Stability of lead magnesium niobate under hydrothermal conditions

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Low-crystalline pyrochlore powder of lead magnesium niobate was treated under various hydrothermal conditions. The perovskite phase crystallized in pure water above 580 °C, but hydrothermal treatments at high temperatures for a long time decreased the amount of the perovskite phase and increased that of the cubic pyrochlore phase. The addition of lead oxide enhanced the formation of the perovskite, but not magnesium oxide. The perovskite phase was not stable in many salt solutions even with the addition of lead oxide, but its stability was increased in solutions consisting of large anions and cations.

1. Introduction

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), is a relaxor ferroelectric with excellent dielectric and electrostrictive properties [1–3]. One of the problems with PMN ceramics is the difficulty in producing a single-phase material of only the perovskite structure without the pyrochlore structure which reduces the dielectric constant in the material [4–6]. A few fabrication processes were developed to minimize the amount of the pyrochlore phases; composition control by addition of excess PbO [7, 8] or MgO [4, 9, 10], and the precursor method by reaction of magnocolumbite ($MgNb_2O_6$) with PbO [11], or by the reaction of lead niobate ($Pb_3Nb_2O_8$) with MgO [12]. The firing temperatures to eliminate the pyrochlore phase by these processes were usually quite high, above 800 °C, though Shrout et al. [13] reported the PMN perovskite was obtained without the pyrochlore phase at 750 °C by the magnocolumbite precursor method.

The sol–gel method has been employed to prepare PMN at low temperatures, about 700 °C [3, 5, 14, 15]. Ravindranathan et al. [5] obtained the pure perovskite phase by calcination of the structurally diphasic gel with 5% seeds at 675 °C for 2 h. The other process to prepare ceramic powders at low temperatures is the hydrothermal method. The hydrothermal synthesis reaction replaces the calcination required by the sol–gel and coprecipitation techniques [16]. Few studies have been reported of the hydrothermal synthesis of PMN. Imoto and Iida [17] showed that the cubic pyrochlore phase crystallized by hydrothermal treatment of the mixture of PMN component oxides at 600 °C. Watanabe and Shimizu [18, 19] prepared a fine powder of low-crystalline cubic pyrochlore at low temperatures, below 200 °C. The present author [20] showed that the hydrothermally prepared low-crystalline pyrochlore could be transformed into the pervoskite phase by hydrothermal treatment in pure water at about 600 °C. No results have been reported on the hydrothermal treatment of PMN in salt solutions. If a solution can be found in which PMN is stable and more or less dissolves, single crystals of PMN could be grown by the hydrothermal method.

The purpose of this investigation was to study the stability of PMN under various hydrothermal conditions. This study especially focuses on the stability and formation of the PMN perovskite.

2. Experimental procedure

The starting powder was synthesized by the hydrothermal method described by Watanabe and Shimizu [18, 19]. Aqueous solutions of $Pb(NO_3)_2$ (1.94 mol l^{-1}) and $Mg(NO_3)_2$ (0.62 mol l^{-1}) was mixed with ethanol solution of $NbCl_5$ (63 wt %) to obtain a solution with the PMN composition. The mixed solution was poured into KOH aqueous solution (7.5 mol l^{-1}) with a mole ratio of PMN/KOH = 1/4, and then hydrothermally treated at 160 °C for 2 h. After the hydrothermal treatment, the solid powder was washed with water and dried at 110 °C. The powder was low-crystalline pyrochlore phase (Fig. 1a).

