Crystal Structural Studies of Thermal Decomposition Process of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ Single Crystal into Pyrochlore Type Compound

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Crystal structure parameters including $B$ thermal parameters of each constituent atom were determined for PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) between 27 and 700°C by the single crystal high temperature X-ray diffraction technique. For lead, and magnesium and niobium atoms, the optimum shift directions from the special positions were not a single direction but "spherical" shifts were observed. For oxygen atom, it was confirmed that the optimum shift direction was not one ring on XY plane but two parallel rings away from XY plane. PMN began to decompose into polycrystalline pyrochlore type compound at 600°C. The mechanism of decomposition was discussed from the viewpoint of crystal structure.

Key-words: Lead magnesium niobium oxide, PMN, Single crystal, Crystal structure determination, Pyrochlore, Thermal decomposition

1. Introduction

PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) has been widely investigated from the viewpoint of its high dielectric constant and diffuse phase transition (DPT). Mizutani et al. reported that PMN decomposed into pyrochlore type compound toward a bulk from a surface at high temperature with the evaporation of PbO and went back into the original PMN phase with the reaction with PbO under the controlled PbO atmosphere. Moreover Jang et al. reported that perovskite PZN decomposed into pyrochlore type compound by annealing a pure PbZn$_{1/3}$Nb$_{2/3}$O$_3$ (PZN) specimen for 1h at various temperatures. However, the behaviors about the decomposition of perovskite into pyrochlore type compound at high temperature have not been discussed yet from the point of crystal structure view in these papers.

The crystal structure of PMN has been tried to determine by many investigators using HRTEM, powder X-ray and neutron diffraction techniques. In these reports, the directions of disordered motions of Pb, (Mg, Nb) and O atoms from the special crystallographic sites of the ideal cubic perovskite structure have been discussed in the wide temperature range. However, no structural correlations on the decomposition of perovskite PMN into pyrochlore type compound have been clarified yet. Therefore the purpose of this work is to investigate the structural correlations using PMN single crystal in the temperature range between 27 and 700°C.

2. Experimental

2.1 Preparation of single crystal

In order to grow PMN single crystal, the pseudobinary PMN–PbO phase diagram was referred. The growth condition was the same as our previous report except for the cooling rate of 1°C/h. The chemical analysis data of grown single crystal were shown in Table 1. The cation ratio was analyzed by ICP-AES (Seiko Instruments, SP5-1500 VR). The oxygen content was measured by LECO's oxygen analyzer (LECO, TC-436).

2.2 Data collection and refinements

The grown crystal was shaped into a sphere of 0.12 mm diameter for the high-temperature X-ray study. The crystal was mounted on a quartz glass capillary with ZrSiO$_4$ cement. A four-circle diffractometer (Philips, PW1100) equipped with a small specimen heating unit was used for the determination of the lattice parameter and the collection of intensity data.

Table 1. Chemical Analysis Data

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<th>ICP-AES (Cation Ratio)</th>
<th>LECO (Oxygen Content)</th>
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<tbody>
<tr>
<td>Sample Weight 52mg</td>
<td>Pb 72.8 ± 0.5wt%</td>
<td>PbO 14.6 ± 0.05wt%</td>
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<tr>
<td></td>
<td>Mg 2.63 ± 0.03wt%</td>
<td>MgO 14.6 ± 0.05wt%</td>
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<tr>
<td></td>
<td>Nb 23.4 ± 0.12wt%</td>
<td>NbO 14.6 ± 0.05wt%</td>
</tr>
<tr>
<td>Analytical Composition</td>
<td>Pb$<em>{0.97}$Mg$</em>{0.32}$Nb$_{0.68}$O$_3$</td>
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tensity data between 27 and 700°C. The specimen was heated in a hot air stream. The temperature of the specimen was measured with a 0.08 mm Pt-PtRh13% thermocouple placed at a point about 0.1 mm away from the specimen and was kept constant within ±5°C during the measurements. Lattice parameter at each temperature was calculated from the 6 reflections in the range 3.5<θ<23° (Mo Kα) using the program RLC-3. Intensities were collected with Mo Kα radiation monochromatized with a graphite plate. The α–2θ scan technique was employed with scanning speeds of 4°/min in αω, and scanning was repeated up to three times when the total counts were less than 10000. The scanning width was 2.0°. Independent reflection data that satisfied the relation \(|F_0| > 3\sigma F_0\) were used in the subsequent refinement. Intensities were corrected for Lorentz, polarization and absorption factors. Extinction corrections were made in the course of refinement. The structure was refined with the full-matrix least-squares program LINUS. The atomic scattering factors for Pb2+, Mg2+ and Nb5+ were referred to International Tables for X-ray Crystallography (1974) and that of O2− was referred to Tokonami.

