JOURNAL OF MATERIALS SCIENCE 27 (1992) 1245–1249

Preparation of lead magnesium niobate by a coprecipitation method

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The ferroelectric complex perovskite lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), was prepared by a coprecipitation method. As the niobium component, niobium oxalate was used. Among the various precipitants, tetramethylammonium hydroxide was effective for the formation of single-phase PMN without pyrochlore phase. The dielectric constant and the dissipation factor of PMN changed either the sintering temperature or the grain size. The maximum dielectric constant at the Curie point was obtained by sintering at 1220 °C in air for 2 h.

1. Introduction

Lead magnesium niobate, $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), has a typical ferroelectric property with a complex perovskite structure. It has a wide range of high dielectric constant values owing to the diffuse phase transition [1, 2], therefore, it has been considered to be an important material for electrostrictive devices [3–5]. However, during the fabrication process of PMN, a lead niobate-based pyrochlore phase with low dielectric constant is formed as a by-product [6, 7], which is slow to transform into the PMN phase. Therefore, the preparation method for single-phase PMN has been strongly requested. The peak maximum dielectric constant reported for ceramic PMN, obtained by an ordinary fabrication process, is about 13 000, on the other hand, that for single-crystal PMN is about 20 000 [8].

From the viewpoint of a solid state reaction, a coprecipitation method can provide a homogeneous, reactive, and sinterable powder. It should be useful to obtain single-phase PMN with the perovskite structure with a high dielectric constant. A coprecipitation method to obtain PMN with a high dielectric constant is described in detail in this report.

2. Experimental procedure

Reagent grade $Pb(NO_3)_2$ and $Mg(OH)_2$ were used as starting materials. For the niobium component, a niobium oxalate solution was prepared by dissolving $Nb_2O_5 \cdot xH_2O$ in a hot oxalic acid solution [9]. The $Nb_2O_5 \cdot xH_2O$ was obtained by reacting $NbCl_5$ powder with an ammonia solution and subsequent filtration. The niobium content in the niobium oxalate solution was determined by gravimetric analysis. Nb_2O_5 was used as weighing form.

The flow diagram of the preparation is shown in Fig. 1. The lead solution was prepared by dissolving $Pb(NO_3)_2$ in water; the magnesium solution was prepared by dissolving $Mg(OH)_2$ in nitric acid. The mixed solution was prepared in a ratio of Pb:Mg:Nb = 3:1:2 and the resultant solution was coprecipitated using the precipitants shown in Table I. The precipitates obtained were washed five times with water, and then dried at 120 °C for 10 h. The precipitates

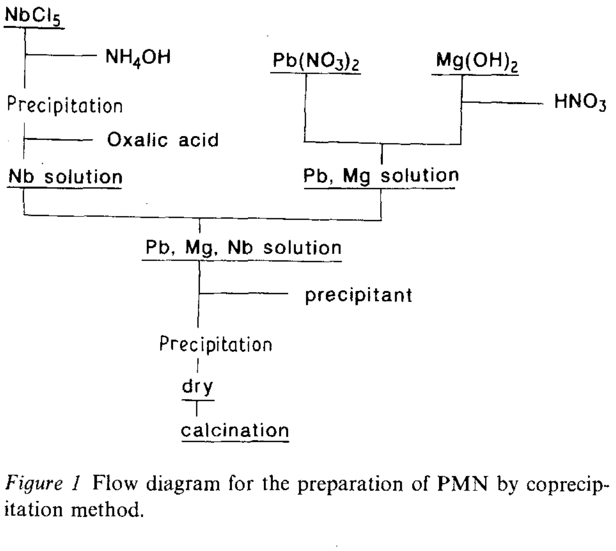

Figure 1 Flow diagram for the preparation of PMN by coprecipitation method.

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TABLE I The various precipitants used and results (remaining ion in filtrate and phases after firing at 1000 °C in air)

Precipitant	Remaining ion in filtrate	Phases after firing at 1000 °C
$(NH_4)_2CO_3$	Mg^{2+}	Perovskite + pyrochlore
Oxine	–	Perovskite + pyrochlore
$(C_2H_5)_2NH$	Mg^{2+}	Perovskite + pyrochlore
$(CH_3)_4NOH$	–	Perovskite
$(CH_3)_4NOH$[a]	–	Perovskite + pyrochlore

[a] Lead and niobium coprecipitated first and then magnesium was precipitated.

were calcined at 800 °C in air for 2 h, and fired in oxygen in the temperature range 900–1250 °C for 2 h.

