

Synthesis of 0.8PMN-0.2PZN perovskite phase by an emulsion method and its dielectric properties

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The perovskite phase was synthesized by an emulsion method in the system of PMN-PZN. $\text{Pb}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Nb}(\text{HC}_2\text{O}_4)_5 \cdot n\text{H}_2\text{O}$ were used as starting materials. Span 80, kerosene and paraffin oil were used to prepare the organic phase. The mixture of aqueous salt solution and organic phase was emulsified at a speed of 4000 rpm for 5 minutes. To evaporate the water, the emulsion was dropped into the kerosene heated at 170 °C in a silicon oil bath and dried at 120 °C in an oven. The as-dried powders were calcined at temperatures from 500 °C to 900 °C for 2 h. A perovskite single phase was formed at 850 °C for 2 h. The mean particle size of the as-dried and calcined powders at 850 °C were 0.25 μm and 0.14 μm respectively. 0.8PMN-0.2PZN sintered at 1050 °C showed a 93% theoretical density, a 12000 dielectric constant, and a 4 °C Curie temperature.

Key words: PMN-PZN system, Emulsion, Perovskite, Powder preparation, Dielectric constant.

Introduction

Lead-base relaxor ferroelectrics have excellent dielectric and electrostrictive properties. Lead zinc niobate, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (hereafter designated as PZN), has a partially disordered perovskite structure. It undergoes a diffuse phase transition around 140 °C from rhombohedral (ferroelectric) to cubic (paraelectric) symmetry [1-3]. PZN ceramics with the perovskite structure may be synthesized only by hot pressing at an elevated temperature [4].

It is well known that the relaxor ferroelectric lead magnesium niobate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (hereafter designated as PMN), has an unusually high dielectric property. But it is also difficult to prepare pure PMN ceramics with the perovskite structure by conventional ceramic processing.

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (hereafter designated as PMN-PZN) ceramics should be prepared by methods using columbite precursor routes [5] and a solid-state reaction by presynthesized P_3N_2 [6]. But it is difficult to synthesize PMN-PZN with a perovskite structure by these methods. The dielectric constant of a 0.4PMN-0.6PZN specimen prepared by the MN + ZN precursor indicated 19000 at T_c (at 1 kHz) [5]. The Curie temperature of PMN-PZN could be arbitrarily controlled and adjusted to near room temperature by suitably varying the content of PZN in a pseudobinary PMN-PZN system (T_c is -12 °C for PMN, 140 °C for PZN at 1 kHz) [2, 3].

The emulsion method using an organic phase divide the mixed metalsalt solution into fine droplets at high speed rotation. All of these divided fine droplets, each has the same and homogenized composition. It is considered that these emulsions could be easily decomposed, reacted and synthesized to a crystalline solid by calcination at a low temperature [7, 8]. A low cost and simple process could produce PMN with the aqueous methods using niobium hydrogen oxalate which is water soluble [9]. In this study, the characteristics of 0.8PMN-0.2PZN powders synthesized by the emulsion method and their dielectric properties were investigated.

Experimental Procedure

Lead nitrate (99+%, Aldrich Chemical Company, Inc.), magnesium nitrate hexahydrate (99%, Aldrich Chemical Company, Inc.), zinc nitrate hexahydrate (Yakuri Pure Chemical Co.,Ltd) and niobium hydrogen oxalate (Assay(Nb_2O_5) 11.3% minimum, Soekawa Chemical Co.,Ltd) were used as starting materials to prepare a mixed aqueous solution (0.05 mol/l for 0.8PMN-0.2PZN). Aqueous solutions of each starting material were mixed by a magnetic stirrer for 24 h. Span 80 (5v/o) for the surfactant, kerosene (92v/o) for the solvent, paraffin oil (3v/o) for the emulsifying agent were mixed by a magnetic stirrer for 24 h to prepare the organic phase.

The mixed aqueous solution and organic phase were mixed in the ratio of 4 : 1 and emulsified at a speed of 4000 rpm for 5 minutes. To evaporate the water included in the water-in-oil type emulsions, the prepared emulsion was dropped into the petroleum heated at 170 °C in a

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silicon oil bath [10]. The as-obtained powders were washed with toluene to remove the organic phase and dried at 120 °C in an oven to evaporate the petroleum. Thermal analysis of the dried powders was carried out from room temperature to 800 °C with a heating rate 10 K·minute⁻¹ using DT-TGA.