A test-tube-type pressure vessel made of Stellite-25, was used for the hydrothermal treatment of the low-crystalline pyrochlore powder. The mineralizers used were pure water, 5N solutions of LiOH, LiCl, NaOH, NaF (added as a solid), NaCl, NaBr, KOH, KF, KI and CsF, and 1N NH_4OH solution. The additives were reagent-grade chemicals, $(CH_3COO)_2Pb \cdot 3H_2O$, $Pb(NO_3)_2$, PbF_2, $PbCl_2$, PbO, Pb_3O_4, and MgO. One of the mineralizers was injected into a platinum capsule of outer diameter 3.0 mm, thickness 0.2 mm and length 30 or 50 mm. The shorter capsules were employed for the experiments using pure water as a mineralizer. The amount of mineralizer was determined to balance the pressure outside and inside the capsule at the hydrothermal treatment temperatures.
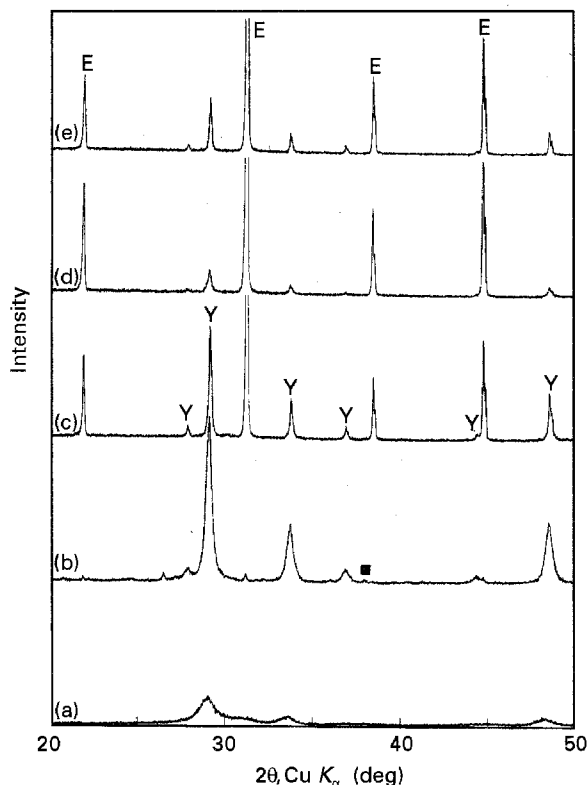
Figure 1 X-ray diffraction patterns of (a) the starting powder, and the reaction products obtained in pure water at (b, c) 580 °C for (b) 3 h and (c) 24 h, and at (d, e) 600 °C for (d) 3 h and (e) 24 h. E, PMN perovskite; Y, cubic pyrochlore; (■) Mg(OH)$_2$.

The starting low-crystalline pyrochlore powder (50 mg) was added to the mineralizer with or without one of the additives (20 mg). The capsule was welded shut with an electric arc. The sealed capsule was placed in the vessel and heated to a desired temperature up to 820 °C. Temperatures were measured on the wall of the vessel at two positions corresponding to the top and the bottom of the capsule. When the shorter capsules were used, the temperature at the top, that is the hydrothermal treatment temperature, was 10 °C lower than the temperature at the bottom. The temperature difference was 30 °C for the longer capsules. The pressure was adjusted to 100 MPa by using water as a pressure medium.

At the conclusion of a run, the vessel was cooled to room temperature by removing the furnace from the autoclave. The capsule was cut open, and the contents were washed with water. The obtained solid was identified by X-ray powder diffraction and observed by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer. The relative amount of the PMN perovskite phase against the pyrochlore phase in the reaction products was estimated from the relative intensity of the X-ray diffraction peaks of the perovskite and the pyrochlore phase:

$$100 \times I_{(1\ 1\ 0)\ \mathrm{perovskite}}/(I_{(1\ 1\ 0)\ \mathrm{perovskite}} + I_{(2\ 2\ 2)\mathrm{pyrochlore}}).$$

3. Results and discussion
3.1. Stability in pure water
X-ray diffraction patterns of hydrothermally treated powders in pure water are shown in Fig. 1. Only the cubic pyrochlore was obtained below 560 °C. Above

580 °C, the PMN perovskite started to crystallize. The hydrothermal method gave the PMN perovskite at a lower temperature than the sol–gel technique [3, 5, 14, 15]. The longer treatment at 580 °C for 24 h (Fig. 1c) gave a larger amount of the perovskite phase than the treatment for 3 h (Fig. 1b), although the longer reaction caused a decrease in the perovskite amount at 600 °C (Fig. 1d, e). The pyrochlore phase was the main phase obtained by reaction at 650 °C for 72 h. At 800 °C, magnocolumbite (MgNb$_2$O$_6$) was produced with the pyrochlore phase.

