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Synthesis of a solid solution of $PbTiO_3$–$PbZrO_3$–Pb $(Mg_{1/3}Nb_{2/3})O_3$ system through use of 8-quinolinol and its properties

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A new method for the synthesis of a solid solution of $PbTiO_3$–$PbZrO_3$–Pb $(Mg_{1/3}Nb_{2/3})O_3$ system (PZTMN) has been developed. An aqueous solution of Ti^{4+}, Zr^{4+}, Mg^{2+} and Nb^{5+} was dropped into a solution of 8-quinolinol in aqueous ammonia. The precipitate formed was washed, dried and fired, then an oxide (ZTMN) was obtained. The best firing temperature for the precipitate was 700 °C. The ZTMN powder was then mixed with PbO powder: when this mixture was fired, PZTMN was formed directly. By a conventional solid-state reaction among PbO, ZrO_2, TiO_2, MgO and Nb_2O_5 ([P + Z + T + M + N] method), $PbTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ were formed as intermediate products during the reaction. The single phase of PZTMN was obtained at 1200 °C for the [P + Z + T + M + N] method and at 800 °C for the new [P + ZTMN] method. The compositional fluctuation of PZTMN prepared by the [P + ZTMN] method was very small, and its dielectric constant was much higher than that of PZTMN prepared by the [P + Z + T + M + N] method. The density of PZTMN prepared by the [P + ZTMN] method practically attained the theoretical density under conditions of calcining at 800 °C and sintering at 1100 °C for 1 h.

1. Introduction

The crystal system of a solid solution of the lead titanate–lead zirconate system (PZT) is tetragonal in the titanium-rich side, and rhombohedral in the zirconium-rich side [1]. The boundary is known as the 'morphotropic phase boundary' (MPB). The dielectric constant and the electromechanical coupling factors near this point have a maximum value [2]. The MPB in $PbZrO_3$–$PbTiO_3$–Pb $(M^{m+}_{Ix}M^{n+}_{IIy})O_3$ $(mx + ny = 4)$ systems extends along a line in the ternary diagram. Many combinations of M_I and M_{II} are possible: Ni–Nb [3], Zn–Nb [4], Mg–W [5], Cd–W [6], Sc–Ta [7], In–Nb [8].

Generally, ceramic solid solutions are prepared by a solid-state reaction among oxides or carbonates of the constituent cations. On the other hand, various 'wet methods' have been developed to produce excellent materials. The wet methods do, however have problems in preparing an aqueous solution containing all the constituent cations; and in finding out the conditions under which all the constituent cations precipitate. For example, it is not easy to prepare an aqueous solution in which Pb^{2+} and Ti^{4+} coexist. Only tetrachloride is a stable water-soluble titanium compound. Pb^{2+} precipitates when chloride ions coexist. Simultaneous precipitation of Mg^{2+} and Nb^{5+} by a simple pH adjustment is also difficult. Mg^{2+} does not precipitate quantitatively as its hydroxide.

It has been found that all the constituent cations need not be precipitated for the preparation of homogeneous solid solutions [9–12]. On this basis, cations of the same site in the perovskite structure are the only ones that should be precipitated simultaneously. The solid-state reaction between these precipitates produces a homogeneous solid solution. We call this method the "wet–dry combination method". For example, for the preparation of Pb(Zr, Ti)O_3, only Zr^{4+} and Ti^{4+} should be precipitated [9].

Cations such as Mg^{2+}, Zn^{2+} and Sn^{2+}, the major constituents in the ternary solid-solution systems, do not precipitate completely by a simple pH adjustment. We have developed a method using organic chelation reagents to prepare ceramics from a solution. The organic chelation reagents can precipitate many kinds of cations. We have succeeded in preparing Pb(Zr, Ti)O_3 [13], $Ba(Mg_{1/3}Ta_{2/3})O_3$ [14] using organic chelation reagents, which form at lower temperatures and have high homogeneity.

