) pair $I_{\mathrm{c-c}}$ by *open circle symbol*, contribution from cation–anion (Pb–chalcogen) pair $I_{\mathrm{c-a}}$ by *cross symbol*, and contribution from anion–anion (chalcogen–chalcogen) pair $I_{\mathrm{a-a}}$ by *plus symbol*

The peak positions of the diffuse scattering intensities in Fig. 3 coincide with those of $\sin(Qr_{\mathrm{Pb-Pb}}) = 1$, where $r_{\mathrm{Pb-Pb}}$ is the inter-atomic distance between second nearest Pb–Pb atoms of lead chalcogenides. The inter-atomic distances between Pb–Pb pair for PbS, PbSe, and PbTe at 294 K are about 0.4193, 0.4379, and 0.4609 nm, respectively. It is shown in Fig. 4 that the diffuse scattering peaks of lead chalcogenides shift to the lower Q region as the inter-atomic distance between cation–cation (Pb–Pb) of lead chalcogenides becomes larger.

In the former reports [3, 14], there are two peaks of diffuse scattering in the 2θ region from 20° to 90° by CuKα radiation. The positions of peaks correspond to those of $\sin(Qr) = 1$, where r is the inter-atomic distance between first nearest neighboring atoms. In the case of lead chalcogenides, there are three peaks of diffuse scattering in the same 2θ range by CuKα radiation as shown in Fig. 2 because of the long inter-atomic distance among Pb and Pb atoms.

It has been shown that the correlated motion among neighboring atoms is important idea for EXAFS analysis [15]. However, the detailed discussion about the values of

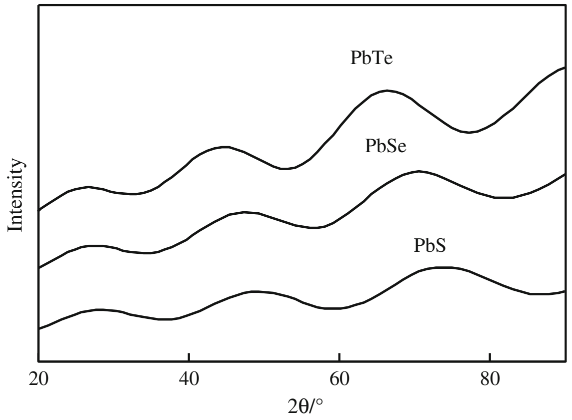

Fig. 4 The calculated diffuse scattering intensities of lead chalcogenides at 294 K by CuKα X-ray diffraction

correlation effects among atoms has not been performed in EXAFS analysis. The diffuse scattering measurements give the values of the correlation effects among atomic motions which are valuable in the analysis of the EXAFS spectrum.

Conclusions

The correlation effects between thermal displacements of atoms were used to explain the profile of the diffuse scattering of lead chalcogenides crystals (PbS, PbSe, and PbTe). The main contribution to oscillatory diffuse scattering of lead chalcogenide compounds is from second nearest neighboring Pb–Pb atoms. The clear contribution from the correlation effects between second nearest neighboring atoms was first obtained.

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