The ideal composition of the PMN perovskite and the pyrochlore is Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and Pb$_2$Nb$_2$O$_7$, respectively. The composition of the pyrochlore phase produced by the ceramics processing was reported to be Pb$_{2.25}$Mg$_{0.27}$Nb$_{1.79}$O$_7$ [4]. The pyrochlore phase has less lead and magnesium components in comparison with the PMN perovskite phase. The release of lead and magnesium components from the PMN composition may stabilize the pyrochlore phase.

The change of the PMN perovskite to the pyrochlore phase and magnocolumbite at high temperatures with long reaction time, was explained by release of lead components from the PMN composition. Fig. 2 shows the inside wall of the platinum capsule and its EDS spectra. Many cracks were observed and lead was detected on the wall of the platinum capsule. When the starting powder was treated with PbO in pure water at 800 °C, Pt–Pb alloy (PbPt and PbPt$_{5-7}$) crystallized. It is considered that the lead component in PMN has a high solubility under the hydrothermal conditions and is easily reduced to metal on the hydrogen-permeable platinum capsule under the reducing atmosphere produced by reaction of the vessel material with water. In order to obtain the pyrochlore phase from the PMN composition, the magnesium component should be released as well as the lead component. A trace of Mg(OH)$_2$ was detected in the products consisting of the pyrochlore phase (Fig. 1b). The EDS spectra showed that the pyrochlore phase obtained in this study included some magnesium. Furthermore, some magnesium component must be dissolved in the hydrothermal solution. In fact, Mg(OH)$_2$ was definitely produced with the pyrochlore and PbO in KOH solution, a strong basic solution, in which the magnesium component must precipitate as hydroxide.

3.2. Effect of additives
In the ceramics processing, excess PbO or MgO was added to obtain the PMN perovskite. In this study, the effect of the addition of Pb$_3$O$_4$ or MgO on the formation of the PMN perovskite was examined by the hydrothermal treatment of the low-crystalline pyrochlore powder at 580 °C for 24 h. X-ray diffraction patterns of the products produced without additives and with MgO, a mixture of Pb$_3$O$_4$ and MgO (10 mg each), or Pb$_3$O$_4$, are shown in Fig. 3a–d, respectively.

