Structural Study of $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ by Single Crystal X-ray Diffraction and EXAFS

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単結晶 X 線回折及び EXAFS による $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ の構造研究

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The structure of $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ ferroelectric relaxor was investigated by the single crystal X-ray diffraction and the extended X-ray absorption fine structure (EXAFS) techniques at room temperature. The crystal has a rhombohedral $R3m$ symmetry with $a=0.40620(4)$ nm and $\alpha=89.93(1)^\circ$. The metal atoms are displaced from the cubic prototype positions by 0.035(1) nm for Pb, and 0.012(2) nm for Zn and Nb. The Pb atoms are statistically distributed at the 9b positions in the hexagonal setting. EXAFS analysis gave mean bond distances of 0.235(1) nm for Pb–O, 0.204(1) nm for Zn–O, and 0.194(1) nm for Nb–O. The coordination number of Pb was estimated to be 3.8(2). Single crystal X-ray diffraction and EXAFS data suggested a pyramidal coordination for the local structure around Pb, which is similar to PbO_4 in PbO . The different bond distances of Zn–O and Nb–O imply a concurrent constriction of NbO_6 and expansion of ZnO_6 octahedra in the crystal, leading to an aperiodic distortion of the corner-shared octahedral network.

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1. Introduction

Since 1961, when Bokov and Myl'nikova reported the growth of $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PZN) perovskite crystals from a molten PbO solvent,¹⁾ the physical and chemical properties of PZN have been investigated extensively,^{1)–13)} as crystals of this family have a potential for relaxor applications. The relaxors show a diffuse dependence of dielectric permittivity on both temperature and frequency. These features were explained by the presence of 1 : 1 ordered regions of B' and B'' cations spread over a disordered matrix for the $\text{PbB}'_{1/2}\text{B}''_{1/2}\text{O}_3$ relaxors, e.g., $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$.^{14)–16)} Attempts were made to model the $\text{PbB}'_{1/3}\text{B}''_{2/3}\text{O}_3$ relaxors, e.g., $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN), by the coexistence of the 1 : 1 ordered Mg-rich region and the disordered Nb-rich regions.¹⁷⁾ However, it was difficult to model the structure by the 1 : 1 ordering because it required electrostatically charged regions to exist in the matrix. No such heterogeneous distribution of electrostatic charges was located by the X-ray photoemission (XPS) study.¹⁸⁾ The electric-field-induced phase transition in PMN^{19)–21)} also supported the compositional homogeneity of the substance at low temperatures. The evolution of nano-polar domains in a disordered matrix at low temperatures proposed by de Mathan et al.²²⁾ was disclaimed by the single crystal synchrotron X-ray experiments.²³⁾ The dipole glass model was proposed by Dorogovtsev and Yushin,²⁴⁾ Vakhrushev et al.²⁵⁾ and Viehland et al.²⁶⁾ for PMN based on a phenomenological point of view.

Structural investigations of cubic PMN revealed atomic displacements from the cubic prototype positions.^{27)–31)} The Pb atoms were statistically distributed on a small sphere surrounding the 'ideal' position in the prototype with no preferential orientation at high temperature,^{30),31)} however the distribution became asymmetric at low temperature.³²⁾ Pair density function studies and extended X-ray absorption fine structure (EXAFS) studies revealed significantly short Pb–O distances in PMN^{33)–35)} and PZN.³⁶⁾

Although the structural origin of relaxors emerged par-

tially in these investigations, some inconsistencies still remain. Thus the present study was undertaken to elucidate the structural characteristics of the PZN relaxor by combining the results from techniques that investigated both the average structure and local environments of the constituent atoms. The single crystal X-ray diffraction technique was employed for a precise structure analysis, using a short wavelength of $\text{Ag K}\alpha$ to reduce the huge absorption that can be attributed mainly to the presence of Pb in the specimen. The EXAFS technique, using synchrotron radiation, was employed to determine the local structures around Pb, Nb and Zn.

