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Variable-Temperature X-Ray Diffraction Analysis of the Behavior of the Mobile Fluorine Ions in a Superionic Conductor, β-PbF$_2$

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We carried out single-crystal X-ray diffraction measurements of β-PbF$_2$ (quenched from 970 K) in the temperature range 131 to 298 K. The structure was refined to $R = 0.008$ at 131 K and $R = 0.008$ at 298 K by the least-squares methods, using about 80 reflections. The behavior of the one independent mobile fluorine ion could not be attributed to split atoms but instead was due to anharmonic thermal vibration. © 1991 Academic Press, Inc.

Introduction

β-PbF$_2$ is the best known superionic conductor of the fluorites. It exhibits a specific heat anomaly and a rapid increase in ionic conductivity at a temperature T_c ($T_c \simeq 710$ K), well below its melting point T_m ($T_m \simeq 1120$ K). These phenomena are associated with a diffuse transition to a phase with extensive dynamic disorder of the anion sublattice in the crystal. It has generally been considered that at low temperature the conductivity of this compound is due to anion Frenkel disorder. Anion disorder should also be responsible for the high conductivity in the superionic state, but the exact nature of this disorder has not been directly established either experimentally or theoretically. It is, however, generally presumed that the superionic and low-temperature disorders are of the same kind, the difference being only one of degree (*1*).

There currently are three models (anharmonic thermal vibration and two split-atom models) proposed to describe the conduction mechanism of the fluorine ion in β-PbF$_2$.

In order to experimentally evaluate these models, we focussed our attention on the behavior of the fluorine ion in a β-PbF$_2$ crystal which was quenched above T_c (970 K). The crystal structure was previously analyzed at high temperature using X-ray (*2*, *3*) and neutron diffraction (*4*).

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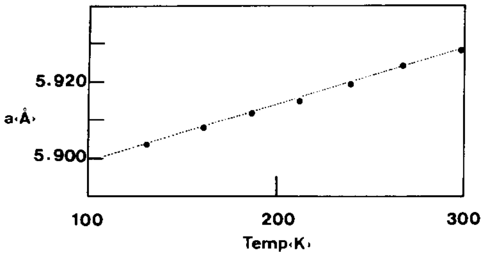

FIG. 1. The cubic lattice parameter of β-PbF$_2$ as a function of temperature.

Experimental

We studied the same crystal (0.18 mm in diameter) that had previously been analyzed by the X-ray diffraction method (5). The crystal was sealed in a quartz capillary under a nitrogen gas atmosphere and then was cooled in a stream of nitrogen gas with a temperature precision of ±5 K. Intensity data set were collected at 131 and 298 K on a four-circle X-ray diffractometer (Rigaku AFC-5) using Mo$K\alpha$ X-rays (0.71069 Å, 60 KV, 200 mA) monochromatized by pyrolytic graphite. The ω-2θ scan technique was applied with scan speed of 2°/min in 2θ. Three standard reflections were measured after every 55 measurements. The cubic lattice parameter was found to decrease linearly with decreasing temperature from 298 to 131 K (Fig. 1). The decrease of intensity of standard reflections was within 5% during the measurements. Symmetry-independent data consisting of ca. 80 reflections for $7° < 2\theta < 100°$ by an $|F_o| > 3\sigma(|F_o|)$ were obtained by averaging of the equivalent reflections in one reciprocal octant under $O_h - m\bar{3}m$ Laue symmetry. Absorption correction was made for each data set. Atomic scattering factors were taken from "International Tables for X-ray Crystallography," Vol. III (6).

Structure refinements were carried out under the assumption that the fluorine ions occupy only normal fixed sites of the fluorite structure. Hence the scale factor and independent isotropic temperature factors for the Pb and F ions were refined, respectively. Least-squares refinements were extended up to anharmonic temperature factors of the third order for F ions and the fourth order for Pb ions. The final R factors for 131 and 298 K were 0.8 and 0.8%, respectively. Positions of interstitial fluorine ions were derived from the difference Fourier synthesis calculated using the refined parameters (anisotropic temperature factors) for the constituent ions. The results of refinements are given in Table I.

The following computer programs were employed in the course of the work: RFINE, full-matrix least-squares (7) and 3DFRS, Fourier synthesis (8).

