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Effect of Pb–Pb correlation in diffuse scattering of powder PbF_2

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Abstract

Diffuse X-ray and neutron scattering from powder PbF_2 are measured at 15 and 294 K. The oscillatory profile of diffuse scattering is explained by including the correlation effects among thermal displacements of atoms. The contribution of correlated thermal vibration of Pb–Pb atoms located at far-off distance to the oscillatory profile of diffuse scattering intensities is first confirmed.

Keywords: X-ray diffraction; Neutron diffraction; Diffuse scattering; Correlation effect; Thermal vibration

1. 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. Anomalously strong and oscillatory diffuse scattering from α-AgI type superionic conductors have been studied by X-ray and neutron scattering experiments [1]. The oscillatory forms were observed even from ordered crystals at room temperature due to the correlation effects among thermal displacements of atoms [2–4]. Usually, the main contribution to the oscillatory profile is from correlated thermal vibration among nearest neighboring atoms, while the contribution from far neighboring atoms is very weak.

High temperature phase of PbF_2 is known as superionic conductor with anion disorder and has a wide potential application in technology [5,6], however the low temperature α-phase of this material is an ordered type. In order to clarify the influence of the correlation effects between far-neighboring atoms to the diffuse scattering profile, the use of ordered crystal of PbF_2 in X-ray and neutron diffuse scattering experiments is important since the atomic scattering factor of Pb by X-ray and the scattering length of Pb by neutron are greater than those of F. In this study, the diffuse scattering measurements by X-ray and neutron diffraction methods have been carried out for powder α-PbF_2 at 15 and 294 K. The influence of correlated thermal vibration of far-neighbor Pb–Pb atoms to the diffuse scattering profile is discussed.

2. Experimental

X-ray diffraction measurements were carried out for a powder α-PbF_2 by using CuKα radiation at 15 and 294 K. The data were collected for 15 s per step at 0.05° intervals over the 2θ range from 10° to 90° by a step-scan mode. The reflection from the (002) plane of a pyrolytic graphite crystal monochrometer was used.

Neutron scattering measurements at 15 and 294 K were performed on powder α-PbF_2 by HRPD (High Resolution Powder Diffractometer) installed at JRR-3 in Japan Atomic

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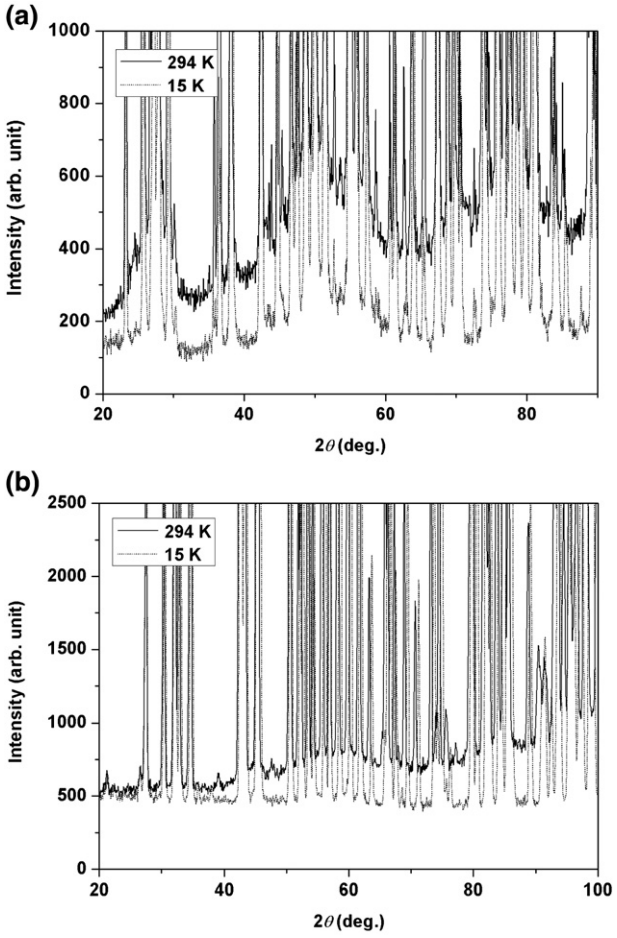

Fig. 1. Diffuse scattering intensities of α-PbF_2 at 15 K (dotted line) and 294 K (solid line) by (a) X-ray and (b) neutron diffraction.