2. Experimental

2.1 Sample preparation

Single crystals were prepared by flux-melting composites of $\text{Nb}_2\text{O}_5 + \text{ZnO} + \text{PbO}$ in a platinum crucible, which was held at 1423 K for 5 h and then cooled at the rate of 1 K/h. The metal atom ratio was confirmed to be stoichiometric by the ICP analysis. The cell dimensions were determined to be $a_R=0.40620(4)$ nm and $\alpha=89.93(1)^\circ$ based on the rhombohedral setting from 25 reflections with $3.01 \leq \sin \theta/\lambda \leq 3.48 \text{ nm}^{-1}$. The cell can be represented in a hexagonal setting with $a_H=0.57411(6)$ and $c_H=0.70440(7)$ nm. Hereafter the subscripts R and H denote quantities based on the rhombohedral and hexagonal settings of the $R3m$ symmetry, respectively. The cell dimensions are identical within error with $a_R=0.4061(1)$ nm and $\alpha=89.92(2)^\circ$ determined by the powder X-ray diffraction technique.^{4),12)} Extra-reflections were not detected using this crystal.

2.2 Single crystal X-ray diffraction

Data collection was carried out on a spherically ground crystal 135 μm in diameter. To reduce the absorption and extinction problems, $\text{Ag K}\alpha$ radiation monochromated by LiF was used rather than the conventional $\text{Mo K}\alpha$. Integrated intensities in reciprocal space up to $\sin \theta_{\text{max}}/\lambda = 11.461 \text{ nm}^{-1}$ were measured by the $\theta/2\theta$ scan technique, with 1.5°

Table 1. Experimental and Refinement Data for PZN

Radiation	Ag K α (0.056083 nm)
Diffractometer	Rigaku Denki Co. LTD. AFC5R
Monochromator	LiF(200)
Scan speed ($^\circ\text{min}^{-1}$)	4
Peak scan width [$a + b \tan\theta$] ($^\circ$)	$a=1.6, b=0.45$
Maximum 2θ ($^\circ$)	80.0
Number of observed reflections	3555
Number of independent reflections with $I > 2\sigma(I)$	522
Linear absorption coefficient for Ag K α (mm^{-1})	44.88
Transmission range min.; max.	0.0259; 0.0637
Extinction type	Zachariasen (1967) ⁴⁸⁾
Extinction, r^*	$0.013 (2) \times 10^4$
Min. extinction y (hkl)	$0.85 (012)_H, (110)_H$
Flack absolute structure parameter	0.5(1)
Rint (F^2)	0.044

receiving slit in front of the detector. Six standard reflections were measured every 100 reflections to monitor the incident beam stability. Experimental details are given in Table 1.

Lorentz and polarization corrections were applied. The absorption correction was applied assuming the crystal to be spherical. The atomic scattering factors and dispersion corrections for Pb^{2+} , Nb^{5+} and Zn^{2+} were taken from the International Tables for X-ray Crystallography,³⁷⁾ while Tokonami's atomic scattering factors for O^{2-} were used.³⁸⁾ Friedel-related reflections were treated as non-equivalent. In all, 522 independent reflections were used in the subsequent structure refinements.

2.3 EXAFS

The EXAFS experiments were carried out at beam-line 14 A at the Photon Factory, High Energy Accelerator Research Organization. Spectral measurements were carried out at room temperature from 12735 to 14239 eV for Pb L_{III}, from 18686 to 20190 eV for Nb K, and from 9363 to 10867 eV for Zn K, with 4 eV step intervals. The synchrotron radiation was monochromated by a Si (111) double crystal monochromator and focused by a toroidal mirror for Pb L_{III} and Zn K measurements. A parallel beam emitted from a Si (311) double crystal monochromator was used for the Nb K measurement. The incident and transmitted beam intensities I_0 and I were measured simultaneously using ion chambers filled with nitrogen or argon gases. The accumulation time was 10 s at each step.