For the analysis of the remaining ions in the filtrate, the filtrate was volatized, dried and fired at 1000 °C. When a residue existed after firing, it was examined by X-ray analysis performed using a Rigakudenki X-ray diffractometer (CuK_α). Thermal analysis was carried out with a Rigakudenki DTA-TG, and particle size distribution was measured with a Seisin Co. SKA5000. Dielectric measurements were carried out with YHP LF impedance analyser 4192A.

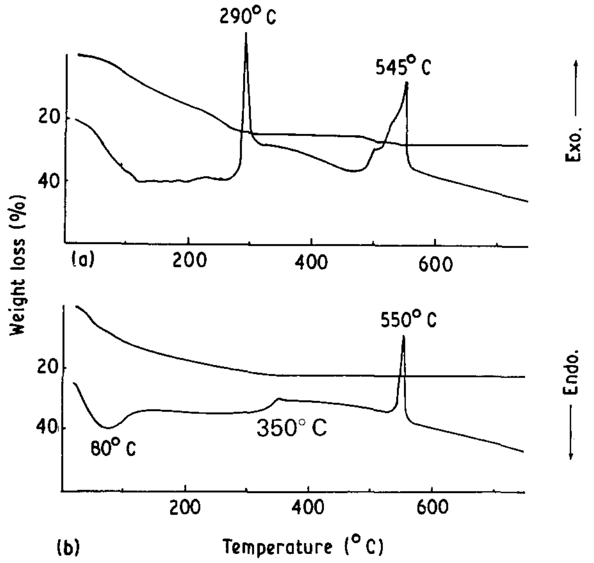

Figure 2 DTA-TG curves of the $Nb_2O_5 \cdot xH_2O$ precipitates for (a) precipitates prepared from Nb oxalate solution and (b) precipitates prepared from $NbCl_5$-hydrochloric acid solution. Heating rate, 10 °C min^{-1}.

3. Results and discussion

3.1. Niobium solution

To clarify the relationship between the precipitation of $Nb_2O_5 \cdot xH_2O$ and pH, a 2N ammonium solution was added to both a niobium oxalate solution and a hydrochloric acid solution with $NbCl_5$. When the ammonium solution was added to the hydrochloric acid solution with $NbCl_5$, $Nb_2O_5 \cdot xH_2O$ immediately began to precipitate. The precipitation had finished at pH 2. On the other hand, for the niobium oxalate solution, $Nb_2O_5 \cdot xH_2O$ did not begin to precipitate before pH 4. The difference between the two phenomena should be related to the high stability of niobium oxalate solution with ammonium ions. In fact, it has been reported that an ammonium oxalate solution stabilizes niobium ions by the co-existence of oxalate radicals [10].

X-ray analysis suggested that the $Nb_2O_5 \cdot xH_2O$ precipitates prepared from both the niobium oxalate solution and the hydrochloric acid solution with $NbCl_5$, were amorphous. They were also measured by differential thermal analysis and thermogravimetry (DTA–TG) as shown in Fig. 2. The dried precipitates prepared from different solutions had different peak shapes in the DTA–TG curves; that is, the precipitate from the niobium oxalate solution showed an exothermic peak around 300 °C, accompanied by a weight loss which is consistent with previous data [11], but the precipitate from the $NbCl_5$ solution did not show an exothermic peak. Thus it is considered that the precipitate from the niobium oxalate solution should have a small number of the oxalate radicals which decomposed at about 300 °C.

3.2. Preparation of PMN precipitations

In preparing PMN by co-precipitation method, the problem exists that it is difficult to precipitate all Mg^{2+} ions from the mixed solution. Therefore, various precipitants were used to try to obtain complete precipitation of Mg^{2+} (Table I).