A solid solution of the $PbTiO_3$–$PbZrO_3$–Pb $(Mg_{1/3}Nb_{2/3})O_3$ system (general formula: $Pb[(Zr_xTi_{1-x})_{1-y}$ $(Mg_{1/3}Nb_{2/3})_y]O_3$, abbreviated as PZTMN) is useful for electronic devices. In order to synthesize PZTMN by a wet method, the constituent cations Pb^{2+}, Zr^{4+}, Ti^{4+}, Mg^{2+} and Nb^{5+} should be precipitated. It is difficult to precipitate Pb^{2+} with the other cations simultaneously. By the wet–dry combination method, Pb^{2+} need not be precipitated; Zr^{4+},

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Ti^{4+}, Mg^{2+} and Nb^{5+} are precipitated simultaneously. An aqueous ammonia containing 8-quinolinol (oxine), an organic chelation reagent, can precipitate all these cations.

In a previous letter [15] the synthesizing method of PZTMN using oxine was reported. The present paper describes the details of the synthesizing conditions and their properties.

2. Experimental procedure

2.1 Preparation of samples

Zirconium oxychloride and titanium tetrachloride were each dissolved in water (~ 1 and 3 M, respectively). Niobium chloride was dissolved in a concentrated hydrochloric acid (~ 1 M). The precise concentrations of Zr^{4+}, Ti^{4+} and Nb^{5+} were determined by gravimetric analysis. These three solutions were mixed in the desired ratio (ZTN solution). The required amount of MgO for this solution was dissolved in a concentrated hydrochloric acid (0.5 M) and the obtained solution was added into the ZTN solution (the resulting solution is hereafter abbreviated as ZTMN solution). Oxine was dissolved into 6N–NH_4OH heated at 70° C, because the solubility of oxine in aqueous ammonia is too low at room temperature. The concentration of oxine was about 0.1 M. The ZTMN solution was dropped into the oxine solution to form a precipitate. Weight changes by firing at temperatures from 250 to 1000° C for 1 h were measured for the dried precipitate. The optimum decomposition temperature was 700° C. The precipitate was fired at this temperature for 1 h to form a ZTMN oxide powder. The ZTMN thus obtained was mixed with equimolar PbO powder and pressed into a powder compact. PZTMN was obtained by firing this powder compact in a closed magnesia crucible with a powder compact of a mixture of PbO and ZrO_2 as a source of PbO vapour (the process is shown in Fig. 1). The mixture of ZTMN and PbO was fired at a range of 400 to 1200° C for 1 h. The X-ray diffraction (XRD) peak heights for phases in these samples were measured.

The following two methods were also investigated for comparison. (i) A mixture of Zr^{4+} and Ti^{4+} solution was dropped into 6N–NH_4OH, resulting in a precipitate. The precipitate was dried at 200° C for 2 h and thermally decomposed at 900° C for 1 h. The resulting oxide (ZT) was mixed with MgO, Nb_2O_5 and PbO and fired to obtain PZTMN ([P + ZT + M + N] method). The use of ZT was effective against reactivity and uniformity in the synthesis of PZT [6]. (ii) Each powder of PbO, ZrO_2, TiO_2, MgO and Nb_2O_3 was mixed thoroughly and fired to form PZTMN ([P + Z + T + M + N] method). This method corresponds to an ordinary dry method.

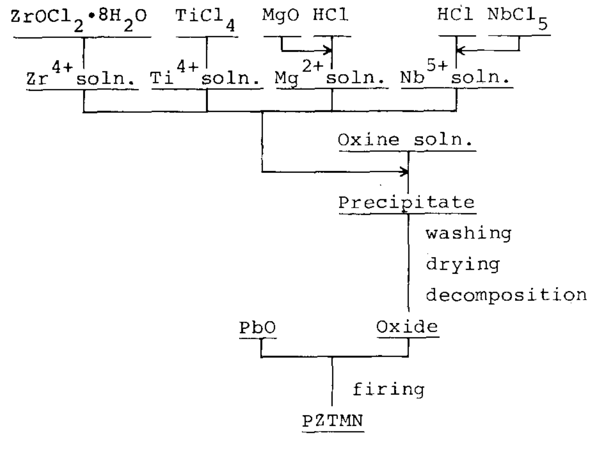


Figure 1 Process for preparing PZTMN by the oxine ([P + ZTMN] method).

