Raman Spectroscopic Determination of Pyrochlore-Type Compound on the Synthesis and Decomposition of Sol-Gel-Derived Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN)

Naoki Wakiya, Jun Shiihara, Kazuo Shinozaki, and Nobuyasu Mizutani[1]

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Raman spectroscopy was applied to the sol-gel-derived Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) powder and thin film. Pyrochlore-type compound which forms on the synthesis of PMN contains Mg in the formula (Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$) instead of Pb$_{1.5}$Nb$_2$O$_{6.5}$, Pb$_2$Nb$_2$O$_7$, or Pb$_{2.8}$Nb$_2$O$_{7.8}$, which have been reported in the literature to form on the synthesis of PMN. It is rather difficult to distinguish these pyrochlore-type compounds by X-ray diffraction since the d-values of these compounds are very close to each other. From the result of Raman spectroscopy, it was also clarified that the pyrochlore-type compound formed by the decomposition of PMN thin film also contains Mg in the formula (Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$). © 1999 Academic Press

INTRODUCTION

There has been much work on the oxide ferroelectric materials and their properties. One of the most complex ferroelectric classes is that characterized by a diffuse and dispersive phase transition of the so-called relaxor ferroelectrics (1, 2). In these relaxor ferroelectrics, lead magnesium niobate, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), has been considered to be one of the most promising materials (3, 4). It is well known that pyrochlore-type compound often forms on the synthesis of PMN and it tends to remain at the end of sintering (5). In addition to the synthesis process, pyrochlore-type compound forms at the thermal decomposition of PMN (6). For the change of the composition with temperature on the synthesis of PMN by solid state reaction, several routes have been reported. Inada reported that the formation reaction of PMN is constructed from the following three steps on the basis of DTA measurement (7):

(A) Pb$_{1.5}$Nb$_2$O$_{6.5}$ (cubic) forms between 530 and 650°C.

(B) Pb$_{1.5}$Nb$_2$O$_{6.5}$ reacts with PbO to form Pb$_2$Nb$_2$O$_7$ (rhombohedral) between 600 and 700°C.

(C) Pb$_2$Nb$_2$O$_7$ reacts with MgO to form both PMN and Pb$_{1.5}$Nb$_2$O$_{6.5}$ between 700 and 800°C.

On the other hand, Lejeune *et al.* (8) reported that Pb$_3$Nb$_2$O$_8$ (tetragonal) forms between 570 and 700°C, Pb$_3$Nb$_2$O$_8$ reacts with MgO to form PMN, and Pb$_2$Nb$_2$O$_7$ and Pb$_{1.5}$Nb$_2$O$_{6.5}$ form as by-products of PMN. Chen *et al.* (9) compared the formation kinetics of PMN from two raw material systems, i.e., Pb$_3$Nb$_2$O$_8$ + MgO and PbO + MgO + Nb$_2$O$_5$. They reported that no considerable difference was detected between the two raw material systems. Swartz *et al.* (10) reported that the formation of pyrochlore-type compound can be suppressed by using MgNb$_2$O$_6$ and PbO as raw materials (so-called "columbite method"). By using this method the amount of pyrochlore type compound can be drastically decreased. They reported that pyrochlore-type compound coexisting with PMN contains Mg in the formula (Pb$_{1.83}$Mg$_{0.29}$Nb$_{1.71}$O$_{6.39}$). For sol-gel-derived PMN, the route to form PMN was examined by Chaput *et al.* (11). They found that the lattice parameter of pyrochlore-type compound continuously decreases with firing temperature for sol-gel-derived PMN powder. They attributed the decrease of lattice parameter to the possibility of the increase of Coulomb interactions due to the additional Mg^{2+} ions in the octahedra of pyrochlore-type compound. However, a detailed reaction is still unknown.