When Pb$_3$O$_4$ was added, PbO (massicot and litharge) was produced (Fig. 3c, d). When MgO was added, PbMg(CO$_3$)$_2$ was detected together with Mg(OH)$_2$ (Fig. 3b). Carbonate ions may be included
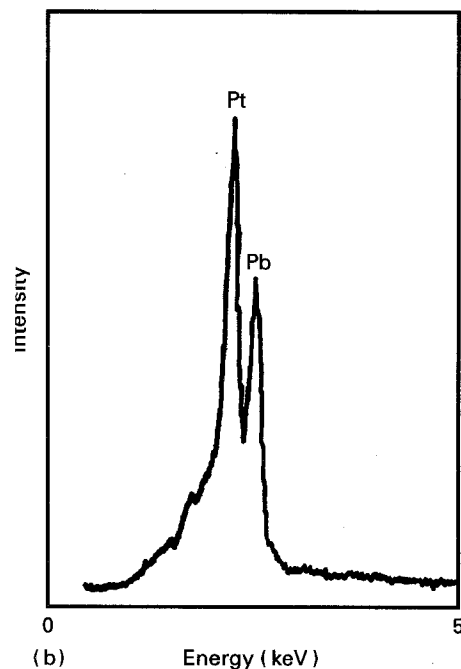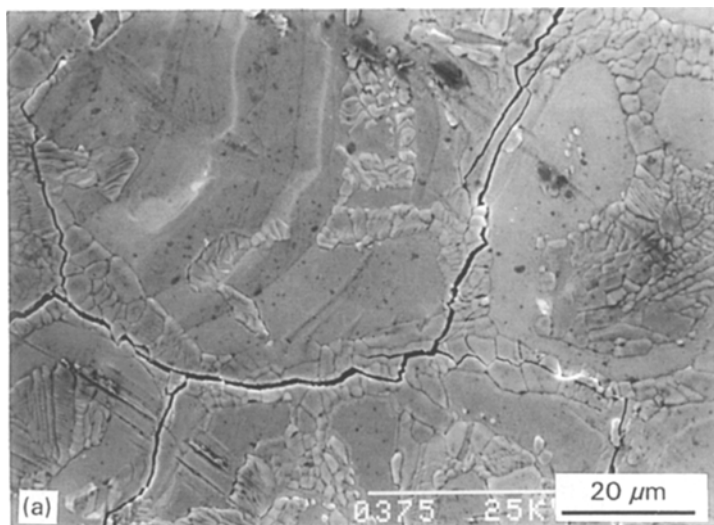
Figure 2 (a) Photograph of the inside wall of the capsule treated at 650 °C for 24 h, and (b) its EDS spectrum.
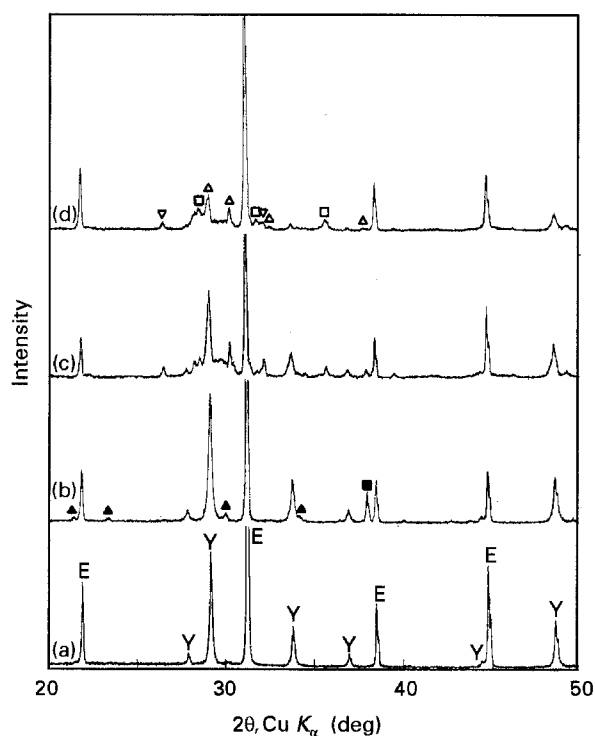

Figure 3 X-ray diffraction patterns of the products obtained in pure water at 580 °C for 24 h (a) without additives, and with (b) MgO, (c) MgO and Pb_3O_4, and (d) Pb_3O_4. E, PMN perovskite; Y, cubic pyrochlore; (■) $Mg(OH)_2$; (▲) $PbMg(CO_3)_2$; (□) PbO (litharge); (△) PbO (massicot); (▽) Pb_3O_4.

in the starting materials, the reagent of MgO and water. The relative amount of the perovskite phase in the reaction products shown in Fig. 3a–d, was estimated to be 74%, 63%, 68%, and 88%, respectively. When massicot (PbO) was produced (Fig. 3c, d), the relative amount of perovskite phase was estimated to be lower because of the coincidence of massicot (1 1 1) and the pyrochlore (2 2 2) diffraction.

The formation of $PbMg(CO_3)_2$ accelerated the release of lead from the PMN composition and resulted in an increase in the amount of pyrochlore. It is concluded that the addition of MgO has no effect on the formation of the PMN perovskite. The addition of Pb_3O_4 promoted the formation of the PMN perovskite in comparison with no additives. Saturation of the hydrothermal solution with the lead component by dissolution of the added lead oxide decreased the dissolution of the lead component from PMN, and the oxidizing atmosphere produced by decomposition of Pb_3O_4 inhibited the deposition of metallic lead on the platinum capsules.

The addition of the lead component may stabilize the PMN perovskite under hydrothermal conditions. The effect of the addition of various lead compounds was examined under hydrothermal conditions at 650 °C for 24 h. X-ray diffraction patterns of the reaction products are shown in Fig. 4.