3. Results

Figure 1 shows the change of integrated intensity of (110) peak with heating temperature. Because of the degradation of intensity by decomposition, the measurement of intensity was carried out after data collection at each temperature was finished. The intensity began to decrease at 600°C due to the decomposition of PMN single crystal.

On the crystal structure determination of PMN, the shift directions for each constituent atom from the special crystallographic sites have been frequently discussed, however, the shift directions proposed for each atom were not always same in these reports. For example the shift direction of Pb atom was reported to be <110>, <110> or <111> and <225>. To determine the shift directions of each constituent atom, the atomic positions were fixed in their special positions and the Fourier difference maps were calculated in the whole temperature range. The directions of residual electron around Pb and (Mg, Nb) atoms were not specified but spherical residual electrons were observed. In all previous reports, only one shift direction model for each atom has been discussed. However, the results of Fourier difference maps suggested that the direction of shifts was not so simple. Consequently, a new model about the shift directions of each constituent atom should be proposed in order to improve the accuracy of refinements. The new model was examined against the data collected at 27°C. At first, for Pb atom, the position was refined using simple <100>, <110> and <111> shift direction models and obtained 14.49, 11.85 and 13.44% of R-factors respectively. Secondly, a new model that was approximated by the spherical residual electron was examined. In this model, Pb site was divided into three sites with different shift directions from the special positions. That is, a third of Pb shifted to <100> direction, next a third of Pb shifted to <110> direction and the last a third of Pb shifted to <111> direction. Hereafter this model was designated as <100/110/111> shift direction model. With this model, the R-factor fell to 8.94%. If the model of spherical shift could be completed, the R-factor would be much improved. In the same way, the position of (Mg, Nb) atoms was examined. Consequently, as well as Pb atom, it was clarified that the <100/110/111> shift direction model was also plausible for (Mg, Nb) atoms.

For the shift direction of O atom, two models have been proposed in the literatures, that is, two parallel rings away from the XY plane model and one ring on the XY plane model. In our refinements, both the two models were examined. Consequently, R-factor fell to 6.83 and 7.02% in the former and the latter models, respectively. From this result it was clarified that the former model was plausible. These shift directions of each constituent atom were examined in the temperature range between 27 and 700°C in the same way, and were found to be valid up to 700°C.

Taking these positions and reported B thermal parameters as starting parameters, the positions of each atom were refined by full-matrix least squares calculation thereafter B thermal parameters were refined by full-matrix least squares calculation. Change of displacements from the special positions for each constituent atom with temperature up to 700°C was shown in Fig. 2. The reported values of displacements were also plotted in Fig. 2 for comparison. Change of B thermal parameters for each constituent atom with temperature up to 700°C was shown in Fig. 3. The final R-factors were between 3.6 and 7.5% in the whole temperature range.
4. Discussion

As mentioned above, the relationship between the change of displacements from the special positions for each constituent atom and temperature has been reported up to 800 K.8,12,14 Comparing these data with our results (Fig. 2), the values of displacements from the special position of each constituent atom were almost identical within the error bars under 600°C in spite of the different shift direction models (spherical shift model for Pb and (Mg, Nb) atoms was adopted in our refinements). The purpose of this investigation is to clarify the structural correlation about the decomposition of perovskite PMN into pyrochlore type compound at high temperature. From Fig. 1, it was clarified that PMN began to decompose at 600°C. Therefore, the data above 600°C in Fig. 2 indicate the change of displacements when PMN thermally decomposed into pyrochlore type compound. For Pb and (Mg, Nb) atoms, the magnitude of displacements from the special positions above 600°C was almost identical to that below 600°C. On the other hand, for O atom vertical to XY plane, the magnitude of displacement from the special position drastically increased above 600°C.

