

Modified chemical route to prepare $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ ceramics

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Lead-based complex perovskite compound $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$ (PMN-PT), is an important relaxor ferroelectric material [1–3]. Owing to its high dielectric performance and superior piezoelectric natures, ceramics based on PMN-PT have good potential to be used as multilayer capacitors, piezoelectric actuators and medical ultrasonic transducers [4–7]. Sol–gel routes [8, 9] are available to synthesize pyrochlore-free PMN-PT powders and enhance the densification of ceramics at relatively low temperature. Previous studies in this system had demonstrated that both the starting material and sintering condition greatly influence the densification process and dielectric properties of the resulting ceramics because of the formation of unwanted pyrochlore phase [10, 11]. Moreover, the metal alkoxide $\text{Nb}(\text{OC}_2\text{H}_5)_5$ and $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were the starting materials for sol–gel method and all the reactions must be carried out in flowing argon atmosphere.

In this paper, a modified process was developed to prepare PMN-PT powders. Low-cost inorganic metal $\text{Nb}(\text{OH})_5$ and $\text{Mg}(\text{NO}_3)_2$ were used as starting materials, and the gel product was obtained in air at room temperature. The composition of 0.65PMN-0.35PT was selected for its optimal piezoelectric property [12]. The phase structure and morphology of calcined PMN-PT powders were investigated. Additionally, the ceramics were sintered and the dependence of sintering temperature on the microstructure and piezoelectric property was studied.

The starting materials were $\text{Nb}(\text{OH})_5$ (99.99% purity), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.5% purity), $\text{Pb}(\text{NO}_3)_2$ (99.9% purity), and TiCl_4 (98% purity). By following the procedures of Yamamura *et al.* [13, 14], aqueous solution of $\text{TiO}(\text{NO}_3)_2$ was prepared from TiCl_4 . In this work, the procedures adopted to prepare gel powder from starting materials were shown in Fig. 1.

The calcined powders were cold pressed (with a load of 10 tons) into pellets with 1 cm in diameter, followed by sintering at 1150, 1200 and 1250 °C for 2 h, respectively. The ceramics were buried in sand of PbZrO_3 powders to decrease PbO volatilization. The calcined powders and sintered specimens were characterized by a Germany Bruker D8 Advance X-ray diffractometer (XRD) using $\text{Cu K}\alpha$. The microstructures of the calcined powders and sintered specimens were studied with a Hitachi S-415A scanning electron microscope. Archimedes' water displacement method was used to

measure density of the sintered specimens. The piezoelectric coefficient (d_{33}) was measured with a quasi-static d_{33} meter of Burlincourt type at 55 Hz.

XRD analysis (Fig. 2) for the calcined powders shows that pyrochlore-free PMN-PT formed at 750 °C. The powders calcined at 750 °C was used to fabricate PMN-PT ceramics. The XRD patterns (Fig. 3) of the specimens show that the single-phase PMN-PT perovskites were obtained at different sintering temperatures.

The morphology of the powders calcined at 750 °C for 2 h is shown in Fig. 4. It shows that the powder with size of about 300 nm was obtained. In the modified

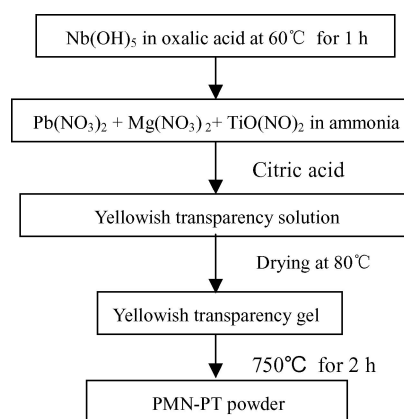


Figure 1 Flow chart of the PMN-PT powders preparation.

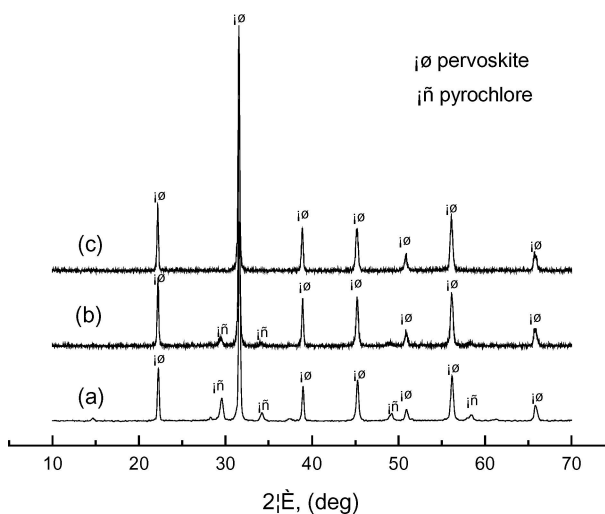


Figure 2 XRD spectra of 0.65PMN-0.35PT powders after calcining the dry gel at different temperature for 2 h: (a) 650 °C, (b) 700 °C, and (c) 750 °C.

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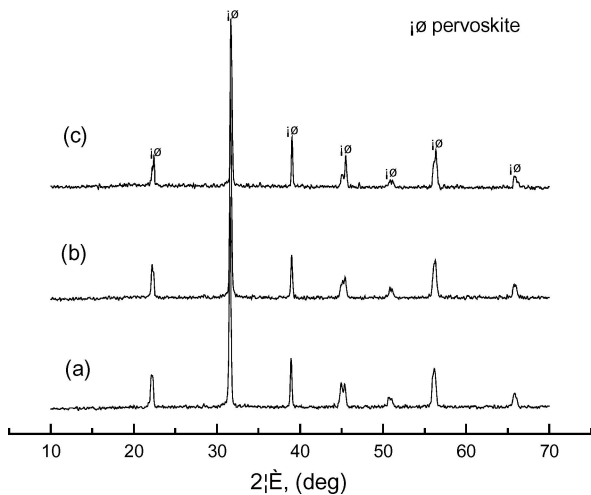


Figure 3 XRD patterns of 0.65PMN-0.35PT ceramics sintered at different temperatures for 2 h: (a) 1150 °C, (b) 1200 °C, and (c) 1250 °C.