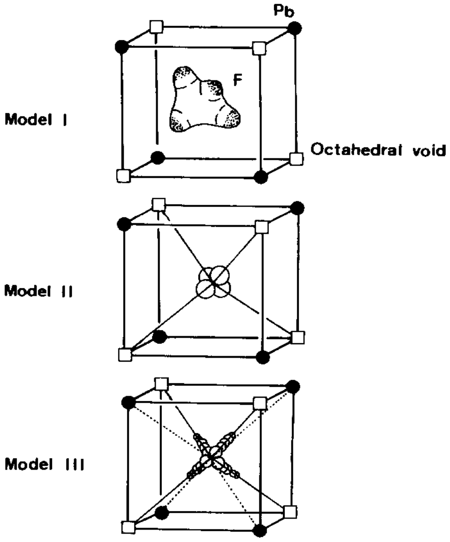

FIG. 2. The distribution models of the fluorine ion in β-PbF$_2$ obtained by X-ray and neutron diffraction methods. Solid circles represent Pb ions and open circles are fluorine ions. Model I involves an anharmonic thermal motion of the independent fluorine ion along the body diagonals in the directions of the tetrahedral faces of the Pb ions (4). Model II involves split-atom sites of the fluorine ion in the Pb tetrahedron which are displaced along the ⟨111⟩ directions (3). Model III also involves split-atom sites of the fluorine ion in the Pb tetrahedron but the F atoms are displaced into several separate sites along the ⟨111⟩ directions (10).

TABLE I

THE RESULTS OF THE REFINEMENTS AT ROOM TEMPERATURE AND 131 K

(a) Crystallographic data for β-PbF$_2$

	298 K	131 K
a (Å)	5.9292 (8)	5.9036 (6)
Space group	$Fm3m$	$Fm3m$
Number of independent reflections	82	79
R (%)	0.8	0.8
R_w (%)	0.8	1.0

(b) Atomic parameters and temperature factors for β-PbF$_2$

	Pb		F	
	298 K	131 K	298 K	131 K
Site symmetry	$m\bar{3}m$		$\bar{4}3m$	
x (= y = z)	0		1/4	
B[a]	0.898 (3)	0.444 (3)	1.49 (5)	0.82 (5)
β_{11} (= β_{22} = β_{33})[b]	0.0064 (1)	0.0033 (1)	0.0106 (3)	0.0059 (3)
β_{12} (= β_{13} = β_{23})	0	0	0	0
$C(123)$[c]	—	—	$10\ (8) \times 10^{-5}$	$3\ (7) \times 10^{-5}$
$D(1111)$[c] (= $D(2222)$ = $D(3333)$)	$16\ (9) \times 10^{-7}$	$36\ (9) \times 10^{-7}$	—	—
$D(1122)$[c] (= $D(1133)$ = $D(2233)$)	$-5\ (4) \times 10^{-7}$	$-12\ (4) \times 10^{-7}$	—	—

[a] Isotropic temperature factors from the last cycle of refinement before changing to anisotropic temperature factors.

[b] The anisotropic temperature factor has the form: $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$.

[c] Anharmonic temperature factors calculated using the expression of the cumulant expansion. Standard deviations are indicated in parentheses in terms of last significant figures.

Results and Discussion

The three different models that have been proposed to account for the conduction mechanism of fluorine ion in β-PbF$_2$ by means of previous X-ray and neutron diffraction results are shown in Fig. 2. In Model I, the fluorine ion has anharmonic thermal vibration. Bachmann and Schulz (*4*) obtained the fluorine ion distribution by reanalyzing the elastic neutron diffraction data (298–973 K) of Dickens *et al.* (*9*). They concluded that the electron density distribution of the fluorine ion in β-PbF$_2$ was due to anharmonic thermal motion, and large anharmonicity of mobile ion at high temperature above T_c was responsible for the conduction to interstitial positions. In Model II, the fluorine ion is considered to have split atoms. Koto *et al.* (*3*) concluded that below the phase transition, the F ions vibrate in a shallow, anharmonic potential, with the largest vibration amplitudes lying along the body diagonals and pointing toward the tetrahedral faces. Above T_c, the F ions occupy split positions around their regular lattice sites. In Model III, from the results (60–640 K) of EXAFS (*10*), it was considered that the independent fluorine ion not only occupies the center of the Pb tetrahedral sites, but is also displaced along the ⟨111⟩ directions into several separate sites at 80 K and that these multiple site displacements are increased in number as temperature rises up to T_c.

