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The Effect of Heating Rate on the Properties of PMN Relaxor Ceramics

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Abstract: The effect of heating rate on the properties of ferroelectric lead magnesium niobate ceramics during calcining and sintering processes was reported in this investigation. Perovskite phase content, density, microstructure, and the dielectric properties of PMN ceramics with the heating rate from 2°C/min to 30°C/min were studied. Perovskite phase content was affected by heating rate, especially on the surface exposed to air. A slow heating rate caused more evaporation of PbO and resulted in porous ceramics with small grains. Increasing PMN content, density, and grain size with increasing heating rate made the dielectric constant increase.

1 INTRODUCTION

The relaxor ferroelectric lead magnesium niobate ($PbMg_{1/3}Nb_{2/3}O_3$; PMN) has been widely investigated in the field of electronic ceramics because of its high dielectric constant and high electrostrictive strain coefficient.[1-3] The main feature of the properties of PMN is a broad maximum dielectric peak just below room temperature. The magnitude decreases while the temperature of this maximum increases as frequency increases. It is well-known that a stable pyrochlore phase often forms when producing PMN ceramics.[4] The presence of this lead-based pyrochlore phase causes the dielectric constant to decrease.[5] Swartz and Shrout proposed a two-stage calcination method to produce pure perovskite PMN ceramics.[1] In the method, columbite $MgNb_2O_6$ is formed first, followed by formation of perovskite PMN.

The effects of parameters in processes such as calcining and sintering, such as temperature[6] and level time,[7] on the properties of PMN have been widely studied. However, studies about the effect of heating rate on the PMN ceramics are seldom reported. Lejeune and Boilot[4] showed that the percentage of PMN phase decreased from 79% to 49% as the heating rate increased from 5°C/min to 170°C/min. Since the increasing step (165°C/min) was so large, what will happen at the middle heating rate was unclear.

In this paper, the effect of heating rate on the dielectric properties of PMN relaxor ferroelectric ceramics will be studied.

2 EXPERIMENTAL PROCEDURE

The PMN ceramics were prepared by a mixed-oxide route from reagent-grade PbO (>99%), MgO (>97%), and Nb_2O_5 (99·9%). MgO and Nb_2O_5 with 10 mol% excess MgO were calcined at 1100°C for 3 h with four heating rates (2, 5, 10, and 30°C/min) to form the columbite precursor $MgNb_2O_6$. The calcined powder was pulverized and the appropriate amounts of PbO were then added. 3 mol% excess PbO and 10 mol% excess MgO were added to suppress the pyrochlore phase formation in this step. After ball-milling in deionized water with agate media, the slurry was dried and the second calcining step was carried out at 850°C for 5 h with different heating rates (2, 5, 10, and 30°C/min). The second calcined powder was thereafter pressed to pellets 10 mm in diameter and 1·5–2 mm thick. The sintering condition of the pellets was 1230°C and 1260°C for 2 h, with four heating rates as in the calcining step. The cooling rate after sintering was 5°C/min.

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The calcined powder and sintered pellets of PMN were analyzed with X-ray diffractometery (XRD) to check the relative amounts of perovskite and pyrochlore phases. Microstructures were analyzed by scanning electron microscopy (SEM), and density was measured by the water immersion method. Before electroding with silver, the dimensions were measured. Dielectric properties were measured with an HP4192A impedance analyzer in a temperature control chamber from –30°C to 45°C at various frequencies between 100 Hz and 100 kHz.

3 RESULTS AND DISCUSSION

The effect of heating rate on $MgNb_2O_6$ and PMN content after the first and second calcination steps, respectively, is listed in Table 1. The relative amounts of $MgNb_2O_6$ were calculated using the following equation:[8]

$$\%MgNb_2O_6 = 100 \times I_{MgNb_2O_6}/(I_{MgNb_2O_6} + I_{Nb_2O_5})$$

where $I_{MgNb_2O_6}$ is the major X-ray peak intensity for (131) columbite $MgNb_2O_6$, while $I_{Nb_2O_5}$ is the unreacted Nb_2O_5 at $2\theta = 23{\cdot}7°$. The relative amounts of perovskite and pyrochlore phases were calculated with the equation described by Swartz and Shrout:[1]

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

where $I_{(110)}$ and $I_{(222)}$ are the major X-ray peak intensities for perovskite and pyrochlore phases, respectively. As shown in Table 1, heating rate did not affect the amounts of $MgNb_2O_6$ and PMN in the first and second calcination. In the first step, the reaction is simple and 10 mol% excess MgO was added to reduce unreacted Nb_2O_5. The reaction in the second calcining step happened at 850°C for 5 h, the effect of heating rate is not obvious.

