

## Temperature dependency of atomic position in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ single crystal

### "Thermal decomposition behavior of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ into pyrochlore-type compound"

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$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) single crystal decomposes into pyrochlore-type compound unaccompanied with topo-chemical reaction. The resultant morphology after PMN thermally decomposed was constructed by two distinct regions, that is, surface layer and intermediate one. The intermediate layer was constructed from pyrochlore-type compound. Since slight composition gradients could be seen in the intermediate region, it was suggested that pyrochlore-type compound in this system is not a line compound, whereas PMN is a line compound. The reason why pyrochlore-type compound often forms in Pb-Mg-Nb-O system was qualitatively explained by this work.

## 1. INTRODUCTION

The general formula of pyrochlore-type oxide is  $\text{A}_2\text{B}_2\text{O}_7$  where ( $\text{A}^{3+}, \text{B}^{4+}$ ) or ( $\text{A}^{2+}, \text{B}^{5+}$ ). Some pyrochlore-type oxides are constructed from mixed cations at the B site [1-3]. The studies of pyrochlore-type oxides with mixed cations at the A site were very few. In our study, the conditions of formation for the pyrochlore-type oxides with mixed cations at the A site were proposed from the view point of crystal structure [4]. On the basis of proposed conditions, four new compounds,  $(\text{Ca}, \text{Ce})_2\text{Sn}_2\text{O}_7$ ,  $(\text{Sr}, \text{Ce})_2\text{Sn}_2\text{O}_7$ ,  $(\text{Cd}, \text{Ce})_2\text{Sn}_2\text{O}_7$  and  $(\text{Ca}, \text{Ce})_2\text{Hf}_2\text{O}_7$  were synthesized [4,5]. For  $(\text{Ca}, \text{Ce})_2\text{Sn}_2\text{O}_7$  and  $(\text{Sr}, \text{Ce})_2\text{Sn}_2\text{O}_7$ , the single phase regions were examined and it was concluded that a part of Ce ion takes tri-valent state in order to satisfy the electrical neutrality in the whole crystal. The coexistence of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  seemed to be due to the crystallographic requirement. The electrical conduction mechanism of  $(\text{Ca}, \text{Ce})_2\text{Sn}_2\text{O}_7$  and  $(\text{Sr}, \text{Ce})_2\text{Sn}_2\text{O}_7$  seemed to be small polaron hopping because of the mixed valence of Ce ion.

Pyrochlore-type compounds often form on the synthesis and decomposition of perovskite ferroelectric relaxor materials with general formula,  $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ . According to Adrianova et al. [7] and Shrout et al. [8], the composition of pyrochlore-type compound in Pb-Mg-Nb-O system was reported to be  $\text{Pb}_{1.85}\text{Mg}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ . From this formula of chemical composition, it was suggested that both of Mg and Nb occupy the B site, and the A and O sites are partially vacant. However, the chemical composition of this

pyrochlore type compound was not identical by different authors [9,10]. To clarify the composition and site occupancy of each constituent atoms, single crystal of this pyrochlore was grown and the crystal structure was determined with an X-ray four-circle diffractometer [11]. Consequently, precious formula of this pyrochlore type compound was determined to be  $\text{Pb}_{1.86}\text{Mg}_{0.24}\text{Nb}_{1.76}\text{O}_{6.5}$  and it was confirmed that Mg and Nb randomly occupy the B site. The oxygen content was 6.5 which was common to other pyrochlore-type oxides including Pb at A site.

The next work of us was to investigate the crystallographic correlation between perovskite PMN and pyrochlore type compound when PMN thermally decomposed into pyrochlore type compound at high temperature. To examine this decomposition behavior, PMN single crystal was mounted to the four-circle X-ray diffractometer equipped with a specimen heating unit. The result of structure determination was interpreted from the point of  $\text{BO}_6$  octahedra linkage [12]. However no topo-chemical reaction was perceived on the decomposition of PMN.

The studies of thermal stability of PMN and PZN were investigated by Kim et al. [13] and Jang et al. [14] respectively. However their works were carried out using polycrystal sample, and their result might include the effects of grain boundary and unhomogeneous mixing. In this work, thermal decomposition behavior of PMN single crystal was examined. The purpose of this work is to clarify the reason why pyrochlore type compound often forms on the decomposition of PMN.