We considered that when the samples were quenched from a temperature above T_c, the high-temperature state of either anharmonic thermal motion or the split atom in β-PbF$_2$ may be preserved, and hence reanalyzed the crystal by the X-ray diffraction

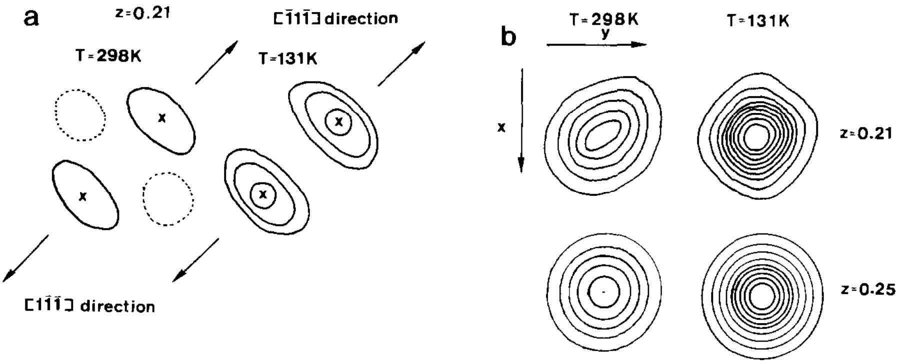

FIG 3. (a) Electron density sections of difference Fourier syntheses at $z = 0.21$ for data collected at 131 and 298 K. Fourier syntheses were calculated up to and including the second tensor (anisotropic temperature factor). Contours are at intervals of 0.25 e/Å^3 with the lowest contour at 0.40 e/Å^3. Peak heights of position xxx, $x = 0.29$ (marked by crosses), are 0.56 and 0.93 e/Å^3 for 298 and 131 K, respectively. Positive contours are represented as solid lines, while negative contours are dotted. (b) Electron density sections around the F ions at 131 and 298 K. At $z = 0.21$ and 0.25, contours are drawn at intervals of 3.2 and 6.4 e/Å^3 with the lowest contours at 3.2 and 6.4 e/Å^3, respectively.

method. Fourier syntheses were calculated, and the resulting atomic electron densities of β-PbF$_2$ at 131 K and room temperature are given in Fig. 3. The features of the sections at $z = 0.21$ in β-PbF$_2$ at 131 K also show the interstitial ions (Fig. 3a) as they exist at 298 K, but do not show such an anharmonicity of the electron density distribution as observed at room temperature (Fig. 3b). These interstitial ions were not observed in β-PbF$_2$, which was cooled at a rate of 0.3 K/min (*5*). Therefore, the existence of interstitial ions may be responsible for having partially preserved the superionic state. The F ions which are located on split positions and several separate sites were not observed around their regular sites. In a recent EXAFS study (*11*) of the quenched β-PbF$_2$ at 60 K, the F ions were found to occupy only the center of the Pb tetrahedral sites, and not the interstitial sites along ⟨111⟩ that were previously reported by Kamijo *et al.* (*10*). This EXAFS result is compatible with that of the single crystal X-ray analysis at 131 K. Although the difference between these EXAFS results will be discussed in detail elsewhere, the difference may be mainly due to the sample preparation for EXAFS. For example, mechanical grinding may produce enough pressure to partially transform cubic β-PbF$_2$ into orthorhombic β-PbF$_2$. In this study we did not observe any evidence to support Models II or III. Consequently, we conclude that Model I, the anharmonic thermal motion, describes the predominant behavior of the F ions in both the superionic and the low-temperature states. This result is consistent with that of the neutron diffraction study (*4*).

Summary

Structural evidence is presented to support the model that describes the conduction of F ions in terms of anharmonic thermal motion and not split atoms in superionic and low-temperature states. Interstitial ions which contribute to ionic conduction in the quenched β-PbF$_2$ were clearly observed at 131 and 298 K. The anion Frenkel disorder in the superionic state is partially quenched, but not completely.

Acknowledgments

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