In the case of $(CH_3COO)_2Pb \cdot 3H_2O$ and $Pb(NO_3)_2$, the additives were decomposed to form a gas phase under the hydrothermal conditions, and all capsules leaked. When PbF_2 or $PbCl_2$ was added, only the pyrochlore was obtained with lead compounds of added anions. The formation of these compounds accelerated the pull-out of the lead component from PMN and resulted in stabilization of the pyrochlore. The addition of PbO (massicot) or Pb_3O_4 gave mainly the PMN perovskite with PbO (litharge and massicot).

Scanning electron micrographs of the perovskite crystals are shown in Fig. 5. The crystals of the PMN perovskite were cubic in shape. This cubic morphology suggested that the formation of the PMN perovskite phase from the pyrochlore phase under hydrothermal conditions proceeded by dissolution and deposition. Each component of PMN might dissolve in water under hydrothermal conditions, but the
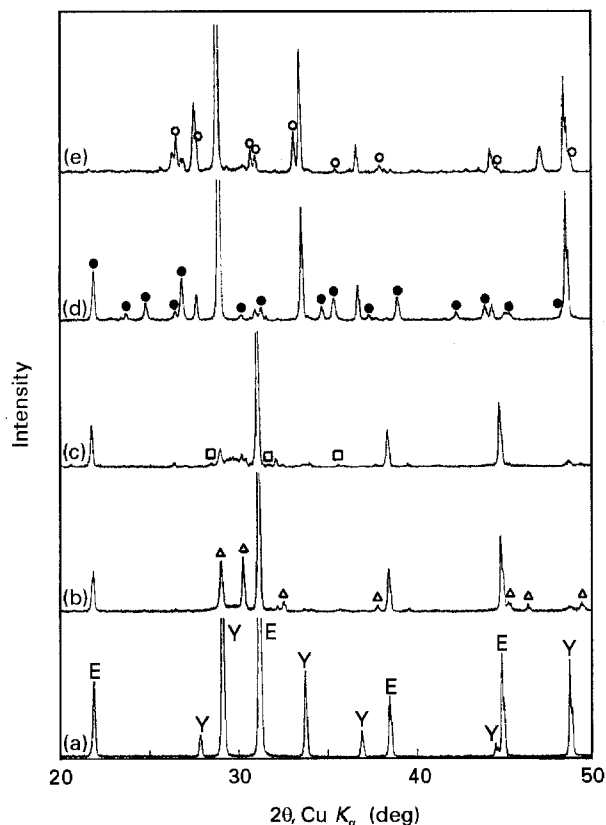
Figure 4 X-ray diffraction patterns of the products obtained at 650 °C for 24 h (a) without additives, and with (b) PbO, (c) Pb_3O_4, (d) $PbCl_2$, and (e) PbF_2. E, PMN perovskite; Y, cubic pyrochlore; (△) PbO (massicot); (□) PbO (litharge); (▽) Pb_3O_4; (●) PbClOH; (○) Pb_2OF_2.

high solubility of the lead component provided opportunity for the formation of the pyrochlore phase.

3.3. Stability in various mineralizers

The stability of PMN under hydrothermal conditions was examined by hydrothermal treatment of the low-crystalline pyrochlore powder in various solutions with or without the addition of lead oxide. The results are summarized in Table I.

First, the stability of PMN in KOH and KF solution was investigated, because KOH solution was used to prepare the starting powder and Barsukova *et al.* [21] grew crystals of $Pb(Ti, Zr)O_3$ under hydrothermal conditions by using KF solution as a mineralizer. X-ray diffraction patterns of the hydrothermally treated powders are shown in Fig. 6.