The as-dried powders were calcined at temperatures of 500 °C–900 °C for 2 h in a magnesia crucible. The crystalline phases of the dried and calcined powder were investigated by powder X-ray diffraction (XRD; Rigaku, D/MAX-111A) operating at 40 kV, 30 mA, scan speed of 4° minute⁻¹ with CuK α radiation. The relative amount of the perovskite phase was determined by the intensities of (110) for the perovskite phase and (222) for the pyrochlore phase from XRD patterns. The percentage of the perovskite phase formed was calculated by the following equation (1);

$$\% \text{ perovskite} = I_{\text{perovskite}(110)} / (I_{\text{perovskite}(110)} + I_{\text{pyrochlore}(222)}) \times 100 \quad (1)$$

The shape of powders and their microstructure were observed by a scanning electron microscope (SEM; JEOL JSM-6400). The surface area was measured by the BET method (Quantachrome, Quantasorb). The relative dielectric permittivity and dissipation factor of the sintered body were measured at 1 kHz by an impedance/gain-phase analyzer (HP 4194A).

Results and Discussion

Characteristics of 0.8PMN-0.2PZN powders

A SEM image of the as-dried powder is shown in Fig. 1. The shape of the powder is spherical with loose agglomerates of small particles. The average particle size measured from SEM images was 0.25 μm and the specific surface area of these powders was 6.10 m²/g. Fig. 2 shows the DT-TGA curves of the as-dried powders. These curves have exothermic peaks and a weight loss associated with exothermic peak from 300 °C to 500 °C. The exothermic peaks and weight loss were due to the oxidation of the organic substances such as the surfactant, kerosene, and paraffin oil and decomposition of metal salts such as

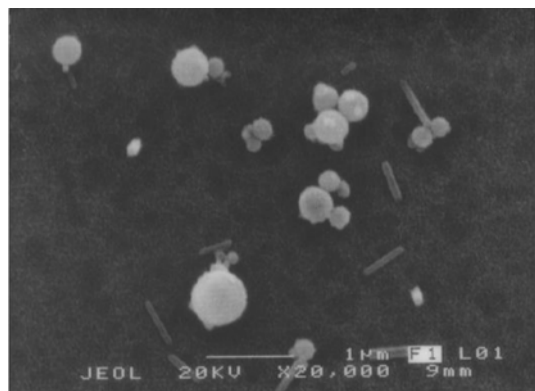


Fig. 1. SEM image of the as-dried 0.8PMN-0.2PZN powder.

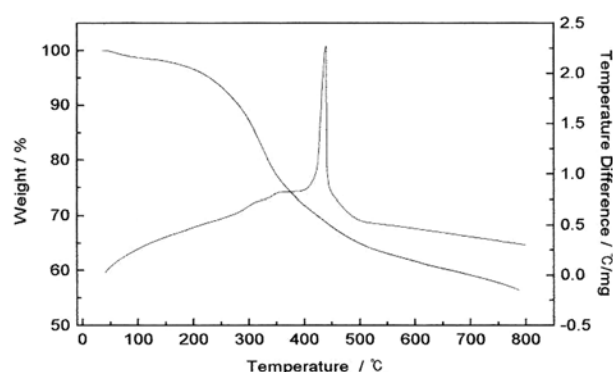


Fig. 2. DT-TGA curves of the as-dried 0.8PMN-0.2PZN powder.

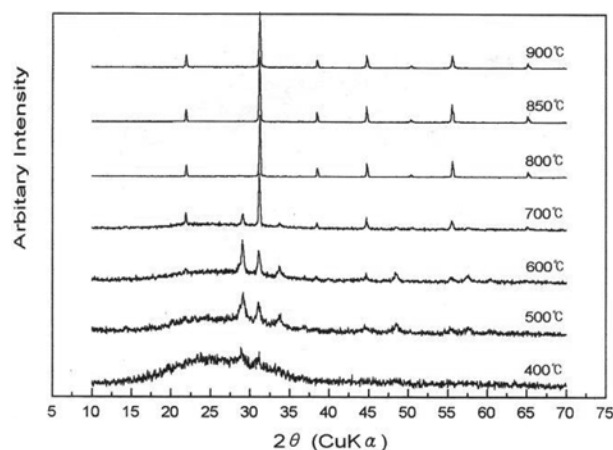


Fig. 3. XRD patterns of calcined 0.8PMN-0.2 PZN powder.

the oxalate and nitrates.