The EXAFS oscillation based on the plane wave approximation is given by

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} |f_j(k, \pi)| \exp \left[-2\sigma_j^2 k^2 - \frac{2R_j}{\lambda(k)} \right] \times \sin \{2kR_j + \phi_j(k)\} \quad (1)$$

where k is the momentum of the photoelectron ejected in the X-ray absorption process, and χ is the normalized oscillation of the fine structure.³⁹⁾ The amplitude of the contribution of each successive shell to the EXAFS depends on N_j , the number of atoms in the j th shell, R_j , the distance of those neighbors from the absorbing atom, σ_j^2 , the variance in that distance, and $|f_j(k, \pi)|$, the backscattering power of the neighboring atoms. The total phase shift, $\phi_j(k)$, experienced by the photoelectron wave in passing through the atomic potentials of the central atom and j th-scattering-shell atom, is given by

$$\phi_j(k) = \phi_a^l(k) + \phi_b(k) - \pi$$

$$l=1 \text{ for K and L}_I \text{ edge,}$$

$$\phi_j(k) = \phi_a^l(k) + \phi_b(k)$$

$$l=0 \text{ and } 2 \text{ for L}_{II} \text{ and L}_{III} \text{ edge}$$

$$(2)$$

where $\phi_b(k)$ is the phase of the back-scattering atom b and $\phi_a^l(k)$ is the phase shift due to the central atom a . Experimentally obtained $\chi(k)$ is expressed by

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} \quad (3)$$

where μ is the absorption spectrum and μ_0 is the background function attributable to absorption from the absorbing atom in the absence of neighbors.

The values of $|f_j(k, \pi)|$, $\phi_a^l(k)$, and $\phi_b(k)$ for all atoms except $\phi_a^l(k)$ for Pb were taken from those tabulated by Teo and Lee.³⁹⁾ The values of $\phi_a^l(k)$ for Pb were calculated using the FEFF8 program,⁴⁰⁾ as the relativistic effects are more significant for heavier atoms. Since there is a large correlation among the parameters $\{\Delta E_0, \lambda, \text{ and } R_j\}$, and among $\{N_j \text{ and } \sigma_j^2\}$, ΔE_0 and λ determined for the reference materials were treated as constants in the calculation for PZN. Powders of PbO, Nb₂O₅ and ZnO were chosen as the reference materials for the measurement of Pb L_{III}, Nb K, and Zn K absorption edges, respectively. Subsequent least-squares refinements were carried out using the Fortran 77 code EXAFS2 published by Udagawa.⁴¹⁾

3. Results

3.1 Single crystal X-ray diffraction

The rhombohedral distortion is quite small ($\alpha=89.93(1)^\circ$). However, it is obvious that the crystal is not cubic as the internal agreement factors among the equivalent reflections, R_{int} , were 0.086 and 0.044 for the $m\bar{3}m$ and $\bar{3}m$ Laue symmetries, respectively.

We initially assumed a basic model structure in which all atoms reside at the special positions of the rhombohedral perovskite with $R3m$ symmetry. Unit-cell relations among the cubic prototype ($Pm\bar{3}m$) and the rhombohedral $R3m$ and $R3c$ perovskites are illustrated in Fig. 1. The R/wR factors were 0.089/0.073 for this basic model. The atomic coordinates and interatomic distances are given in Tables 2 and 3, respectively.

The magnitudes of metal atom displacements along the three-fold axis were 0.025(3) nm for Pb and 0.008(3) nm for Zn/Nb from respective positions in the cubic prototype. The equivalent temperature factor, U_{eq} , for Pb is 0.00066(2) nm², which is approximately twice as large as that for other lead-containing perovskite compounds, such as PbZrO₃.⁴²⁾

The difference Fourier map of the plane at $z_H=0.53$ is shown in Fig. 2. The accumulation of electrons around Pb suggested a possible static displacement of Pb along $\langle 210 \rangle$. Therefore, another model (hereafter referred to as 'model A') was examined by considering the statistical disorder of Pb atoms in the vicinity of the positions in the basic model.