2.2. X-ray diffraction

For the measurement of powder XRD, a Cu target was used with a Ni filter. As an optical system for the qualitative measurements, a divergence slit of 1°, a scattering slit of 1°, and a receiving slit of 0.3 mm were used. For the measurement of peak widths and diffraction angles, a receiving slit of 0.15 mm was used. Lattice constants were determined from 0 0 2 and 2 0 0 diffraction peaks of tetragonal PZTMN using Si powder (99.99%) as an internal standard.

The XRD peak profiles were fitted to the following equation using the least-squares analysis:

$$I(2\theta) = \frac{A}{1 + B(2\theta - C)^2} + \frac{0.5A}{1 + B(2\theta - C - \Delta)^2}$$

where $I(2\theta)$ is the intensity at an angle 2θ, Δ is the line splitting by the doublet of Cu$K\alpha_1$ and $K\alpha_2$, and A, B, and C are constants. By means of this fit, widths at half-maximum intensity (WHI) for an X-ray of single wavelength of $K\alpha_1$ were obtained. From this method, WHIs of Si were determined. The WHI of Si can be seen as a width establishing the resolving power of the apparatus. These values were plotted against 2θ in order to obtain the resolution width at any angle. The resolution width at the diffraction angle of the sample was subtracted from the WHI of the sample, resulting in a value β, which is the net width of the sample.

2.3. Sintering properties

Sintered density was measured by Archimedes' method with water. Microstructures of the samples were observed with the scanning electron microscope (SEM: Jeol, JSMM-T20).

2.4. Dielectric measurements

Silver paste was painted on both sides of a sintered pellet (about 1 mm thick and 13 mm in diameter) and baked at 500° C for 10 min. The capacitance of the sample at 1 KHz was measured by a low-frequency impedance analyser (YHP, 4192A), and the dielectric constant was calculated.

The relation between dielectric constant and composition was measured for the samples, which were poled under an electric field of 30KV cm^{-1} at 100° C for 30 min in a silicone–oil bath.

3. Results and discussion

A precipitate, which was prepared by an addition of

ZTMN solution into oxine solution, was washed and dried at 200° C. This material was fired at various temperatures from 250 to 1000° C for 1 h and weighed. Fig. 2 shows the relation between weight after firing and firing temperature. The weight was normalized to a value of 100 for the material before the firing. The weight loss below 200° C is due to a desorption of adsorbed water. A decomposition of the chelate took place between 300 and 500° C. The sample fired at 600° C was greyish, indicating that it has small amounts of free carbon. The sample fired at 650° C was white. Consequently, the slight weight loss between 600 and 650° C is due to combustion of the free carbon. For the subsequent reaction between this decomposed material and PbO, this free carbon is harmful. On the other hand, if this material was fired at a very high temperature, it might exhibit poor reactivity. Therefore, the optimum firing temperature of the precipitate is 700° C at which the free carbon is completely eliminated by combustion.

A mixture of PbO, ZrO_2, TiO_2, MgO and Nb_2O_5 was fired at various temperatures for 1 h. The heights of XRD peaks for the resulting phases are plotted against firing temperature in Fig. 3. This corresponds to the [P + Z + T + M + N] method. A part of PbO (yellow) transformed into red in the vicinity of 500° C. $PbTiO_3$, an intermediate product, was formed at a temperature of 600° C or above. $PbTiO_3$ is also an intermediate product for the formation of PZT from a mixure of PbO, ZrO_2 and TiO_2. $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), a second intermediate product, was formed at a temperature of 800° C or above. PZTMN, the desired compound, was formed at 900° C or above. The intermediate products did not disappear below 1200° C.