**Fig. 4 (a)** shows an ideal linkage of (Mg, Nb)O₆ octahedra in PMN along <100> direction. Because of the displacements of (Mg, Nb) and O atoms from the special positions, there exist long and short (Mg, Nb)-O distances locally as shown in Fig. 4 (b) even at room temperature. According to Hazen and Prewitt,22) mean coefficient of linear thermal expansion from 23 to 1000°C is 14.3 × 10⁻⁶/°C while 0/°C for Mg²⁺-O and Nb⁵⁺-O distances, respectively. Considering this difference of linear thermal expans-
sion coefficients, the difference between long and short (Mg, Nb)-O distances are magnified at high temperature. Figure 5 shows the change of short (Mg, Nb)-O distance with temperature. From this figure, it was clarified that the short (Mg, Nb)-O distance actually began to decrease above 500°C.

Figures 6(a) and (b) shows arrangement of BO₆ octahedra in the perovskite and pyrochlore structure, respectively. As shown in this figure, B-O-B angle along <100> direction in the perovskite structure is 180°, while that along <110> direction in the pyrochlore structure is around 138°, therefore the BO₆ octahedra link in zig-zag line. Figure 4(c) shows a schematic figure of BO₆ octahedra linkage in PMN at 600°C. At this temperature the short (Mg, Nb)-O distance is 1.89 Å. Figure 4(d) shows schematic figure of BO₆ octahedra linkage in the pyrochlore type compound at 600°C. The B-O distance determined from the structure refinement using pyrochlore single crystal at this temperature was 2.02 Å. Because of the similarity between the perovskite and pyrochlore shown in Fig. 6, the orthogonal projection of B-O distance of pyrochlore on <110> direction was calculated and obtained 1.89 Å.

This value of the orthogonal projection was in good agreement with the short (Mg, Nb)-O distance shown in Fig. 4(c). From this fact, it was considered that the decrease of short (Mg, Nb)-O distance caused access of electron cloud and that would give rise to the instability of linear linkage of BO₆ octahedra then brought about the slight rotation of BO₆ octahedra to release the instability. This slight rotation would give a chance to form pyrochlore type compound. As shown in Fig. 4(d), the slight rotation of BO₆ octahedra causes local cutting of the BO₆ octahedra linkage unaccompanied with topo-chemical reaction and form polycrystal pyrochlore type compound. Actually it was difficult to construct the lattice of pyrochlore type compound after PMN single crystal decomposed at high temperature by using four-circle diffractometer. Figure 5 also shows the change of the orthogonal projection of pyrochlore B-O distance along <110> direction. From this figure, it was shown that the decomposition temperature of PMN (600°C) shown in Fig. 1 is in good agreement with the temperature which the short (Mg, Nb)-O distance of PMN coincides with the orthogonal projection of pyrochlore B-O distance along <110> direction.

5. Conclusions

Crystal structure parameters including B thermal parameters were determined for PbMg₁/₃Nb₂/₃O₃ (PMN) between 27 and 700°C using a single crystal high temperature X-ray diffraction technique. Several kinds of shift directions for each constituent atom have been reported until now. However, from our refinements, it was clarified that for Pb and (Mg, Nb) atoms the optimum shift directions were not a single direction but "spherical" shifts were plausible, and for O atom the distribution is two parallel rings away from XY plane. On the basis of this model, the mechanism of thermal decomposition of perovskite PMN into polycrystal pyrochlore type compound was interpreted by the slight rotation of BO₆ octahedra that was brought about the difference of linear thermal expansion coefficient against Mg-O and Nb-O distances at high temperature.

Fig. 5. Change of short (Mg, Nb)-O distance in PMN (●) and the orthogonal projection of (Mg, Nb)-O distance along <110> direction of pyrochlore type compound (○) with temperature.

Fig. 6. Arrangement of BO₆ octahedra in the perovskite and pyrochlore structure.
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72, 593–98 (1989).