The sintered PMN ceramics are yellowish on the surface exposed to air. This is caused by the evaporation of PbO, therefore, the pyrochlore phase increased on the surface.[8] Figure 1 shows the perovskite phase amounts of the topmost pellet along the thickness from the surface exposed to air under the sintering condition of 1260°C for 2 h with four various heating rates. Note that the amounts of perovskite phases of the pellets are small (<50%) on the surface, and increase along the thickness. This was mainly due to decreased PbO evaporation with increasing depth. Also in Fig. 1, the amounts of perovskite phases increased with heating rate due to decreased evaporation of PbO.

Table 1. Effect of heating rate on $MgNb_2O_6$ and PMN content in calcined powder

Heating rate (°C)	1st calcination $MgNb_2O_6$ (%)	2nd calcination PMN (%)
2	100	100
5	100	100
10	100	100
30	100	100

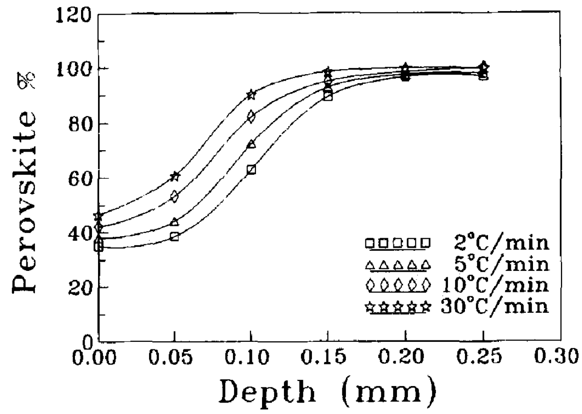

Fig. 1. Perovskite phase amounts along thickness of the topmost pellets sintered at 1260°C/2 h with various heating rates.

Table 2 shows the effect of heating rate on PMN content and grain size of sintered pellets at 1230°C and 1260°C. For 1230°C, PMN content and grain size are obviously not affected by heating rate. The PMN content increases with heating rate at 1260°C due to decreased evaporation of

Table 2. Effect of heating rate on PMN content and grain size of sintered pellets

Sintering temp. (°C)	Heating rate (°C/min)	PMN (%)	Grain size (μm)
	2	99·5	3·2
1230	5	100	3·4
	10	100	3·7
	30	100	3·8
	2	97·6	4·5
1260	5	99·2	4·8
	10	100	5·6
	30	100	6·1

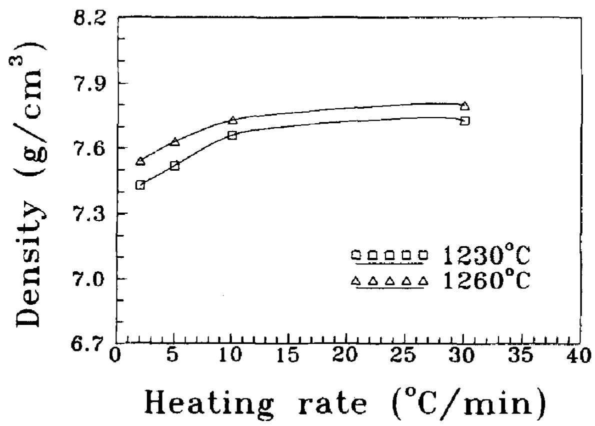

Fig. 2. Dependence of density on heating rate for PMN ceramics.