By crystal structure determination, the accurate composition of Pb$_3$Nb$_2$O$_8$ has been revised to Pb$_{2.8}$Nb$_2$O$_{7.8}$ (12) and that of Pb$_{1.83}$Mg$_{0.29}$Nb$_{1.71}$O$_{6.39}$ has been revised to Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ (13). In these pyrochlore-related compounds mentioned above, Pb$_{1.5}$Nb$_2$O$_{6.5}$ and Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ are both ideal cubic pyrochlore-type compounds (13, 14). On the contrary, Pb$_2$Nb$_2$O$_7$ is reported to be rhombohedral; pyrochlore blocks are separated by regular shear planes (15, 16). Pb$_{2.8}$Nb$_2$O$_{7.8}$ is reported to have orthorhombic symmetry (12). In this way, many pyrochlore-related compounds exist in a Pb–Mg–Nb–O system. However the d-values of these pyrochlore-type compounds are close to each other. Therefore it is

---

[1] To whom correspondence should be addressed.

rather difficult to distinguish these compounds by X-ray diffraction. Raman spectrum is sensitive not only to the defects, such as shear structure, but also to the substitution by another cation since the force constants between cations and oxygen are changed by the kind of cation even in the same crystallographic sites (17). Therefore it is expected that it will be possible to identify the pyrochlore-type compound forms on the crystallization process of PMN from sol using Raman spectroscopy. The target of this work is to clarify this point.

EXPERIMENTAL

A PMN alkoxide-based solution was synthesized in (18) from the starting materials of Pb(CH$_3$COO)$_2$·3H$_2$O, Mg(OC$_2$H$_4$OCH$_3$)$_2$, Nb(OC$_2$H$_5$)$_5$. 2-methoxyethanol, CH$_3$OC$_2$H$_4$OH, was used as a solvent. To prepare gel powders, the solution was spread over a petri dish and hydrolyzed by humidity in air. The films were deposited by spin coating (2000 rpm) onto (100)MgO single crystal substrate. After hydrolyzation, the samples were heated at 350°C for 30 min, then rapid thermally annealed at a prescribed temperature for 2 h. The details of the thin film preparation can be found in Ref. (19).

Raman spectra were measured with a spectrometer with a triple monochrometer and a CCD detector (T64000, Atago-Jobin Yvon, Japan). The green laser line (514.5 nm) of an argon-ion laser was used. X-ray diffraction was measured with an automated powder X-ray diffractometer using CuKα radiation with a single crystal graphite monochromator (PW-1700, Philips, Netherlands).

In this work, PMN and several pyrochlore-type compounds, Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$, Pb$_{1.5}$Nb$_2$O$_{6.5}$, Pb$_2$Nb$_2$O$_7$, and Pb$_{2.8}$Nb$_2$O$_{7.8}$, were used as references. To synthesize these compounds, conventional solid state reaction was used from PbO, MgO, and Nb$_2$O$_5$ powders of reagent grade. The powders were weighted out and mixed using ball milling with ZrO$_2$ balls for 18 h in ethanol. The wet slurry was dried using a rotary evaporator and calcined at 800°C for 2 h, ground and pressed into pellets, put into a MgO crucible, and covered with powders having the same composition as the pellets. The samples were sintered at 1100°C for 2 h for PMN, 1000°C for 4 h for Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$, Pb$_{1.5}$Nb$_2$O$_{6.5}$, and Pb$_2$Nb$_2$O$_7$, and 800°C for 4 h for Pb$_{2.8}$Nb$_2$O$_{7.8}$, and single phase samples were obtained. After sintering, the pellets were ground into powders.

RESULTS AND DISCUSSION

Raman Spectra of PMN and Several Pyrochlore-Type Compounds

Figure 1 shows Raman spectra of PMN, Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$, Pb$_{1.5}$Nb$_2$O$_{6.5}$, Pb$_2$Nb$_2$O$_7$, and Pb$_{2.8}$Nb$_2$O$_{7.8}$
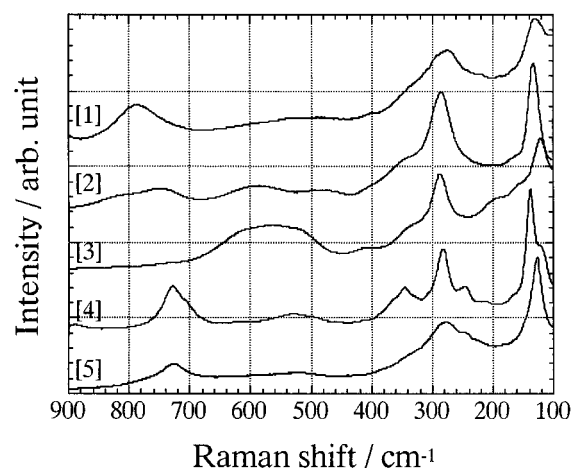
FIG. 1. Raman spectra of [1] Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), [2] Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$, [3] Pb$_{1.5}$Nb$_2$O$_{6.5}$, [4] Pb$_2$Nb$_2$O$_7$, and [5] Pb$_{2.8}$Nb$_2$O$_{7.8}$ synthesized by solid state reaction in the 100–900 cm^{-1} wave number range.