The contamination of the capsules with metal lead was not serious in either solution. In KOH solution, the pyrochlore crystallized well at 650 °C together with PbO (litharge) and $Mg(OH)_2$ (Fig. 6a). The extraction of lead and magnesium components from the PMN composition resulted in stabilization of the cubic pyrochlore phase in KOH solution. In KF solution, a perovskite phase was obtained at high temperatures (Fig. 6b–d). X-ray diffraction peaks due to the perovskite phase were broad and shifted to a higher angel than those of the PMN perovskite. A few large crystals were grown at the top of the capsule (Fig. 7) and many small crystals at the bottom. EDS spectra
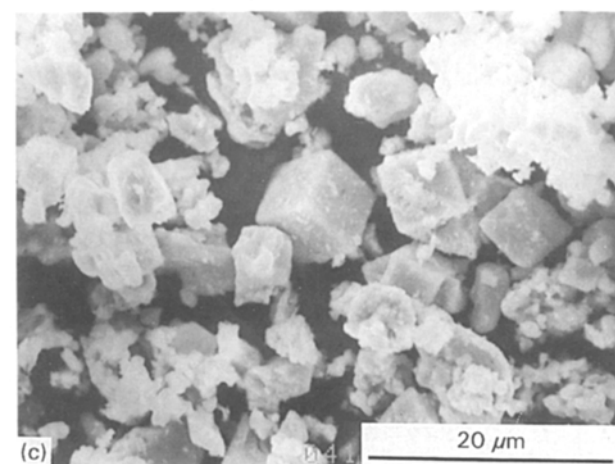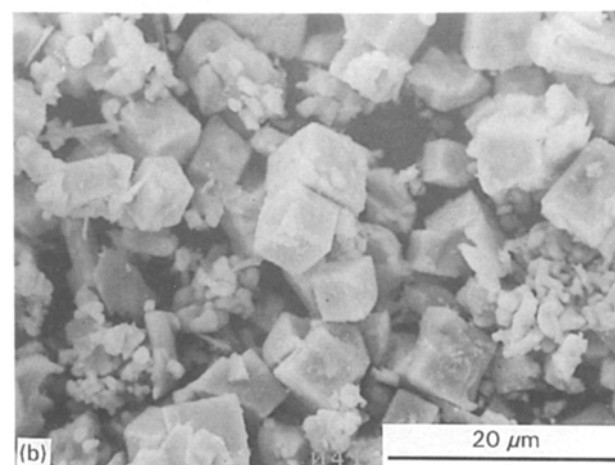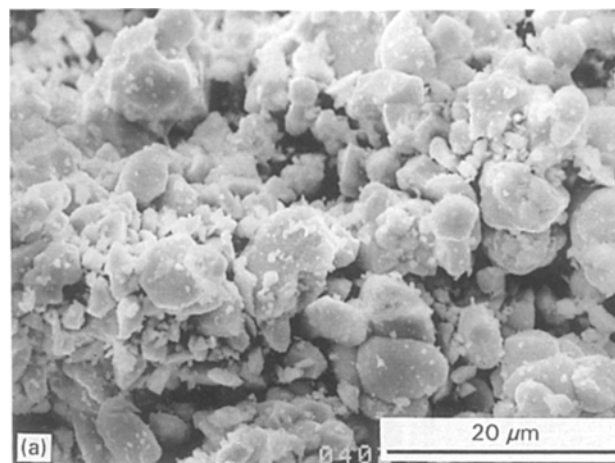

Figure 5 Photographs of the PMN perovskite crystals obtained by (a) heating in air at 800 °C for 80 h, and by hydrothermal treatment at 650 °C for 24 h with addition of (b) PbO, and (c) Pb_3O_4.

show the crystal grown at the top of the capsule contained potassium, lead, niobium, magnesium and fluorine. The intensity of potassium from the small crystals at the bottom increased and that of lead decreased in comparison with the crystals grown at the top. It is concluded that the perovskite phase obtained in KF solution contains potassium and fluorine, and the heterogeneity of these contents in the perovskite causes the broadness in the X-ray diffraction peaks. When the starting powder was hydrothermally treated in KF solution with Pb_3O_4, the platinum capsules were very seriously damaged and