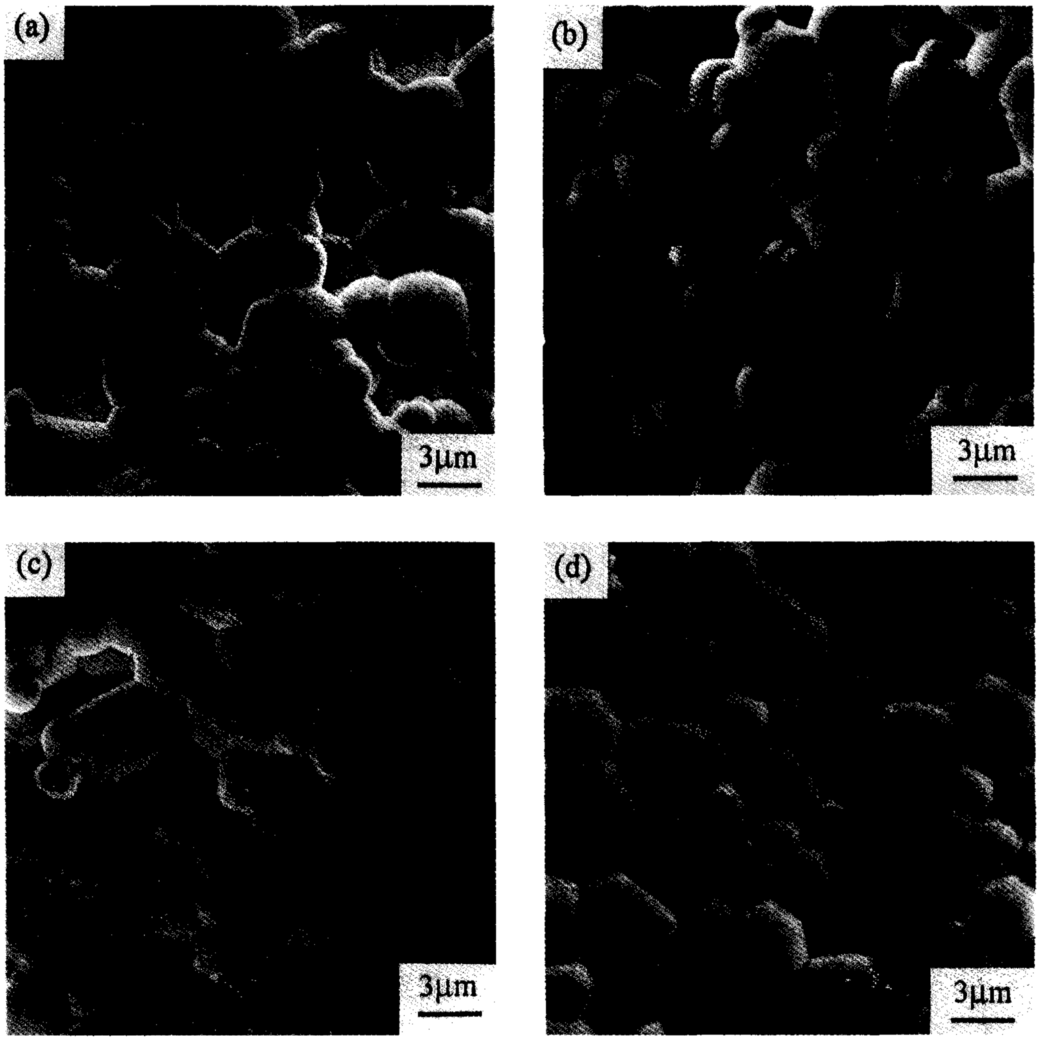

Fig. 3. SEM photographs of the as-fired surface for PMN ceramics with heating rate (a) 2°C/min, (b) 5°C/min, (c) 10°C/min and (d) 30°C/min.

PbO. The grain size also increases as evaporation of PbO decreases. Therefore, the effect of heating rate on PMN content and grain size is obvious at high sintering temperature. The density of sintered PMN ceramics with various heating rates is shown in Fig. 2. Density increases with heating rate as a result of decreasing PbO loss. With the same heating rate, density increases at high sintering temperature. Figure 3 shows the SEM photographs of the as-fired surface of the PMN ceramics sintered at 1260°C. The microstructure becomes more dense as heating rate increases, as shown in Fig. 2.