Energy Agency (JAEA). Powder samples were set in a vanadium container of 10 mm in diameter. Incident neutron wavelength of 1.823 Å which is monochromatized by Ge (331) was used and the data were collected in the 2θ range from 20° to 100° with step angle 0.05°.

Table 1
Structure parameters (a, b, c: lattice constants; x, y, z: atomic coordinates; B: Debye–Waller temperature parameter) obtained by Rietveld refinement analysis

	X-ray		Neutron	
	15 K	294 K	15 K	294 K
a (Å)	6.408	6.442	6.404	6.442
b (Å)	3.877	3.898	3.876	3.896
c (Å)	7.647	7.653	7.648	7.651
x_{Pb}	0.252	0.253	0.254	0.254
y_{Pb}	0.250	0.250	0.250	0.250
z_{Pb}	0.104	0.104	0.105	0.105
$x_{F(1)}$	0.856	0.857	0.858	0.860
$y_{F(1)}$	0.250	0.250	0.250	0.250
$z_{F(1)}$	0.063	0.062	0.063	0.063
$x_{F(2)}$	0.467	0.470	0.470	0.468
$y_{F(2)}$	0.250	0.250	0.250	0.250
$z_{F(2)}$	0.842	0.843	0.843	0.844
B_{Pb} (Å^2)	0.025	1.016	0.027	0.983
B_F (Å^2)	0.397	1.826	0.350	1.715

Table 2
Coordination numbers Z and interatomic distances r in the crystal α-PbF_2

	Z	X-ray		Neutron	
		$r_{15\ K}$ (Å)	$r_{294\ K}$ (Å)	$r_{15\ K}$ (Å)	$r_{294\ K}$ (Å)
Pb–F	1	2.422	2.432	2.427	2.430
–F	2	2.431	2.438	2.433	2.448
–F	1	2.556	2.571	2.558	2.555
–F	1	2.632	2.642	2.628	2.628
–F	2	2.677	2.673	2.651	2.676
Pb–Pb	2	3.877	3.899	3.876	3.896
–Pb	2	3.905	3.920	3.899	3.910
–Pb	2	4.048	4.057	4.025	4.058
–Pb	2	4.089	4.118	4.117	4.129
–Pb	4	4.287	4.295	4.288	4.293
F–F	2	2.845	2.845	2.824	2.825
–F	1	2.927	2.961	2.948	2.962
–F	2	3.012	3.014	3.001	3.032
–F	2	3.098	3.109	3.094	3.103
–F	1	3.178	3.183	3.189	3.192

3. Results and discussion

The observed diffuse X-ray and neutron scattering intensities of α-PbF_2 are shown in Fig. 1. The observed intensities show temperature dependence clearly. In Fig. 1(a), large diffuse scattering peaks are observed at 2θ around 28 and 50° at 15 K. These peaks would be related to static disorders that occurred because of the grinding process in the X-ray sample preparation. In the case of neutron measurement where no grinding in the sample preparation was performed, such a peak does not occur at 15 K in Fig. 1(b).

Rietveld refinement analysis has been performed on the X-ray and neutron scattering intensities of α-PbF_2 using RIETAN-2000 [7]. Low temperature α-phase of PbF_2 belongs to orthorhombic structure with the space group *Pnma* where Pb and F atoms occupy 4(c) sites [8]. The structure parameters (a, b, c: lattice constants; x, y, z: atomic coordinates and B: Debye–Waller temperature parameter) obtained by Rietveld refinement analysis are shown in Table 1. From these parameters, the coordination numbers and interatomic distances are calculated. The result is shown in Table 2.

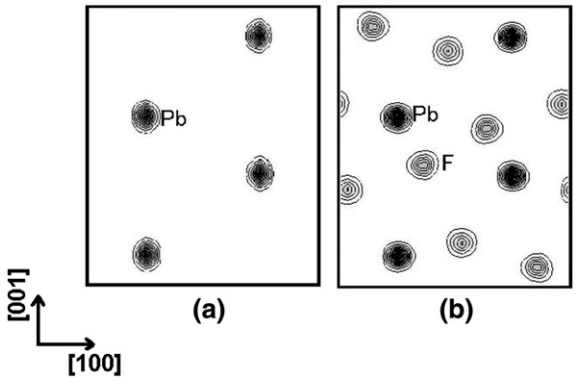

Fig. 2. (a) Electron density distribution by X-ray diffraction and (b) nuclear density distribution by neutron diffraction for α-PbF_2 at (010) plane.