## 2. EXPERIMENTAL

The growth of PMN single crystal was referred to our pervious paper [11,12]. The decomposition behavior of PMN single crystal was observed using two different experiments. The one was examined using X-ray four-circle diffractometer equipped with a specimen heating unit and the dependence of peak intensity and lattice parameter upon temperature was measured. The other was the observation of microstructure and composition change using a SEM (scanning electron microscope) with a EDS (energy dispersive spectroscopy). The grown single crystals were planed off and polished on the surface of the sample. In this way, three samples normal to (100), (110) and (111) planes were prepared. These crystals were put on the silica grass plate and heat treated in the same time. These samples were heated up to 1000°C in 2h and kept for 6h then cooled to room temperature in the muffle furnace.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the relationship between intensities of (100), (110) and (111) peaks on heating temperature of PMN single crystal. From this figure, it was found that the peak intensities are almost constant between 27 and 600°C, and above 600°C the peak intensities decrease. The intensities at 700°C decrease about 20% against the intensities below 600°C irrespective of the three different orientations. This tendency was similar to other (hkl) peaks and suggests that the decomposition of PMN single crystal proceeds isotropically.

Figure 2 shows the relationship between the lattice parameter of PMN single crystal and heating temperature. The data reported by Bonneau et al. [15] are also shown. From this figure, the change of lattice parameter of single crystal is in good agreement with that of powder.

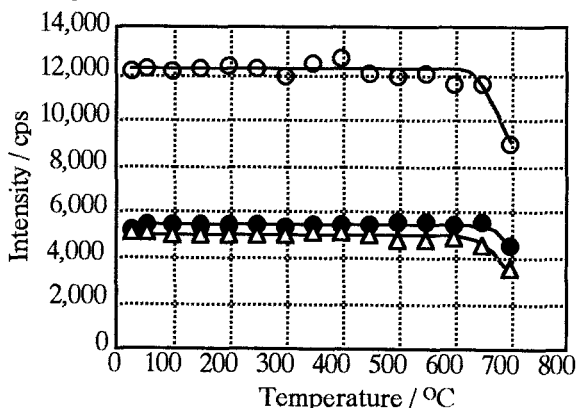


Figure 1. Relationship between intensities of (100)(●), (110)(○) and (111)(△) and heating temperature

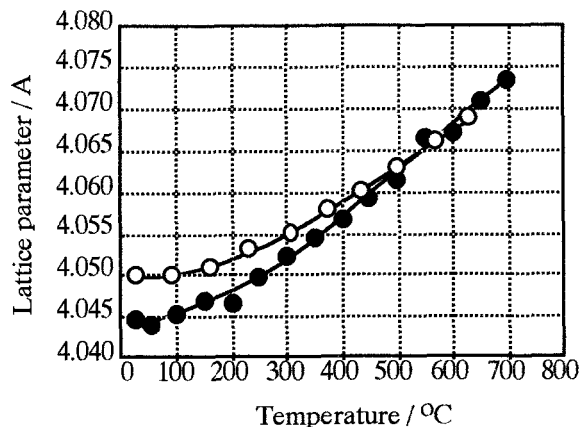


Figure 2. Relationship between lattice parameter of PMN single crystal (●) and temperature. Powder data after Bonneau et al. are also plotted (○)

Figure 3 shows scanning electron micrographs of the cross sections of (100)(a), (110)(b) and (111)(c) planes of PMN single crystal after heat treatment in the furnace at 1000°C for 6h. All of three micrographs show that the resultant morphology of decomposed PMN single crystal is constructed from two regions having layer structures. The schematic morphology is shown in Figure 3(d), in which three regions are indexed. Regions (1), (2) and (3) correspond to the surface, intermediate layer and original PMN single crystal respectively. The thicknesses of Regions (1) and (2) are shown in Table 1. From this Table, it was found that the thicknesses of Regions (1) and (2) are almost constant against three directions. The composition change along the cross section of Figure 3(a) is shown in Figure 4(a). Figure 4(b) shows the dependence of Pb/Nb, Mg/Nb, and Pb/(Mg+Nb) atomic ratios on the distance from the surface. From Figure 4(a) and 4(b), there is the marked difference in the composition profile. Pb is hardly detected in Region (1), on the other hand, Mg and Nb contents show the drastic change of concentration in this region. Namely, Mg is rich on the surface of this region and its concentration decreases with distance from the surface. Nb concentration reveals maximum value near the boundary of Region (1) and (2). To form this profile, migration of both Mg and Nb can be expected. In Region (2), Pb is detected. From Figure 4(a), it is shown that the concentrations of the three elements are almost constant but the tendency of slight increase of Mg and slight decrease of Nb with the distance from the surface can be seen in Region (2). Because of this tendency, the Pb/Nb