Distributing the Pb atoms at the 9b ($x_H, -x_H, z_H$) positions instead of 3a (0, 0, z_H) resulted in R/wR of 0.0547/0.0506 with $x_H = -0.0222(3)$ and $z_H = 0.538(2)$. If there is no preference in the orientation of the Pb displacements as in the cubic PMN,^{30),31)} a 60° rotation of the Pb arrangement should provide similar R/wR factors. However such a model (referred to as model B) converged with R/wR of 0.0576/0.0540 when $x_H = 0.0212(3)$ and $z_H = 0.539(2)$. Hamilton's R test⁴³⁾ indicated that model A was better than model B at the 90% confidence level. Neither significant depletion nor accumulation of electrons was observed around the Zn/Nb position in the difference Fourier maps, suggesting that the Zn and Nb atoms are statistically distributed at the same position.

The atomic coordinates and interatomic distances for the

Fig. 1. Relationship between ABO_3 perovskite structures; (a) Prototype cubic unit cell ($Pm\bar{3}m$) with $a \approx 0.4$ nm, $\alpha_R \approx 90^\circ$, (b) $R3m$ unit cell with $a_R \approx 0.57$ nm, $\alpha \approx 60^\circ$, (c) $R3c$ unit cell with $a \approx 0.57$ nm, $\alpha \approx 60^\circ$, (d) $R3m$ hexagonal unit cell with $a_H \approx 0.57$ nm, $c_H \approx 0.7$ nm, $-1/2 \leq x_H, y_H \leq 1/2$ and $0 \leq z_H \leq 1$, and (e) $R3c$ hexagonal unit cell with $a \approx 0.57$ nm, $c \approx 1.4$ nm, $-1/2 \leq x, y \leq 1/2$ and $0 \leq z \leq 1$. Subscripts R and H conform to the text.

Table 2. Atomic Coordinates, Isotropic Temperature Factors ($U/10^{-2}$ nm²) and Site Occupation Parameters for the Basic Model and Model A

Basic model				Model A		
Atom	Pb	Zn/Nb	O	Pb	Zn/Nb	O
x_H	0	0	$2y$	-0.0222(3)	0	$2y$
y_H	0	0	0.177(3)	$-x$	0	0.168(2)
z_H	0.535(4)	0.011(4)	1/6	0.538(2)	0.017(2)	1/6
U_{eq}	0.066(2)	0.0094(8)	0.03(1)	0.030(2)	0.0088(6)	0.026(7)
Pop.	1.0	0.333/0.667	1.0	0.333	0.333/0.667	1.0

Basic model				Model A		
Atom	Pb	Zn/Nb	O	Pb	Zn/Nb	O
U_{11}	$2U_{12}$	$2U_{12}$	$2U_{12}$	0.025(1)	$2U_{12}$	$2U_{12}$
U_{22}	$2U_{12}$	$2U_{12}$	0.034(7)	U_{11}	$2U_{12}$	0.031(5)
U_{33}	0.055(3)	0.0070(6)	0.04(1)	0.044(2)	0.0055(5)	0.027(7)
U_{12}	0.0359(8)	0.0053(3)	0.012(6)	0.0151(9)	0.0052(2)	0.008(2)
U_{13}	0	0	$2U_{23}$	0.0058(4)	0	$2U_{23}$
U_{23}	0	0	-0.000(4)	$-U_{13}$	0	-0.003(2)

Fig. 2. Difference Fourier map on the ab plane at $z_H = 0.53$, obtained after the refinements assuming the basic model. The contour interval is 1000 e/nm^3 . Solid and dashed lines denote positive and negative levels, respectively.

Table 3. Interatomic Distances (nm) in the Basic Model and Model A

	Basic model	Model A
Pb-O	0.261(3) $\times 3$	0.259(2) $\times 2$
	0.288(2) $\times 6$	0.270(1) $\times 2$
	0.314(3) $\times 3$	0.279(2)
		0.289(1) $\times 2$
		0.299(2)
		0.308(1) $\times 2$
Nb/Zn-O	0.199(3) $\times 3$	0.198(2) $\times 3$
	0.207(3) $\times 3$	0.209(2) $\times 3$

model A are shown in Tables 2 and 3. The magnitudes of metal atom displacements from the cubic prototype positions were 0.035(1) nm for Pb and 0.012(2) nm for Zn and Nb.