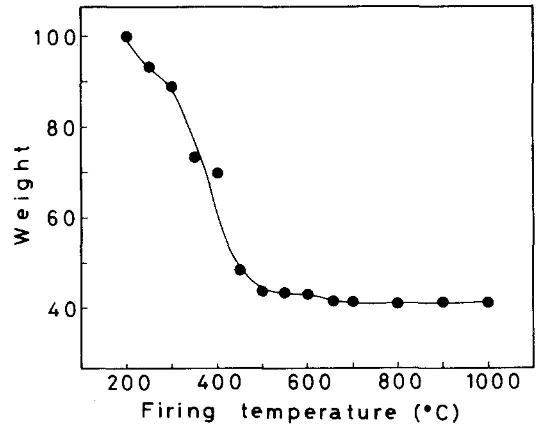


Figure 2 Relation between firing temperature for Zr^{4+}, Ti^{4+}, Mg^{2+} and Nb^{5+}-8-quinolinol chelate and weight of fired powder (normalized to a value of 100 for starting dried material).

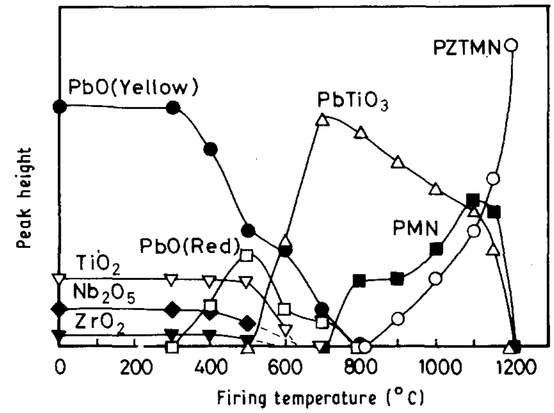


Figure 3. Phase composition against firing temperature for mixture of PbO, ZrO_2, TiO_2, MgO and Nb_2O_5 ([P + Z + T + M + N] method).

Mixtures of PbO, ZT, MgO and Nb_2O_5 were fired at various temperatures for 1 h. The heights of XRD peaks for the resulting phases are plotted against firing temperature in Fig. 4. This reaction corresponds to the [P + ZT + M + N] method. It has been reported [16] that the formation reaction of PZT from a mixture of PbO and ZT gives no intermediate products. It is seen from Fig. 4 that the reaction among PbO, ZT, MgO and Nb_2O_5 did not form $PbTiO_3$ as the intermediate product. Nevertheless the second intermediate product, PMN, was formed. PMN did not disappear below 1200° C. Thus temperatures of 1200° C or above are required for the formation of the single-phase PZTMN from this mixture (firing period, 1 h).

Mixtures of PbO and ZTMN were fired at various temperatures for 1 h. The heights of XRD peaks for the resulting phases are plotted against firing temperature in Fig. 5. This reaction corresponds to the [P + ZTMN] method. The XRD pattern of ZTMN agreed with that of a compound $ZrTiO_4$. Magnesium oxide and niobium oxide in ZTMN may be dissolved in the $ZrTiO_4$ phase or may be in amorphous phases. The reaction between PbO and ZTMN gave no intermediate product. PZTMN was formed at 600° C or above. The transformation of PbO from yellow to red, seen in Figs 3 and 4, was not observed. The formation reaction of PZTMN occurred before the transformation. A single-phase PZTMN was obtained at 800° C in this reaction. This reaction gave PZTMN at considerably lower temperatures than those in the other two methods mentioned above. Thus the [P + ZTMN] method is useful with respect to reactivity.

Generally, solid solutions have a compositional fluctuation. The compositional fluctuation of PZTMN extends two-dimensionally in the ternary-phase diagram. We have already reported [17] a

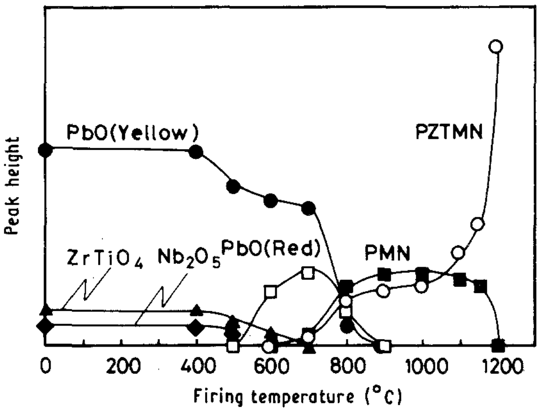


Figure 4. Phase composition against firing temperature for mixture of PbO, ZT, MgO, and Nb_2O_5 ([P + ZT + M + N] method).