in the 100–900 cm^{-1} wave number range. As shown in Fig. 1, many bands were observed in this range. In this work, special attention was paid to the 700–900 cm^{-1} range to distinguish the individual compounds, as shown in Fig. 2. For PMN, the band observed at 788 cm^{-1} was considered to be generated by the different force constant for stretching mode between Mg–O and Nb–O although Mg^{2+} and Nb^{5+} cations occupy the same site (B site of perovskite-type compound) statistically (20). For Pb$_{1.5}$Ta$_2$O$_{6.5}$, which is isostructure with Pb$_{1.5}$Nb$_2$O$_{6.5}$, the Raman bands have been assigned (21). According to Ref. (21), no band was reported between 700 and 900 cm^{-1} (no such band is shown in Fig. 2). Although Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ is also isostructure with Pb$_{1.5}$Nb$_2$O$_{6.5}$ (cubic having the same content of oxygen vacancy), two characteristic bands were observed at 745 and 815 cm^{-1}, as shown in Fig. 2. Since the B site of Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ was occupied by two different cations, i.e., Mg^{2+} and Nb^{5+}, the two bands would be derived from the different force constants between oxygen. Pb$_{2.31}$Nb$_2$O$_{7.31}$ is one of the pyrochlore-related compounds having rhombohedral symmetry in which pyrochlore blocks are separated by regular shear planes (12, 15); Pb$_{2.8}$Nb$_2$O$_{7.8}$ is another such compound. For Pb$_{2.31}$Nb$_2$O$_{7.31}$, a Raman spectrum has been assigned (21). According to Ref. (21), the Raman band at about 700 cm^{-1} is assigned to be the shear planes. In Fig. 2, a large Raman band can be observed for Pb$_2$Nb$_2$O$_7$ and Pb$_{2.8}$Nb$_2$O$_{7.8}$ at around 730 cm^{-1}. Although no Raman spectrum is reported for Pb$_2$Nb$_2$O$_7$ and Pb$_{2.8}$Nb$_2$O$_{7.8}$, the band would be assigned due to the regular shear planes. Regardless, the two Raman bands at 745 and 815 cm^{-1} are characteristic for Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ only, and the bands are not observed for PMN, Pb$_{1.5}$Nb$_2$O$_{6.5}$, Pb$_2$Nb$_2$O$_7$, and Pb$_{2.8}$Nb$_2$O$_{7.8}$.
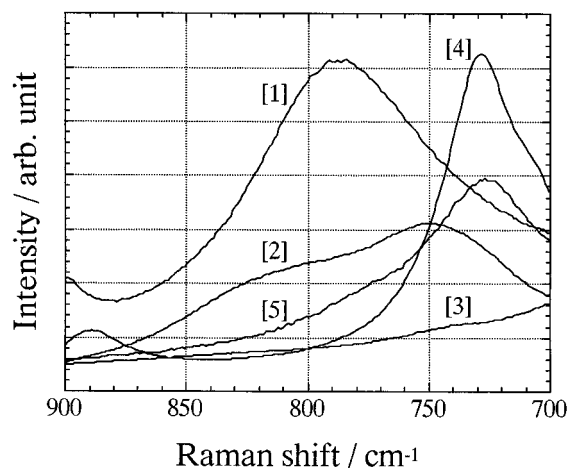
FIG. 2. Enlargement of Raman spectra shown in Fig. 1 in the 700–900 cm^{-1} wave number range. [1] Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), [2] Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$, [3] Pb$_{1.5}$Nb$_2$O$_{6.5}$, [4] Pb$_2$Nb$_2$O$_7$, and [5] Pb$_{2.8}$Nb$_2$O$_{7.8}$ synthesized by solid state reaction.