3.2 EXAFS

Fourier transforms of k^3 -weighted χ without the phase-shift corrections of the Pb L_{III}, Nb K and Zn K edges are shown in Figs. 3, 4 and 5, respectively. The coordination numbers, interatomic distances and Debye-Waller factors were obtained from least-squares calculations of the first oxygen neighbors in PZN, and are given in Table 4.

The Nb-O distance is approximately 0.01 nm shorter than that of Zn-O, reflecting the different ionic radii of Nb⁵⁺ (0.064 nm) and Zn²⁺ (0.074 nm).⁴⁴ These results indicate that the Nb⁵⁺ cations allow the O₆ coordination octahedra to

Fig. 3. Fourier transforms of Pb L_{III} EXAFS in PbO (a) and PZN (b) as a function of the radial distance R from the absorbing atom.

Fig. 4. Fourier transforms of Nb K EXAFS in Nb_2O_5 (a) and PZN (b) as a function of the radial distance R from the absorbing atom.

Fig. 5. Fourier transforms of Zn K EXAFS in ZnO (a) and PZN (b) as a function of the radial distance R from the absorbing atom.

constrict while the Zn^{2+} cations cause them to expand.

The Pb–O distance and the coordination number of Pb in PZN were calculated to be 0.235(1) nm and 3.8(2). This bond distance is close to 0.232 nm in PbO and approximately 0.024 nm smaller than the two shortest Pb–O interatomic

Table 4. Results of Fitting EXAFS Data to the First O Neighbors in PZN. N_O and R_O Represent the Coordination Number and Interatomic Distances (nm) of the First Oxygen Shell, Respectively. σ_O (nm) is the Debye–Waller Factor

Absorbing atom	N_O	R_O	σ_O
Pb	3.8(2)	0.235(1)	0.0117(3)
Nb	5.2(3)	0.194(1)	0.0075(3)
Zn	6.0(3)	0.204(1)	0.0072(5)

distances in PZN listed in Table 3. The coordination number of Pb is close to 4 that corresponds to the value for the reference material PbO.

4. Discussion

The atomic coordinates of Pb in the model A structure are (0.582, 0.516, 0.516)_R in the rhombohedral $R\bar{3}m$ cell. The absolute value of the Pb atom shift from the cubic prototype position is (0.0333, 0.0065, 0.0065)_R in nm. The direction of the shift corresponds approximately to $\langle 100 \rangle_R$. Such a Pb atom shift towards the O_4 square results in four short bonds (0.259 nm $\times$ 2, 0.270 nm $\times$ 2), leading to a PbO_4 pyramidal configuration as in PbO.

The local structure around Pb is schematically illustrated in Fig. 6. It is worth noting that this pyramidal configuration has, locally, a tetragonal symmetry comprised of a four-fold rotation axis. The pyramidal configuration of PbO_4 explains the EXAFS results qualitatively, though the Pb–O distance of 0.235 nm observed by EXAFS is still rather small com-

Fig. 6. Schematic drawing of PbO_4 pyramidal polyhedra in PZN (a) and PbO (b). The rhombohedral distortion is omitted in (a). The Pb–O bond distance in (a) is the value obtained by the EXAFS analysis.

pared with the single crystal X-ray result. A possible disorder of oxygen atom positions as discussed later may obscure this disagreement.

Cohen^{(45), (46)} demonstrated the stabilization of tetragonal distortion of PbTiO_3 by the hybridization of lead 6s and oxygen 2p orbitals using the full potential linearized augmented plane wave method. The local tetragonal distortion in PZN presumably has a similar origin to that of PbTiO_3 . However, there is a difference in that the Zn and Nb atoms in PZN occupy the B sites statistically with a ratio of 1 : 2. As seen in the EXAFS results, the expansion and constriction of BO_6 coordination octahedra that occur in PZN depend on the B species. Due to the Zn/Nb ratio, this relaxation of the oxygen lattice is basically aperiodic in the octahedral topology of the perovskite-type structure.