When an ammonium carbonate or a diethylamine was used as precipitant, some Mg^{2+} ions were left in the filtrate, so that the pyrochlore phase was formed as well as the perovskite phase. When a tetramethylammonium hydroxide was used, PMN (pyrochlore free) was formed. It is considered that a tetramethylammonium hydroxide was strongly basic and all Mg^{2+} ions were changed to $Mg(OH)_2$. However, the pyrochlore phase was also formed when tetramethylammonium hydroxide was used. In this case, the mixed solutions with Pb^{2+} and Nb^{5+} ions were titrated first, and a solution with Mg^{2+} ions was next titrated. Because the preparation sequence was different from the above-mentioned case, it is considered that $Pb(OH)_2$ and $Nb_2O_5 \cdot xH_2O$ were homogeneously mixed, but $Mg(OH)_2$ was not mixed well. The compositional fluctuation in the precipitate would cause the formation of the pyrochlore phase.

On the other hand, when an oxine was used as precipitant, the pyrochlore phase as well as the perovskite phase was formed, even if no Mg^{2+} ions remained in the filtrate. The formation of a pyrochlore phase when an oxine was used as precipitant, may also be explained by the presence of a compositional fluctuation in a precipitate. To make the magnesium oxine complex, the oxine solution was kept at pH 9–10 [12]. As the solution was kept at pH 9–10, lead and niobium were precipitated as $Pb(OH)_2$ and $Nb_2O_5 \cdot xH_2O$. The precipitates of $Pb(OH)_2$ and $Nb_2O_5 \cdot xH_2O$. were colloidal and were not easy to filter. On the other hand, the precipitate of the magnesium oxine complex was not colloidal and was easy to filter.

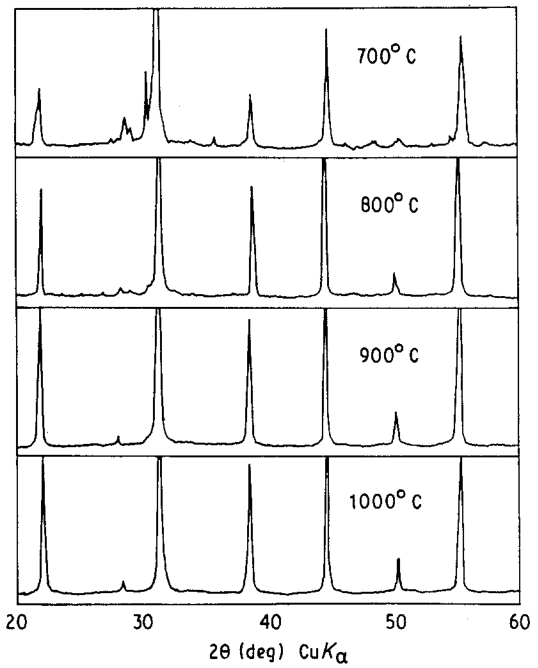

Figure 3 X-ray diffraction patterns of fired material in air for 2 h.

Although all precipitates were formed at the same time, they might be separated into magnesium oxine complex-rich and magnesium oxine complex-poor precipitates by stirring during titrating and washing.

Fig. 3 shows the X-ray diffraction pattern of the fired sample of PMN at various temperatures in the range 600–900 °C in air for 2 h. At 700 °C, PMN was already formed and a small amount of pyrochlore was formed. At 800 °C, almost all pyrochlore was transformed to PMN; above 900 °C, there was only PMN. This PMN formation mechanism may be very different from that from mixed oxides [6, 7].

Fig. 4 shows a scanning electron micrograph of material calcined at 800 °C in air for 2 h. As can be seen, the particle size was about 0.3 μm. Fig. 5 shows

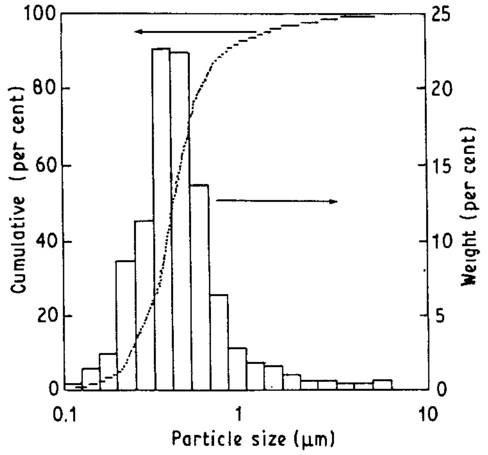

Figure 5 Particle size distribution of the calcined material at 800 °C in air for 2 h.

the particle size distribution of the same material. The average particle size was coincident with that from SEM observation.