Raman Spectra of Sol-Gel-Derived Powder

Figure 3 shows changes in the Raman spectra of sol-gel-derived powder after it has been heated at various temperatures for 2 h in air. Raman spectra of PMN and Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ are also shown as references. This figure indicates that the Raman spectra of sol-gel-derived powder drastically changed between 700 and 750°C. The spectra below 700°C show the same bands of Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$, which strongly suggests that pyrochlore-type compound forming on the synthesis of PMN contains Mg in the formula. However, the pyrochlore-type compound synthesized by solid state reaction is reported to be Pb$_{1.5}$Nb$_2$O$_{6.5}$, Pb$_2$Nb$_2$O$_7$, or Pb$_{2.8}$Nb$_2$O$_{7.8}$ (7, 8), which do not contain Mg in the formula. For the explanation of this disagreement, the following can be considered.

(A) In the literature, Mg containing pyrochlore-type compound (Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$) was identified as Mg free pyrochlore-type compound since it is rather difficult to distinguish pyrochlore-type compound precisely by X-ray diffraction as mentioned above.

(B) For sol-gel-derived powder, it is believed that the mixing state of elements is uniform in the atomic level and Mg containing pyrochlore-type compound forms instead of other Mg free pyrochlore-type compounds.

Comparing the Raman spectrum of Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ with sol-gel-derived powder after it has been heated at 500, 600, and 700°C, the band near 745 cm^{-1} shows the tendency to shift from 755 cm^{-1} (500°C) to 745 cm^{-1} (700°C). This shift is simply due to the thermal dilation of the crystal cell and of the bonds when the temperature increases. In this work, it was impossible to measure Raman spectrum for sol-gel-derived powder
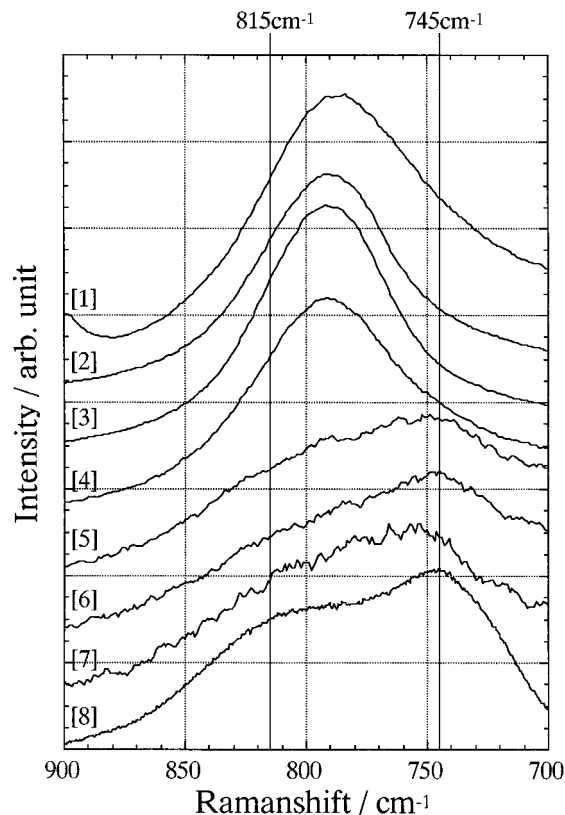

FIG. 3. Changes of Raman spectra for sol-gel-derived powder after it has been heated at the following temperatures for 2 h in air: [1] PMN powder (as a reference), [2] 900°C, [3] 800°C, [4] 750°C, [5] 700°C, [6] 600°C, [7] 500°C, and [8] Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ powder (as a reference).

heated at 350°C due to the strong fluorescence. Figure 3 also shows that perovskite PMN drastically forms in a narrow temperature range. In the case of PMN, the band of sol-gel-derived powder is shifted about 5 cm^{-1} toward large wave numbers compared with that of reference PMN powder synthesized by solid state reaction; however, a difference of 5 or 10 cm^{-1} is not significant since the Raman bands observed are very large. Figure 4 shows changes of XRD patterns for sol-gel-derived powder after it has been heated at various temperatures. Figure 4 indicates that the powder was X-ray amorphous below 600°C and the broad peaks of pyrochlore type compound were detected at 700°C followed by the formation of PMN above 750°C. Comparing Fig. 3 with Fig. 4, the following can be pointed out.

(A) The Raman spectrum is very sensitive to detect pyrochlore-type compound even if the sample is X-ray amorphous since the Raman spectrum does not require correlation lengths as large as those for diffraction experiments.