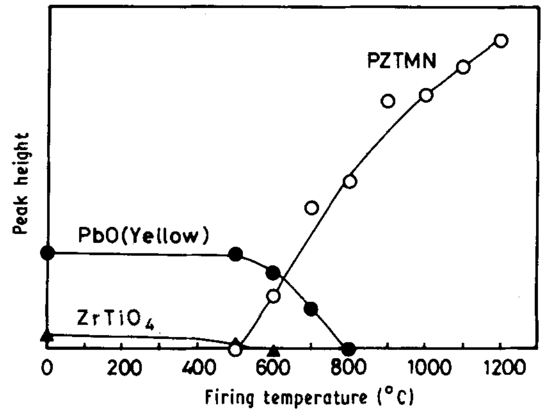


Figure 5. Phase composition against firing temperature for mixture of PbO and ZTMN ([P + ZTMN] method).

method to determine such a compositional fluctuation. This fluctuation causes a fluctuation of lattice spacings, which can be determined by XRD analysis: the slope of plots of $\beta \cos \theta$ against $\sin \theta$ (where θ is the Bragg angle) corresponds to the fluctuation of lattice spacings, $\Delta d/d$. Thus we can determine the region of fluctuating lattice spacing to be from $d_0 - \Delta d/2$ to $d_0 + \Delta d/2$ (d_0 = average lattice spacing). The compositions with such lattice spacings are not fixed to a certain composition, but are on a line in the ternary phase diagram. The compositional fluctuation region should extend to such lines. Compositions having lattice spacing of the fluctuation limit for different lattice planes are on different lines. Thus we can estimate the fluctuation region of composition [18].

The curves in Fig. 6 indicate compositions with lattice spacing of the fluctuation limit for some lattice planes of the sample prepared by the [P + Z + T + M + N] method. The region of compositional fluctuation can be determined to be the area surrounded by the solid line, namely the ellipse. It can be seen that the compositional fluctuation region for this sample is very large. This result is consistent with that for PZT [9], (Ba, Pb)TiO_3 [19], and Pb[(Zr, Ti), ($Mg_{1/3}Ta_{2/3}$)]O_3 [18] prepared by the solid-phase reaction.

The compositional fluctuation region of PZTMN by the [P + ZT + M + N] method (1200° C, 1 h) is shown in Fig. 7. The compositional fluctuation region of this sample is smaller than that of the sample prepared by the [P + Z + T + M + N] method. This may be due to the high reactivity of ZT powder. It is especially noteworthy that the width of fluctuation of the direction of $PbTiO_3$–$PbZrO_3$ is small.

The compositional fluctuation region of PZTMN by the [P + ZTMN] method (1200° C, 1 h) is shown in Fig. 8. The compositional fluctuation region is extremely small. This method is also useful with respect to homogeneity.

The sinterability of PZTMN samples prepared by the three methods was examined. Fig. 9 shows the relation between sintered density and calcining temperature for PZTMN samples sintered at 1100° C for 1 h. PZTMN was also sintered without calcining: the results without calcining are plotted on the left ordin-

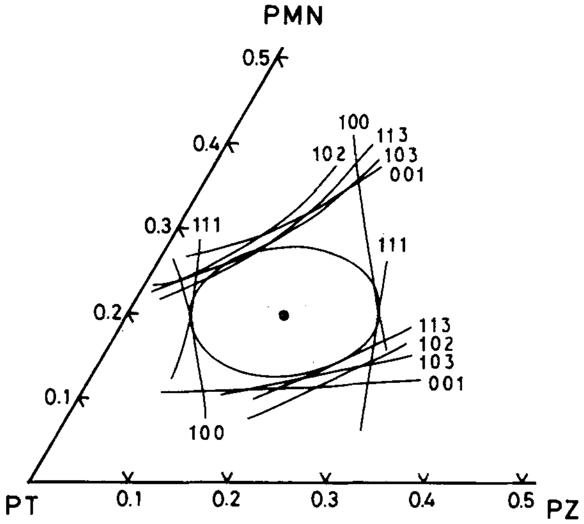


Figure 6. The compositional fluctuation region of PZTMN prepared by the [P + Z + T + M + N] method. Firing conditions: 1200 °C, 1 h.