Fig. 6 gives the change of the relative density as a function of the sintering temperature. The relative density is maximum (97.3%) at 1000 °C. Fig. 7 shows the change in grain size of the sintered material as a function of sintering temperature. This result shows the PMN powder prepared by a coprecipitation method is more sinterable than that prepared from mixed oxides [13]. As the sintering temperature was increased to above 1100 °C, the relative density decreased rapidly. According to the relative density change, the grain size increased rapidly when the sintering temperature was higher than 1100 °C. The X-ray diffraction pattern of the material sintered at 1250 °C showed that the PMN single phase alone caused PbO volatilization.

As mentioned above, the well-mixed powder prepared by a coprecipitation method began to form PMN near 700 °C, and the PMN formed did not decompose by PbO volatilization until 1250 °C. This result supports that the formation of the pyrochlore is

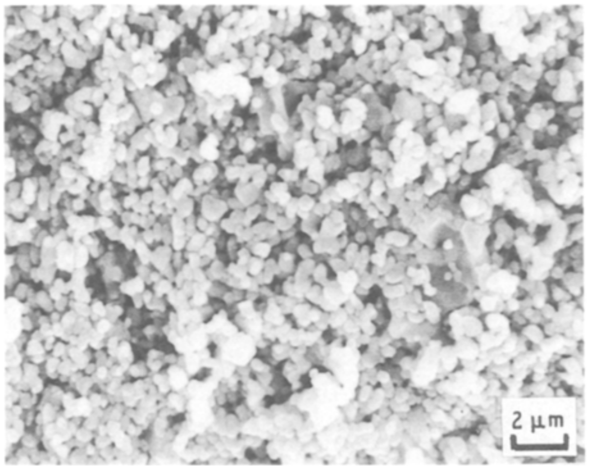

Figure 4 SEM picture of the calcined material at 800 °C in air for 2 h.

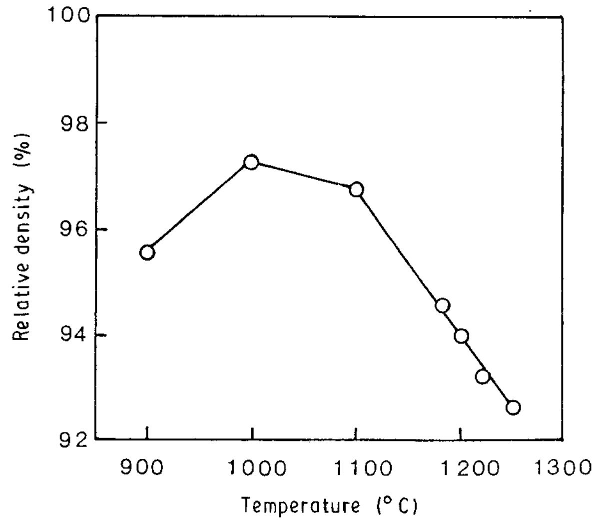

Figure 6 Relative density of the sintered material as a function of the sintering temperature.

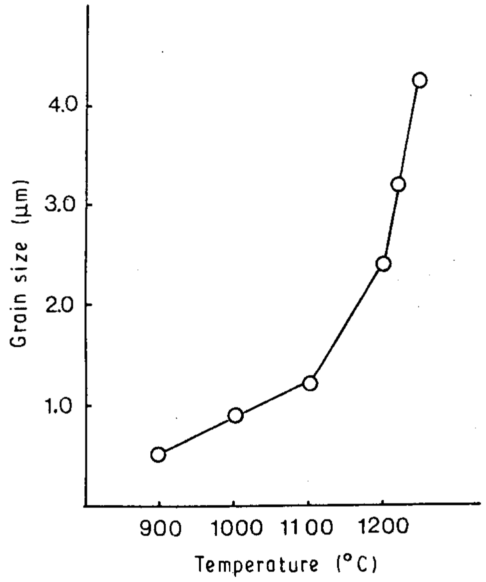

Figure 7 Grain size of the sintered material as a function of the sintering temperature.

mainly due to insufficient mixing of the starting materials, and not to the volatilization of PbO during sintering [14]. A similar result was reported for PZT [15].