Solution	Additive	Time (day)	Main phase[b]	Minor phase[b]
5N KOH	No	1	Py	PbO(L), Mg(OH)$_2$
5N KF	No	3	Pe'	Py
4N KCl	No	3	Py	U
5N KI	No	3	Py	PbIOH
5N CsF	No	3	Py	PbO(M, L)
Water	Pb$_3$O$_4$	6	Pe	PbO(M), Pb$_3$O$_4$
5N KOH	PbO(M)	1	Py	PbO(L), Mg(OH)$_2$, Pe
5N NaOH	PbO(M)	1	Py	PbO(L), Pe, Mg(OH)$_2$
5N LiOH	PbO(M)	1	Py	PbO(L), Pe, Mg(OH)$_2$
1N NH$_4$OH	Pb$_3$O$_4$	6	Pe	PbO(M), Pb$_3$O$_4$
5N NaF[a]	Pb$_3$O$_4$	6	Py	PbO(L,M), U
5N KF	Pb$_3$O$_4$	1	Py	PbO(M,L)
5N CsF	Pb$_3$O$_4$	3	Py	PbO(M,L)
5N LiCl	Pb$_3$O$_4$	6	Py	Pb$_2$Cl(O,OH)$_2$
5N NaCl	Pb$_3$O$_4$	6	Py, Pe, Pb$_2$O$_2$Cl	PbO(L,M)
5N KCl	Pb$_3$O$_4$	3	Pe, Pb$_2$O$_2$Cl, Py	U
5N NaBr	Pb$_3$O$_4$	6	Pe, Pb$_4$O$_3$Br$_2$, Py	Pb$_2$OBr$_2$

[a] Added as a solid.
[b] Pe, PMN perovskite; Py, cubic pyrochlore; PbO(M), massicot; PbO(L), litharge; U, unknown phase.
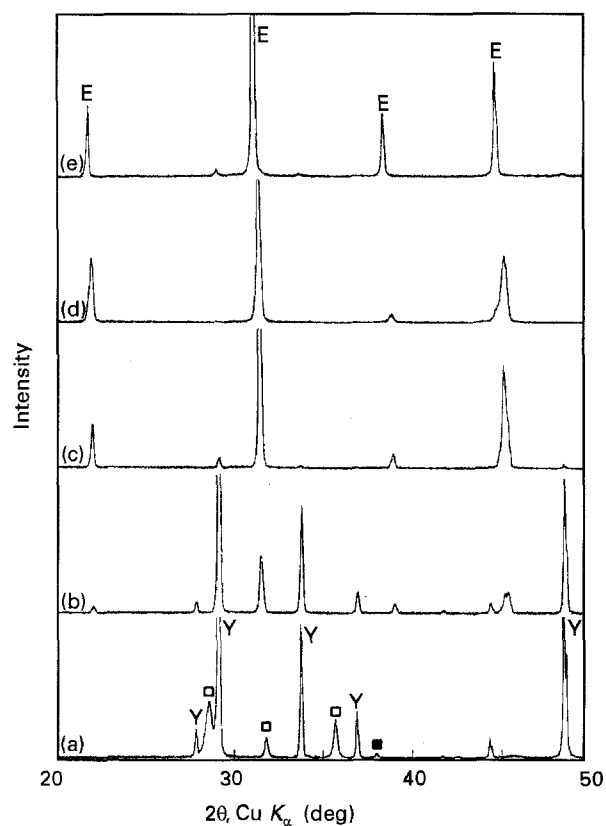

Figure 6 X-ray diffraction patterns of the products obtained in (a) 5N KOH solution at 650 °C for 24 h, (b–d) 5N KF solution (b) at 600 °C for 72 h, (c) at 650 °C for 72 h, (d) at 820 °C for 24 h, and (e) by heating in air at 800 °C for 3 h. E, PMN perovskite; Y, cubic pyrochlore; (□) PbO (litharge); (■) Mg(OH)$_2$.

all runs at 650 °C for 72 h resulted in leakage. The reaction products obtained in KF solution with Pb$_3$O$_4$ at 650 °C for 24 h, were only the pyrochlore and lead oxides without the perovskite. These results suggested that the dissolution phenomenon of PMN into hydrothermal solutions was very complicated

and the stability of the PMN perovskite was limited in KF solution.