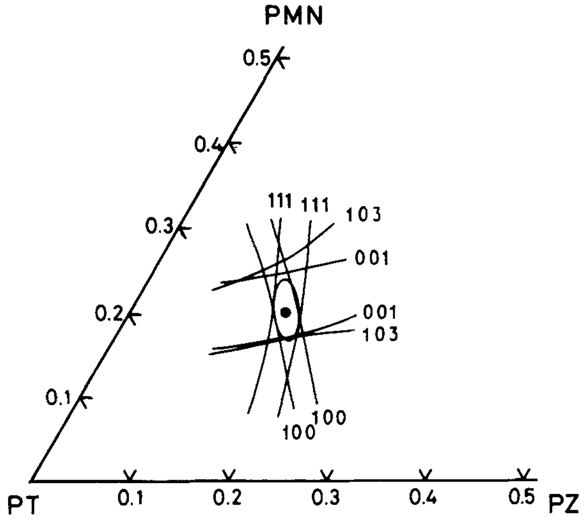


Figure 7. The compositional fluctuation region of PZTMN prepared by the [P + ZT + M + N] method. Firing conditions: 1200 °C, 1 h.

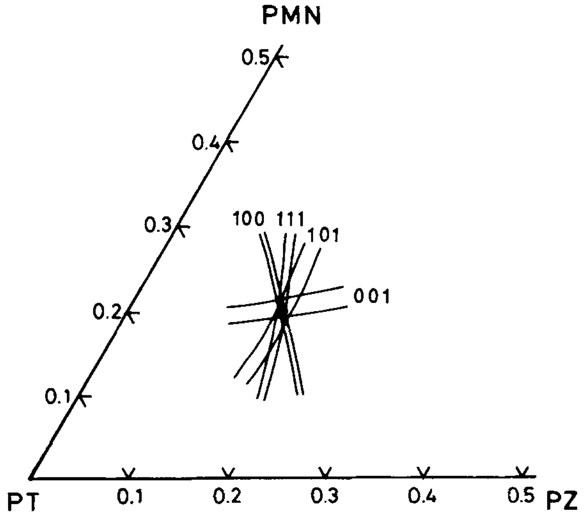


Figure 8. The compositional fluctuation region of PZTMN prepared by the [P + ZTMN] method. Firing conditions: 1200 °C, 1 h.

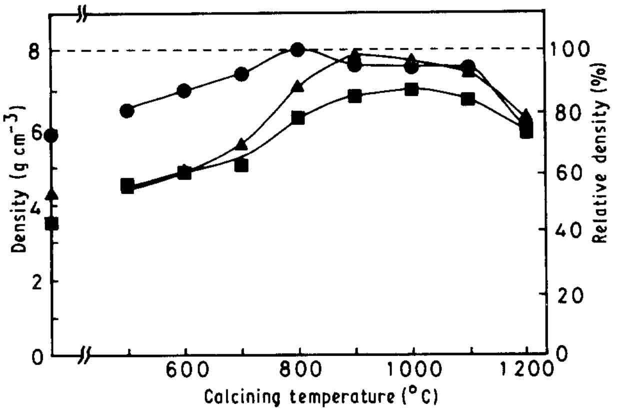
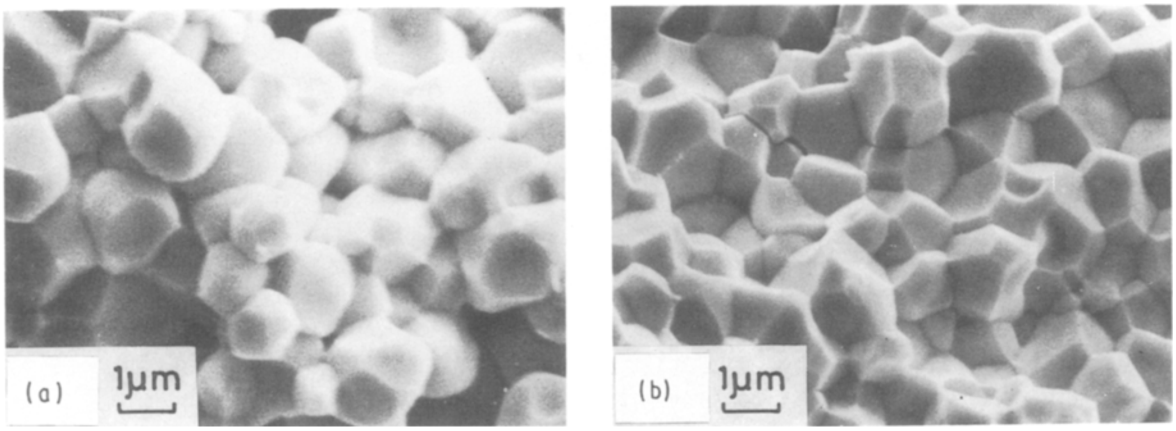