(B) Since the X-ray diffraction peak of the resultant pyrochlore-type compound at 700°C was very weak, it is almost impossible to determine the lattice parameter of the pyrochlore-type compound unless special a strong X-ray beam
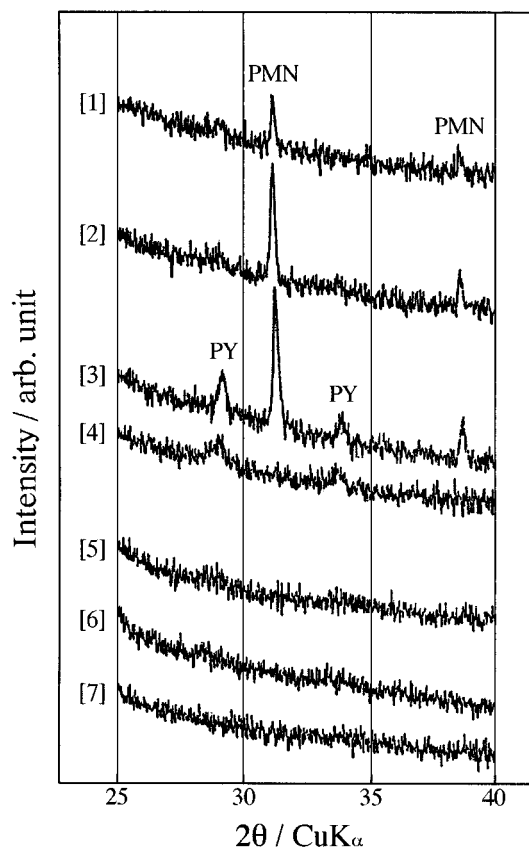
FIG. 4. Changes of XRD pattern for sol-gel-derived PMN powder after heated at the following temperatures for 2 h in air. [1] 900°C, [2] 800°C, [3] 750°C, [4] 700°C, [5] 600°C, [6] 500°C, and [7] 350°C.

FIG. 5. Changes of Raman spectra for sol-gel-derived PMN thin film after it has been heated at the following temperatures for 2 h in air: [1] PMN powder (as a reference), [2] 900°C, [3] 800°C, [4] 700°C, and [5] Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ powder (as a reference)

generated by a rotating anode or synchrotron orbital radiation (SOR) are used. This indicates that it is almost impossible to identify the resultant pyrochlore-type compound.

(C) For a mixed phase sample, X-ray diffraction is more sensitive to identify the phases since the width of the Raman spectrum is relatively wider than X-ray diffraction. However, at least, the formation of PMN at 750°C is clearly observed by Raman spectroscopy.

X-ray diffraction is sensitive to the long-range order whereas Raman spectroscopy is sensitive to the short-range order. Consequently, it can be mentioned that Raman spectroscopy is very effective for identification of samples for which X-ray diffraction is not effective due to the lack of long-range order. Raman spectroscopy is also very effective to determine whether a crystallographic site of a compound was occupied by a single cation (e.g., Pb$_{1.5}$Nb$_2$O$_{6.5}$) or by multiple cations (e.g., Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$) even for the samples with low crystallinity.