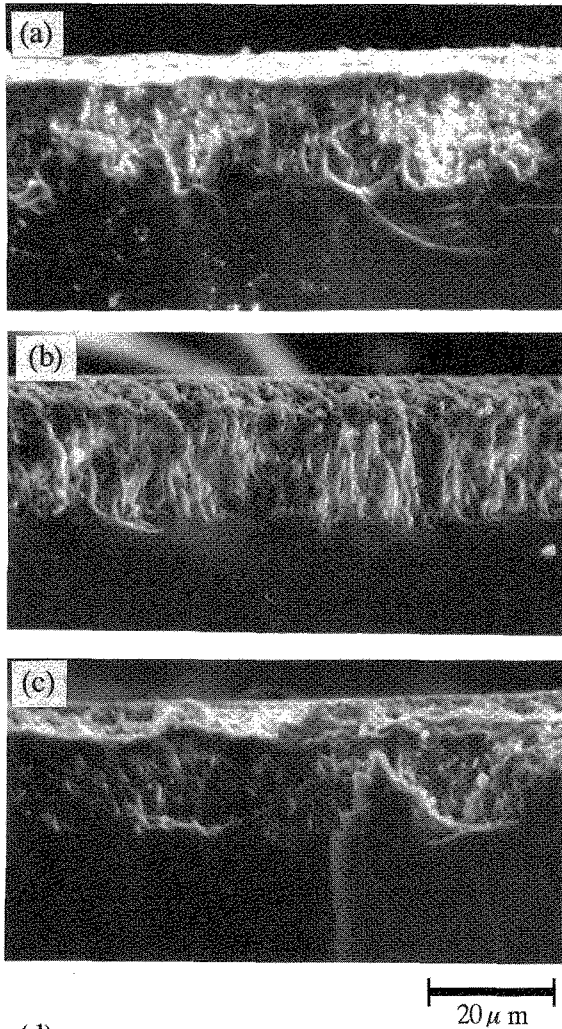


Figure 3. SEM photographs of cross sections after PMN single crystal was thermally decomposed: (100)(a), (110)(b) and (111)(c). Figure 3(d) is a schematic illustration of the three regions.

Table 1  
Thickness of Regions (1) and (2) of samples shown in Figure 3(a), (b) and (c)

	Region (1)	Region (2)
(100)(a)	3.9 μm	16.1 μm
(110)(b)	4.1 μm	17.5 μm
(111)(c)	4.3 μm	15.8 μm

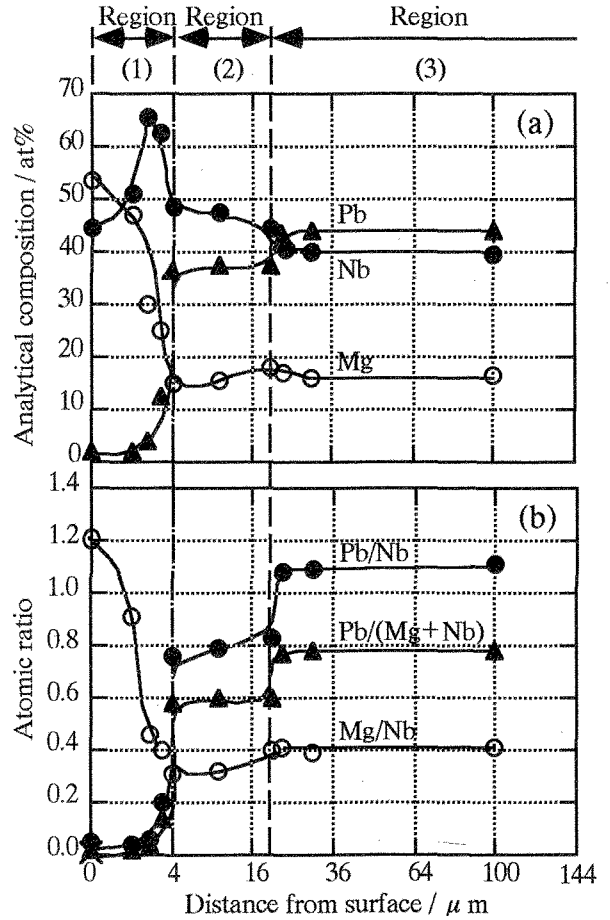


Figure 4. Dependence of analytical composition (a) and atomic ratio (b) on the distance from the surface