The as-dried 0.8PMN-0.2PZN powder was calcined at the temperatures of 400–900 °C for 2 h and the crystal phases were analyzed by an X-ray diffractometer. The X-ray diffraction patterns of the calcined powder are shown in Fig. 3. Broad peaks of the pyrochlore and perovskite phases were appeared simultaneously at 400 °C and the intensity of these peaks became higher with an increase in the calcination temperature to 600 °C. From 700 °C, the intensity from the pyrochlore phase decreased and almost disappeared at 800 °C, but the intensity from the perovskite phase increased and formed as a single phase at 850 °C. Fig. 4 shows the percentage of the perovskite phase of the calcined powder calculated with equation (1). The amount of the perovskite phase in the calcined powder increased with an increase of the calcination temperature. The percentage of the perovskite phase was 98.8% at 800 °C. A single perovskite phase was obtained at a calcination above 850 °C.

A SEM image of the powder calcined at 850 °C is shown in Fig. 5. The average particle size was 0.14 μm from SEM images and the specific surface area was 12.1 m²/g. The specific surface area of calcined powders, 12.1 m²/g was larger than that of the as-dried powders 6.12 m²/g and the average particle size of calcined powders, 0.14 μm was smaller than that of the as-dried powders 0.25 μm .

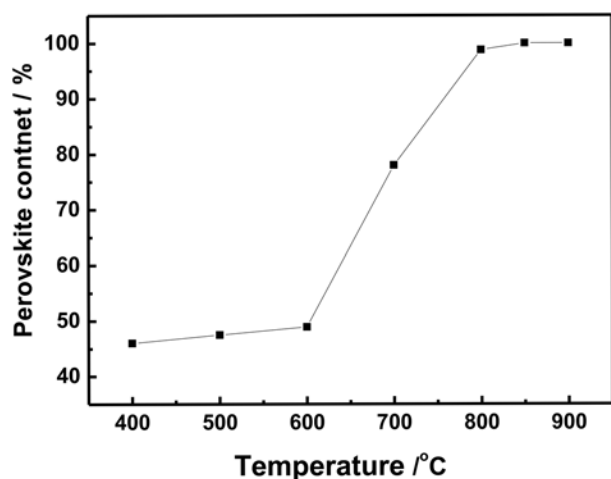


Fig. 4. The change of perovskite content with calcination temperature.

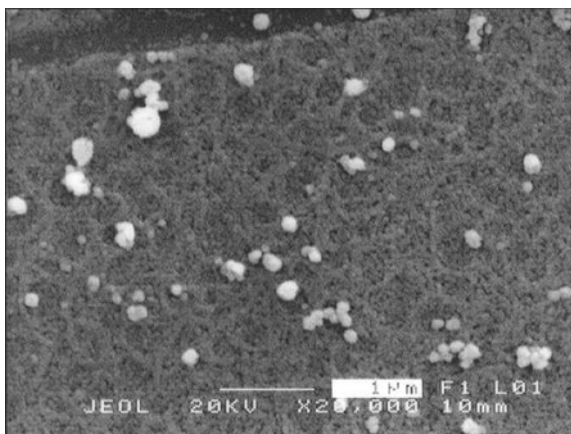


Fig. 5. SEM image of the powder calcined at 850 °C.

These results suggest that the as-dried powder composed of metal salts including an organic phase were decomposed to fine perovskite particles by calcination. The powder prepared by the emulsion method has a low calcination temperature because it is fine (mean particle size is 0.25 μm for as-dried powders) and compositionally homogeneous.

Sintering and dielectric properties

As shown in Fig. 6, the relative density of a 0.8PMN-0.2PZN sintered body became higher as the sintering temperature increased below 1050 °C but lower above 1050 °C. The specimen sintered at 1050 °C has a maximum density, 93% of theoretical density. It is considered that the decrement of density was due to PbO evaporation from the specimens above 1050 °C. The microstructure of the 0.8PMN-0.2PZN specimen sintered at 1050 °C is shown in Fig. 7. The mean grain size on the fractured surface was 2.90 μm and the crystal phase of the sintered body was single perovskite phase from the XRD pattern.