Raman Spectra of Sol-Gel-Derived PMN Thin Film

Figure 5 shows the change of Raman spectra of sol-gel-derived PMN thin film after it has been heated at 700, 800,
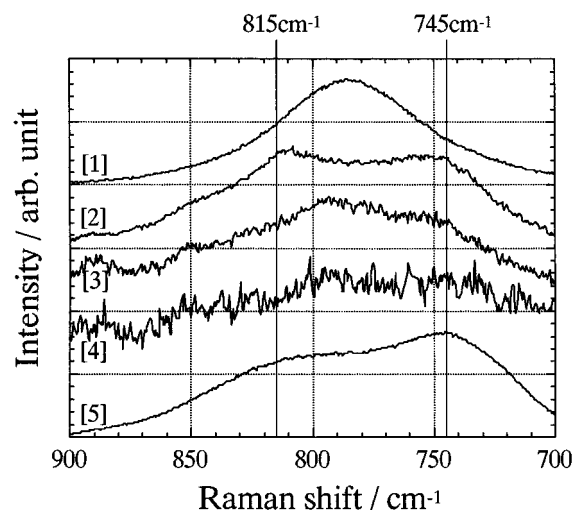
and 900°C for 2 h in air. In this figure Raman spectra of PMN powder and Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ powder synthesized by solid state reaction are also shown as references. For the thin film heated at 700°C for 2 h, only weak and broad bands were observed, and therefore it is difficult to identify by this spectrum. For thin film heated at 800°C, two apparent bands can be observed at 745 and 792 cm^{-1}. The band at 745 cm^{-1} coincides with the band of Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$, however, the band observed at 792 cm^{-1} is far from another characteristic band observed at 815 cm^{-1}. The band observed at 792 cm^{-1} is close to that of PMN powder observed at 788 cm^{-1}. Therefore it can be considered that the Raman spectrum of thin film heated at 800°C consists of mixed phase of PMN and Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$. The Raman spectrum of thin film heated at 900°C agreed well with that of Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$. This indicates that PMN decomposed into Pb$_{1.86}$Mg$_{0.24}$Nb$_{1.76}$O$_{6.5}$ at 900°C. Figure 6 shows the changes of XRD pattern for the thin film after it was heated at various temperatures. This figure shows that PMN was only detected for thin film heated at 800°C, and the PMN decomposed into pyrochlore-type compound at 900°C, which indicates that the information gathered by X-ray diffraction can be obtained by Raman spectroscopy, and in addition to the information gathered by X-ray diffraction, more information can be obtained by Raman spectroscopy such as the composition of the pyrochlore-type compound after the decomposition of PMN.

Comparing the crystallization process of gel powder with that of thin film, the following could be mentioned.

(1) Gel powder. On the way of heating, Mg containing cubic pyrochlore-type compound first crystallized from
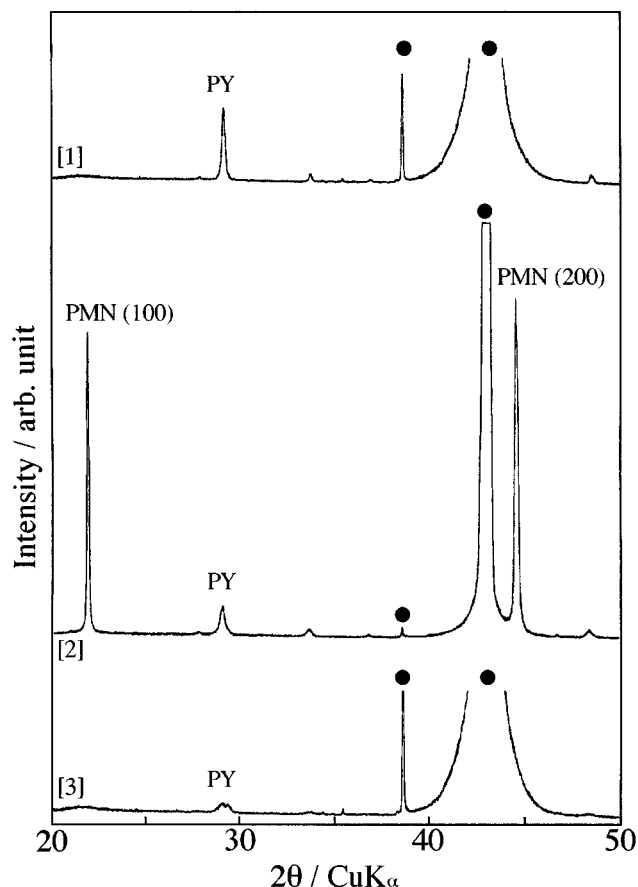
FIG. 6. Changes of XRD pattern for sol-gel-derived PMN thin film it has been after heated at the following temperatures for 2 h in air. [1] 900°C, [2] 800°C, [3] 700°C. (●) Diffraction peak of MgO substrate.

Consequently, both for powder and for thin film, Raman spectroscopy is effective for the distinction of Mg containing pyrochlore-type compound from Mg free pyrochlore-type compound.