Figure 9. Relation between density of sintered body and calcining temperature (calcining period, 1 h; sintering conditions, 1100 °C, 1 h). Method of sample preparation: ●, [P + ZTMN]; ▲, [P + ZT + M + N]; ■, [P + Z + T + M + N].



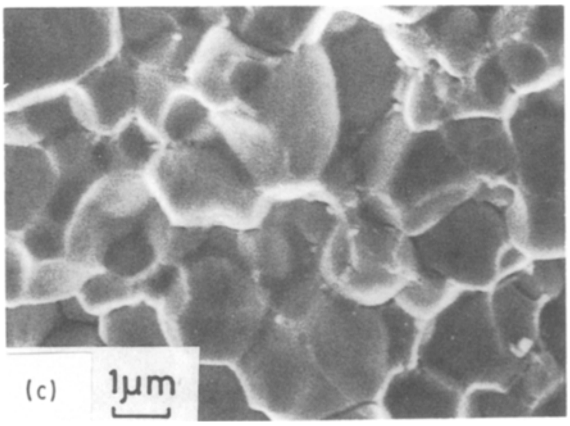


Figure 10. Scanning electron micrographs of fracture surfaces of PZTMN. (a) [P + Z + T + M + N] method, clacined at 1000 °C for 1 h, sintered at 1100 °C for 1 h. (b) [P + ZT + M + N] method, calcined at 900 °C for 1 h, sintered at 1100 °C for 1 h. (c) [P + ZTMN] method, calcined at 800 °C for 1 h, sintered at 1100 °C for 1 h.

ate. The optimum temperature of calcination was 1000° C for the sample prepared by the [P + Z + T + M + N] method. The density of this sample was about 82% of theoretical. The optimum temperature of calcination for the sample prepared by the [P + ZT + M + N] method was 900° C and its maximum density was 98% of theoretical. The optimum temperature for the sample prepared by the [P + ZTMN] method was 800° C and its density was almost equal to the theoretical density.

The optimum calcining temperature was decreased in the order of the [P + Z + T + M + N], [P + ZT + M + N] and [P + ZTMN] methods. This order corresponds to reactivity. All the samples calcined at the optimum calcining temperature consisted of the single phase of PZTMN. The method using oxine is useful for sintering properties.

Fig. 10 shows scanning electron micrographs of the fracture surfaces of the samples prepared by the three methods (calcined at the optimum temperature and sintered at 1100° C for 1 h). Fig. 10b is for the sample prepared by the [P + ZT + M + N] method. A very dense structure is observed as expected from measured density. Fig. 10c is for the sample prepared by the [P + ZTMN] method. A face which was formed by an intergranular crack is found: this is due to sufficient sintering, which causes tight intergranular bonds. Fig. 10a is for the sample prepared by the [P + Z + T + M + N] method: this sample had the lowest density of the three. All of the three samples had a similar grain size.