Fig. 8 shows the temperature dependence of the dielectric constant and dissipation factor of the sintered body at 1050 °C. It may be seen that the maximum dielectric constant was 12000, and the Curie temperature was 4 °C. The Curie

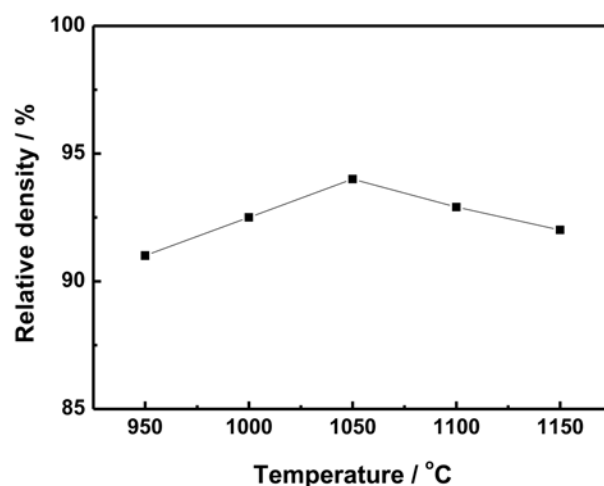


Fig. 6. The relative density of sintered bodies at various sintering temperatures.

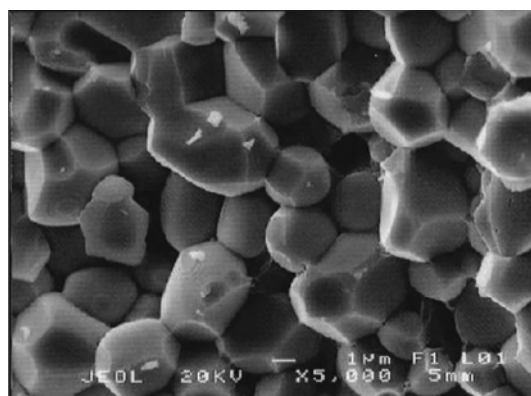


Fig. 7. SEM image of a fractured surface of 0.8PMN-0.2PZN sintered at 1050 °C.

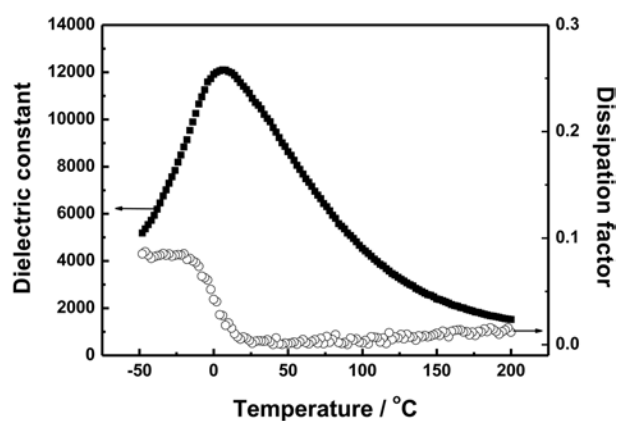


Fig. 8. The dielectric constant and dissipation factor of 0.8PMN-0.2PZN sintered at 1050 °C.

temperature of 0.8PMN-0.2PZN ceramics was shifted between that of PMN (−12 °C) and PZN (140 °C). The dielectric constant of 0.8PMN-0.2PZN prepared by the emulsion method was lower than PMN-PZN prepared by the columbite precursor route. This seems to be associated with low a relative density.

Conclusions

The results of this study are summarized as follows.

(1) The emulsion-derived powder was fine and had a spherical shape. The mean particle size of the as-dried and calcined PMN-PZN powders were 0.25 μm , 0.14 μm respectively.

(2) As-dried PMN-PZN powders began to crystallize simultaneously to the pyrochlore and perovskite phases at 400 °C and a single perovskite phase appeared at 850 °C.

(3) The dielectric constant and Curie temperature of 0.8PMN-0.2PZN were 12000 and 4 °C, respectively.

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