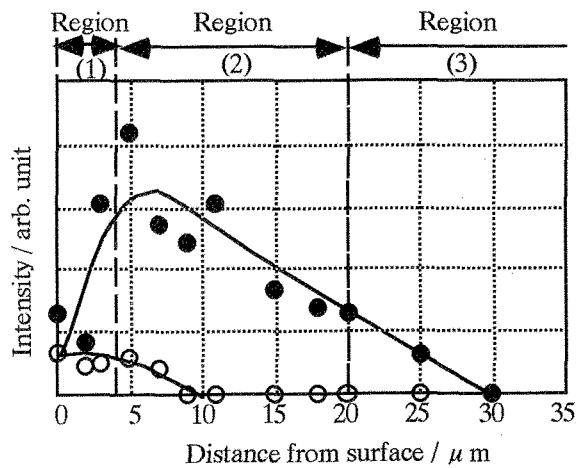


Figure 5. Relationship between resultant phases and the distance from the surface. Pyrochlore-type compound (●), MgNb<sub>2</sub>O<sub>6</sub> (□)

and Mg/Nb ratios may show slight increase with the distance from the surface, that suggests that there is a possibility of concentration gradient in this region. In Region (3) the concentration of all elements turns out completely constant.

The change of resultant phases with distance from the surface was analyzed with a powder diffractometer. For this experiment, the sample in Figure 3(a) was repeatedly polished and analyzed. The depth profile is shown in Figure 5. Since the plane of sample was tilted at 4° against (100) plane, no diffraction of PMN was detected in Figure 5. The range of Regions (1), (2) and (3) is also shown in Figure 5. From the data in Figure 5 and the data reported by Kim et al. [13], it can be considered that Region (1) is consisted of  $\text{MgNb}_2\text{O}_6$  and slight pyrochlore, Region (2) of Pyrochlore and Region (3) of PMN. However the boundary of each region observed with SEM and EDS is not necessarily corresponded to this Figure. The reason may reflect both the difficulty to polish the sample perfectly parallel and the fluctuation of the thickness of each layer.

From the data shown Figures 4(a), (b) and 5 comprehensively, it can be concluded that Region (3) is consisted of PMN and no concentration gradient can be seen in this region, that is, PMN is a line compound. On the other hand, Region (2) is consisted of pyrochlore type compound and there is a possibility of concentration gradients in both Pb/Nb and Mg/Nb ratios in this region. This suggests that pyrochlore type compound is not a line compound and has the range of composition to a certain content. In our previous work [16], it was presumed that pyrochlore type compound in this system is not a line compound from the point of crystal structure. This work may support our previous work.

The fact that pyrochlore-type compound may not be a line compound but PMN is a line compound would suggest that pyrochlore type compound is more stable than PMN against the fluctuation of composition. Consequently, pyrochlore-type compound may often form on both the synthesis and decomposition of PMN.

#### 4. CONCLUSIONS

Thermal decomposition behavior of PMN was examined using single crystal. The decomposition of PMN proceeds isotropically and unaccompanied with topo-chemical reaction. When PMN single crystal decomposed, the resultant morphology was constructed by two distinct regions having layer structures. Surface layer was poor in Pb, and the possibility of concentration gradient in the intermediate layer was shown. This region was resulted in pyrochlore type compound. That is, pyrochlore-type compound may not be a line

compound, and Mg and Nb may migrate toward the surface on the decomposition of PMN. On the other hand, the region of original PMN had no concentration gradient, that is, PMN is a line compound. These facts would suggest that pyrochlore-type compound is more stable than PMN against the fluctuation of composition. Therefore the reason why pyrochlore-type compound often forms on both the synthesis and decomposition of PMN is qualitatively explained by this work.

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