As such, the disordered distribution of Nb and Zn will perturb the long-range ordering of tetragonal distortion around Pb in contrast with PbTiO_3 . Three possible orientations of the PbO_4 pyramids in a nanometer-sized region are compatible with the three-fold global symmetry along $[111]_R$. This could be one reason that PZN crystals exhibit rhombohedral instead of tetragonal symmetry.

A slight shift of the y parameter from 1/6 for the O atom in PZN may be indicative of a small distortion of the O_6 octahedra. On the other hand, the ORTEP diagram, as shown in Fig. 7, depicts the thermal ellipsoids of oxygen atoms elongated along the direction orthogonal to the B–O bonds projected onto the horizontal plane. This is suggestive of (a) a disordered nature of the oxygen atom positions or (b) the remnant rigid tilting of the regular octahedron about $[001]_H$ axis. The former may account for the disagreement between the EXAFS and single crystal diffraction results for the interatomic distance. The latter rigid tilting throughout the crystal is not allowed in $R3m$ symmetry, but are possible in $R3$ and $R3c$. If an ordering of the octahedral tilt occurs, $R3c$ or $R3$ phases with double cell edges may arise at low temperature. However, the $R3c$ or $R3$ phases have not yet been observed in PZN.

These structural characteristics of PZN are similar to those found in the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) system.⁽⁴⁷⁾ Corker et al. characterized the crystal structure of $R3c$ PZT with various x values by the Pb shifts nearly along $\langle 100 \rangle_R$. It should be recalled that the subscript R refers to the $R3m$ cell edges, and not to the $R3c$. He also pointed out the four-fold coordination of the O atoms for the Pb, which leads to $[111]_R$ cation-shifts on average in X-ray and neutron diffraction experiments. This is essentially the case for the present study of PZN.

Fig. 7. Thermal ellipsoids of BO_6 projected along $[001]_H$ with 50% probability.

Perovskite-type ferroelectrics such as BaTiO_3 , are normally characterized by the displacement of ferroelectrically active B cations from the center of BO_6 octahedra. Though the ferroelectricity in PZN is supposed to have a similar origin as in BaTiO_3 , several intrinsic geometrical problems in the PZN structure give rise to a complicated manifestation of ferroelectricity. One is the ratio of Zn/Nb, which does not allow a commensurate concurrence of NbO_6 constriction and of ZnO_6 expansion, leading to an aperiodic distortion of the corner-shared octahedral topology. Another is the covalent nature of the Pb–O bonding, which is responsible for the formation of the PbO_4 pyramidal coordination with a local four-fold symmetry. The Pb atom can rattle within the twelve-fold cage to align the local four-fold symmetry along one of the equivalent $\langle 100 \rangle_R$ directions. The formation of PbO_4 pyramids with various orientations will also complicate the distortion of the octahedral network and retard the ferroelectric switching. These geometrical characteristics are supposedly the cause for the diffuse behavior of various properties typical for the $\text{PbB}_{1/3}\text{B}_{2/3}\text{O}_3$ relaxors.

5. Conclusion

The PZN ferroelectric cluster has a rhombohedral $R3m$ symmetry with $a = 0.40620(4)$ nm and $\alpha = 89.93(1)^\circ$ at room temperature. The Pb atoms are distributed statistically at the 9b positions ($x_H, -x_H, z_H$) with $x_H = -0.0222(3)$ and $z_H = 0.538(2)$. The direction of the Pb shift from the position in the cubic prototype is approximately $\langle 100 \rangle_R$. The EXAFS analysis gave mean bond distances of 0.235(1) nm for Pb–O, 0.204(1) nm for Zn–O, and 0.194(1) nm for Nb–O. The coordination number of Pb was estimated to be 3.8(2). The different bond distances of Zn–O and Nb–O imply a concurrence of the constriction of NbO_6 and expansion of ZnO_6 octahedra in the crystal. The single crystal and EXAFS data suggested a pyramidal coordination configuration around Pb, which is similar to the PbO_4 moiety in PbO . The configuration around Pb with the tetragonal local symmetry is considered to have an orientation distribution within a nanometer-sized region, which is supposedly responsible for the rhombohedral global symmetry of the crystal.

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