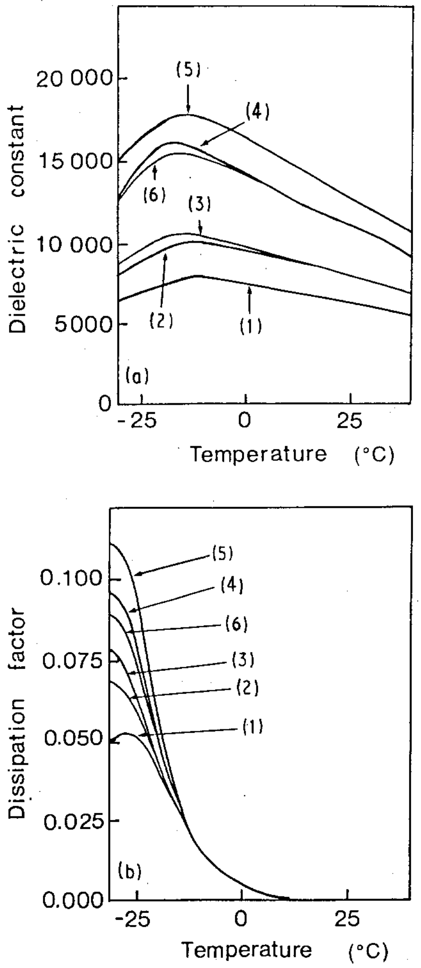

Figure 8 Temperature dependence of (a) dielectric constant and (b) dissipation factor at 1 kHz: sintered at (1) 900 °C, (2) 1000 °C, (3) 1100 °C, (4) 1200 °C, (5) 1220 °C and (6) 1250 °C.

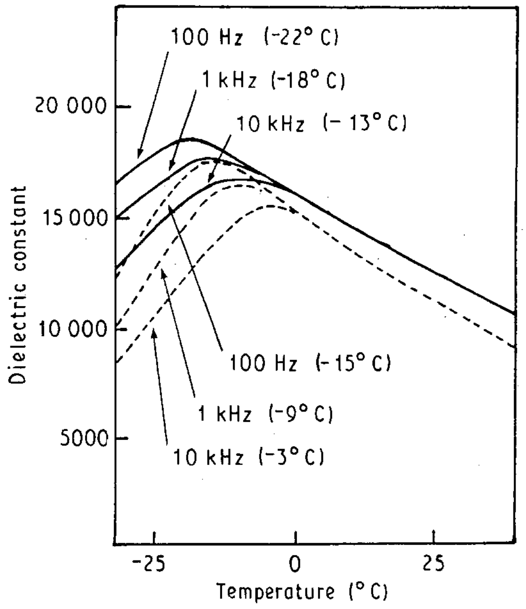

Figure 9 Temperature dependence of dielectric constant of the sintered material at 1220 °C compared with Swartz' result (broken line) (16).

3.3. Dielectric characteristics

Fig. 8 shows the temperature dependence of dielectric constant and dissipation factor at 1 kHz for the samples sintered at various temperatures. As the sintering temperature was increased, the dielectric constant increased. The dielectric constant at the Curie point increased rapidly when the sintering temperature was increased to above 1100 °C. This change was in agreement with grain size change. This grain-size dependence of the dielectric constant of PMN ceramics has also been reported by Swartz *et al.* [16], and sintering at 1220 °C gave the maximum dielectric constant at the Curie point.

Fig. 9 shows the temperature dependence of the dielectric constant of material sintered at 1220 °C and various frequencies. At each frequency, the dielectric constant was greater than that reported by Swartz *et al.* The Curie temperature was slightly lower, and the frequency dispersion of the dielectric constant maxima was also smaller than that reported by Swartz *et al.* Generally, the diffuse phase transition at the Curie point and the frequency dispersion of the dielectric constant maxima of PMN could be explained by the composition fluctuation in the PMN crystal [17]. Thus this difference in Curie point and frequency dispersion between these results and Swartz *et al.*'s results might originate in the compositional uniformity of PMN ceramics.

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Receieved 26 November 1990
and accepted 10 April 1991