Relations between dielectric constant and temperature were measured for PZTMNs $\{Pb[(Zr_{0.46}Ti_{0.54})_{0.8}(Mg_{1/3}Nb_{2/3})_{0.2}]O_3\}$ prepared by the three methods. The results are shown in Fig. 11. The PZTMN prepared by the [P + ZTMN] method has a remarkably high peak.

PZTMNs prepared by the three methods were poled. Relations between dielectric constant and composition for these samples are shown in Fig. 12. In this figure, the value of y was fixed at 0.2. The morphotropic phase boundary of PZTMN ($y = 0.2$) lies at $x = 0.475$. The peak of the dielectric constant was shifted slightly to the tetragonal side. Such a shift is not strange. The peak of the dielectric constant in PZT system also shifts to the tetragonal side [20]. The dielectric constant of PZTMN prepared by the [P + ZTMN] method was much higher than those by the [P + Z + T + M + N] and [P + ZT + M + N] methods.

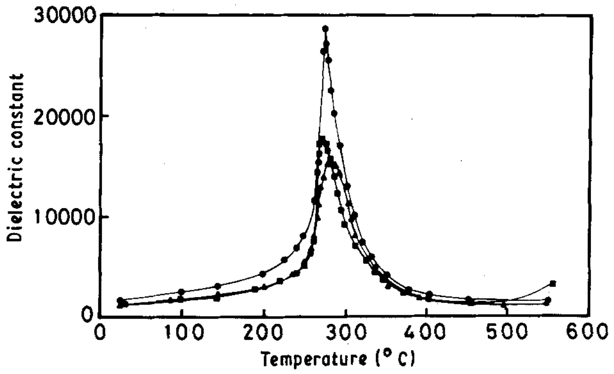


Figure 11. Dielectric constant as a function of temperature for Pb $[(Zr_{0.46}Ti_{0.54})_{0.8}(Mg_{1/3}Nb_{2/3})_{0.2}]O_3$. Method of sample preparation: ●, [P + ZTMN]; ▲, [P + ZT + M + N]; ■, [P + Z + T + M + N].

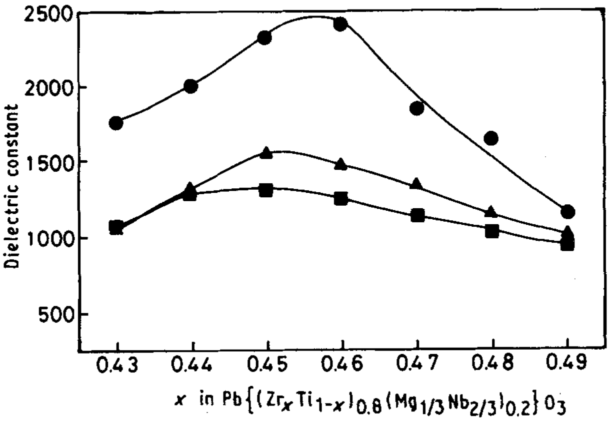


Figure 12. Relation between dielectric constant and composition x in Pb $[(Zr_xTi_{1-x})_{0.8}(Mg_{1/3}Nb_{2/3})_{0.2}]O_3$. Poling conditions: 30 kV cm^{-1} for 30 min at 100 °C. Method of sample preparation: ●, [P + ZTMN]; ▲, [P + ZT + M + N]; ■, [P + Z + T + M + N].

4. Conclusions

Pb[(Zr, Ti), $(Mg_{1/3}Nb_{2/3})]O_3$ (PZTMN) was synthesized by a new method. A precipitate containing zirconium, titanium, magnesium and niobium was formed using 8-quinolinol. The precipitate was thermally decomposed, mixed with lead oxide and fired, resulting in PZTMN. The conditions of the formation process were investigated. The temperature at which single-phase PZTMN was formed by the [P + ZTMN] method was lower than that of the conventional method by about 400° C. PZTMN prepared by the [P + ZTMN] method had a high sintered density and high dielectric constant. The compositional fluctuation of this sample was very small.

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