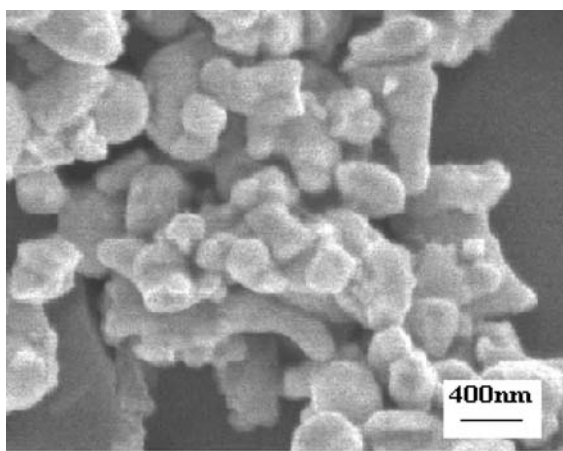


Figure 4 The morphology of the powder calcined at 750 °C for 2 h in air.

TABLE I Physical properties of PMN-PT ceramics and the loss of PbO for various temperatures

Sintering temperature (°C/2 h)	Density (g/cm ³)	Loss of PbO (mol%)	d_{33} (PC/N)
1150	7.81	1.0	508
1200	8.06	1.1	631
1250	7.92	1.3	555

sol-gel process, the gel-forming rate can be controlled by adjusting the hydrolyzing rate and the synthesis temperature can be decreased to 750 °C. In this way, fine powders with narrow particle-size distribution were prepared, which are favorable to improve the reactivity of powders.

Fig. 5 shows the microstructure of PMN-PT ceramics sintered at various temperatures. The results indicate that grain size tends to increase with an increase in sintering temperature, in agreement with other works [15–17]. At the sintering temperature of 1200 °C, the grain size of the sample was refined to 2–3 μm. This may due to the use of fine and uniform starting powders. The micrographs also demonstrate the dependence of fracture pattern on sintering temperature. For the ceramics sintered at 1150 °C, the fracture shows almost intergranular behavior. As the sintering temperature elevates to 1200 °C, the surface tends to transform to transgranular fracture. While the sintering temperature enhances to 1250 °C, the transgranular fracture is dominant over intergranular fracture. It indicates that the strength of grain boundary is enhanced at elevated sintering temperature. The data of densities and PbO loss shown in Table I demonstrate that the PbO loss enhances as the sintering temperature elevates and

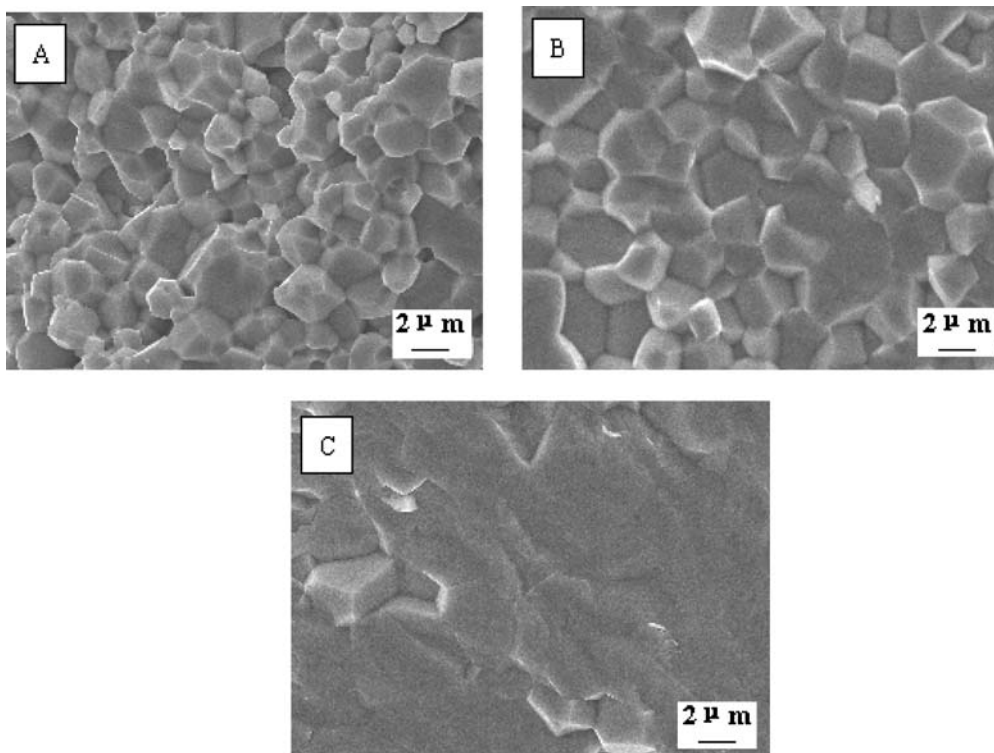


Figure 5 Scanning electron micrographs (fracture surface) of samples: (A) 1150 °C, (B) 1200 °C, and (C) 1250 °C.

the density comes to maximum (8.06 g/cm^3) at the sintering temperature of 1200°C for 0.65PMN-0.35PT. This infers that the modest sintering temperature are favorable for the densification of PMN-PT ceramics and enhancement of piezoelectric performance. In addition, an optimal piezoelectric coefficient d_{33} of 631 PC/N (shown in Table I) was obtained at 1200°C .

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