Figures 4(a) and (b) show typical plots of dielectric constant and dissipation factor vs

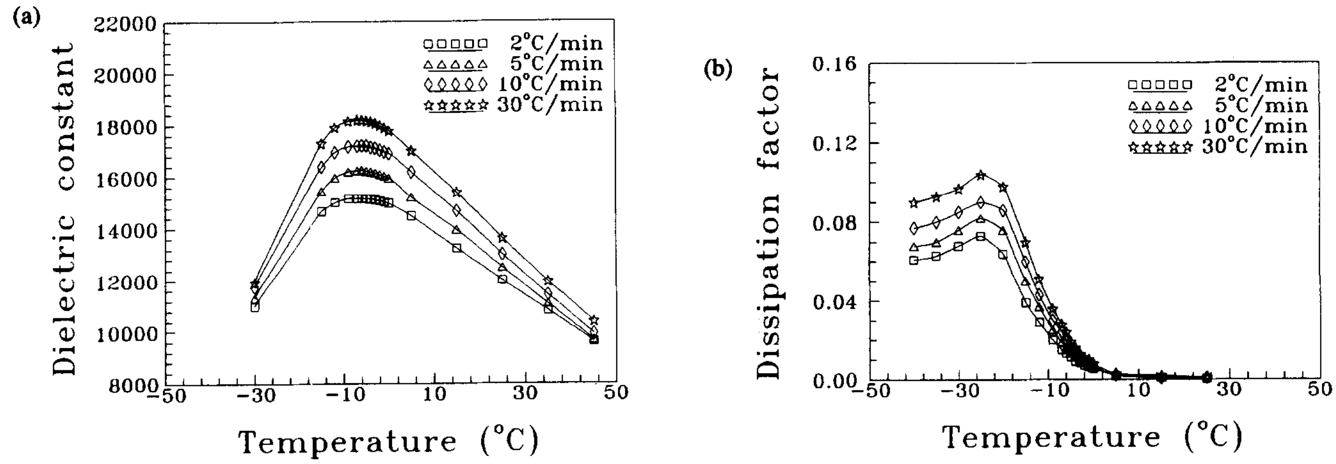

Fig. 4. Dependence of (a) dielectric constant at 1 kHz, and (b) dissipation factor at 1 kHz, on temperature for PMN ceramics sintered at 1260°C/2 h.

Table 3. Effect of heating rate on dielectric properties of sintered PMN pellets

Sintering temp. (°C)	Heating rate (°C/min)	K_{max} (1 kHz)	T_{max} (°C)
1230	2	14900	−5
	5	15800	−6
	10	16500	−6
	30	17300	−7
1260	2	15200	−6
	5	16300	−6
	10	17200	−7
	30	18200	−8

temperature under 1 kHz, for PMN sintered at 1260°C with various heating rates. Dielectric constant increases with heating rate due to the increasing density, grain size, and PMN content. From the reduced equation proposed by Wang and Schulze,[8] the dielectric constant of the sample (K_s) is related to that of PMN grain (K_g) and grain boundary (K_{gb}) by

$$1/K_s = 1/K_g + 1/RK_{gb}$$

where $R = D_g/D_{gb}$, i.e. the thickness ratio of the grain to grain boundary layer. Larger grain size results in a thinner grain boundary, therefore R and K_s increase. The dissipation factor increases with heating rate as a result of increasing dielectric constant. For the same electric field, samples with high dielectric constant induce more polarization. As an alternating electric field is applied, more polarization results in more dielectric loss. The effect of heating rate on dielectric properties (maximum dielectric constant and temperature of maximum dielectric constant) of sintered PMN ceramics is listed in Table 3. K_{max} increases with heating rate in the PMN ceramics sintered at 1230°C and 1260°C. This could be due to two major causes: one is the increasing density as shown in Fig. 2, and the other is the increasing grain size as listed in Table 2.

4 CONCLUSION

The columbite and perovskite content in the first and second calcined powder were not affected by heating rate. The perovskite amount in sintered PMN ceramics increased as heating rate increased from 2°C/min to 30°C/min. It is affected not only by excess MgO and PbO (shown in other studies) but also, in this study, by heating rate. Density and grain size increased with heating rate, and this resulted in the increasing of the dielectric constant.

In the process of producing PMN ceramics, heating rate is a parameter to be considered to get better dielectric properties.

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