CONCLUSIONS

It is rather difficult to distinguish several pyrochlore-type compounds in the Pb–Mg–Nb–O system by X-ray diffraction, especially when the crystallinity is low. Raman spectroscopy is effective in distinguishing the pyrochlore-type compounds. In this work, Raman spectroscopy was applied to the sol-gel-derived $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder and thin film, and it was clarified that pyrochlore-type compound which forms on the synthesis of PMN contains Mg in the formula $(Pb_{1.86}Mg_{0.24}Nb_{1.76}O_{6.5})$ instead of $Pb_{1.5}Nb_2O_{6.5}$, $Pb_2Nb_2O_7$, or $Pb_{2.8}Nb_2O_{7.8}$, which have been reported in the literature to form on the synthesis of PMN. It was also clarified that the pyrochlore-type compound formed by the decomposition of PMN thin film also contains Mg in the formula $(Pb_{1.86}Mg_{0.24}Nb_{1.76}O_{6.5})$.

REFERENCES

1. G. A. Smolenskii, *J. Phys. Soc. Jpn.* **28,** Suppl. p. 26 (1970).
2. L. E. Cross, *Ferroelectrics* **76,** 241 (1987).
3. M. Lejenue and J. P. Boilot, *Ceram. Int.* **8,** 99 (1982).
4. S. L. Swartz, T. R. Shrout, W. A. Schulze, and L. E. Cross, *J. Am. Ceram. Soc.* **67,** 311 (1984).
5. T. R. Shrout and S. L. Swartz, *Mater. Res. Bull.* **8,** 663 (1983).
6. B. H. Kim, O. Sakurai, N. Wakiya, and N. Mizutani, *Matter. Res. Bull.* **32,** 451 (1997).
7. M. Inada, *Japanese Natl. Tech. Rep.* **23,** 954 (1977).
8. M. Lejeune and J. P. Boilot, *Ceram. Int.* **8,** 99 (1982).
9. S. Y. Chen, C. M. Wang, and S. Y. Cheng, *J. Am. Ceram. Soc.* **74,** 2506 (1991).
10. S. L. Swartz and T. R. Shrout, *Mater. Res. Bull.* **17,** 1245 (1982).
11. F. Chaput and J. P. Boilot, *J. Am. Ceram. Soc.* **72,** 1335 (1989).
12. H. B. Wulf and W. Hoffmann, *Z. Krist.* **164,** 129 (1982).
13. N. Wakiya, N. Ishizawa, A. Saiki, K. Shinozaki, and N. Mizutani, *Matter Res. Bull.* **28,** 137 (1993).
14. F. Beech, W. M. Jordan, C. A. Catlow, A. Santoro, and B. C. H. Steele, *J. Solid State Chem.* **77,** 322 (1988).
15. H. B. Wulf and W. Hoffmann, *Naturwissenschhaften* **67,** 141 (1980).
16. H. G. Scott, *J. Solid State Chem.* **43,** 131 (1982).
17. M. Kakihana *et al.*, *Trends Appl. Spectrosc.* **1,** 261 (1993).
18. L. F. Fracis, Y. J. Oh, and D. A. Payne, *J. Mater. Sci.* **25,** 5007 (1990).
19. K. Okuwada, M. Imai, and K. Kakuno, *Jpn. J. Appl. Phys.* **28,** L1271 (1989).
20. E. Husson, L. Abello, and A. Morell, *Mater. Res. Bull.* **25,** 539 (1990).
21. M. T. Vandenborre and E. Husson, *J. Solid State Chem.* **53,** 253 (1984).

X-ray amorphous sample at 500°C. Then resultant phase changes into perovskite PMN at 750°C. However, as shown in Fig. 4, the intensity of X-ray diffraction decreases at 900°C which is due to the decomposition of PMN into pyrochlore type compound. However, it was difficult to identify the pyrochlore type compound after decomposition since PMN was a major phase.

(2) Thin film. On the way of heating, formation of pyrochlore-type compound was first confirmed at 700°C, and then formation of PMN was confirmed at 800°C by X-ray diffraction. Further heating brought about the decomposition of PMN into pyrochlore-type compound. From the Raman spectrum, it was difficult to determine the phase for thin film after it was heated at 700°C. On the contrary, at 900°C, the resultant phase was clarified to be Mg containing pyrochlore-type compound by Raman spectrum. The discrepancy of the resultant phase at 900°C between powder and thin film is ascribed to the rate of evaporation of lead from the sample since the decomposition of PMN into pyrochlore-type compound is brought about by the evaporation (6).