The PMN perovskite was not obtained in KCl, KI, and CsF solution. The addition of lead oxide had a slight effect on the stabilization of the perovskite phase in alkaline solutions, but the amount of perovskite was small, except in 1N NH$_4$(OH) solution, probably because of low alkalinity. In fluoride solutions, the perovskite was not obtained, even with the addition of Pb$_3$O$_4$. In chloride solutions, lead compounds containing chlorine were produced. In these solutions, the amount of the perovskite was increased with increasing cation size. A comparison of the products obtained in sodium salt solutions showed that the solutions of large anions gave the larger amounts of perovskite.

Crystals of the PMN perovskite phase contaminated by potassium and fluorine were grown in KF solution at the top of the capsules with transportation from the bottom by thermal convection. In other solutions, no crystals were grown at the top of the capsules. Further experiments with a large temperature difference between the top and the bottom of the capsules in solutions which gave the PMN perovskite phase, are in progress, to grow PMN crystals under hydrothermal conditions.

4. Conclusion

The stability of PMN under various hydrothermal conditions was investigated by hydrothermal treatment of the low-crystalline pyrochlore powder prepared by hydrothermal crystallization from a solution with the PMN composition. The powder crystallized to the PMN perovskite in pure water above 580 °C. The amount of perovskite was decreased by long-term reactions at high temperatures because of the release of lead from the PMN composition. The addition of lead oxide stabilized the perovskite, but not Mg(OH)$_2$.
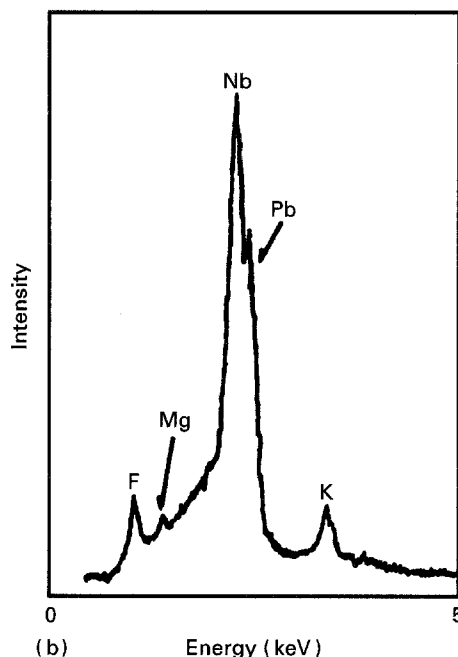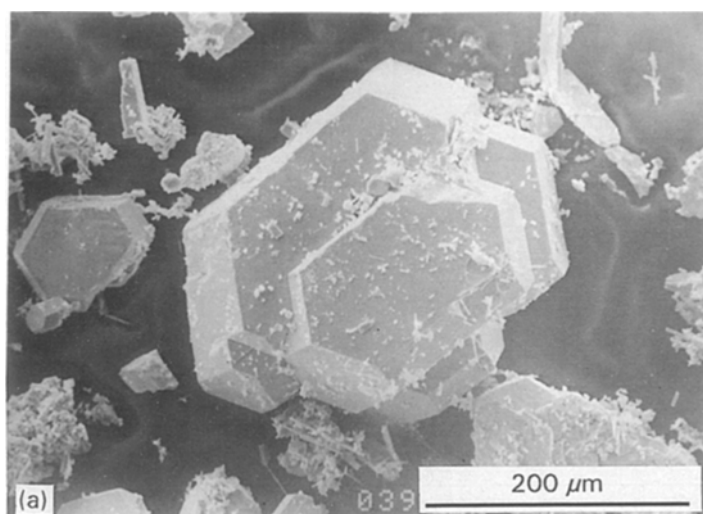
Figure 7(a) Photograph of crystals grown at the top of the capsule in 5N KF solution at 650 °C for 72 h and (b) the EDS spectrum.

In KF solution, a perovskite phase containing potassium and fluorine was obtained. The PMN perovskite was decomposed to the cubic pyrochlore and $Mg(OH)_2$ in alkaline solutions. Fluoride solutions also gave the pyrochlore phase even with the addition of lead oxide. The amount of the perovskite was increased in a salt solution consisting of large anions and cations.

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