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Ceramics International 30 (2004) 1377–1381

CERAMICS INTERNATIONAL

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The effect of lead deficiency on the dielectric properties of $0.80Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.20PbTiO_3$ ceramics

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Received 28 November 2003; received in revised form 9 December 2003; accepted 22 December 2003

Abstract

The $0.80Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.20PbTiO_3$ ceramics with different PbO deficiency in starting raw powders were synthesized by the columbite method, and the effect of lead deficiency on phase structure, microstructure, and dielectric properties were investigated. With the increase of lead deficiency, the amount of perovskite phases of both calcined powders and sintered ceramics decreased, and at the same time, the density, linear shrinkage, and grain size also decreased greatly. When the lead deficiency varied from 0 to 1 mol%, the maximum dielectric constant jumped from 25,000 to 35,000; however, when lead deficiency was more than 1 mol%, the dielectric constant began to decrease. With the increase of lead deficiency ($<1\%$), the increase of dielectric constant resulted from the elimination of low-permittivity PbO-rich inter-granular layers. However, this investigation proved that pyrochlore phase is less harmful to dielectric properties than PbO-rich inter-granular layers.

Keywords: C. Dielectric properties; $Pb(Mg_{1/3}Nb_{2/3})O_3$; Lead deficiency; Phase structure

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$-based ceramics (abbreviated as PMN) is a promising candidates for multilayer ceramics capacitors and electrostrictive devices because of its high dielectric constant, low firing temperature, and large electric field-induced strain [1]. However, the synthesis of this family of compounds has been found to be most difficult due to the pyrochlore phase formation, the problem can be effectively solved by employing the columbite precursor method [2]. However, the loss of PbO during sintering can also result in the formation of pyrochlore phase, thus addition of excess PbO has been the most widely used method to compensate PbO loss. Though excess PbO is helpful in the elimination of pyrochlore phase and enhance density through liquid phase sintering, the excess PbO segregates in the grain boundary leads to a reduction in dielectric constant. Furthermore, excess PbO alters the dielectric behavior of PMN more severely than the pyrochlore phase [3,4]. In principle, removing PbO through volatilization during sintering can eliminate the detrimental effects of excess PbO on the dielectric properties. Such a step in the processing will require knowledge of the exact amount of PbO to be eliminated and a precise sintering schedule, which is difficult to achieve. Though annealing after sintering could eliminate PbO-rich inter-granular layers, lead cations within crystal cells also would loss during annealing, which is certain to create new defects and thus affect dielectric properties of the specimen.

In the present investigation, the effect of lead deficiency in starting powders on phase structure, ordered micro-regions and dielectric properties of $0.80Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.20PbTiO_3$ ceramics was explored.

2. Experimental procedure

The specimens studied in this investigation were fabricated according to formula $0.80Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.20PbTiO_3$ (abbreviated as PMN–PT hereafter). The specimens were prepared by columbite precursor method [2]

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doi:10.1016/j.ceramint.2003.12.102

and the purity of all starting raw powders was 99.9%. The columbite precursor ($MgNb_2O_6$) was first prepared by mixing pre-determined amounts of MgO and Nb_2O_5 and ball-milled for 12 h in polyethylene jars, then the slurry was dried and calcined for 4 h at temperature 1000 °C to form $MgNb_2O_6$. The columbite precursor was then mixed and ball-milled with pre-determined amounts of PbO and TiO_2 powders and calcined at 880 °C for 4 h. The calcined powders were ground, ball-milled again and compressed under 150 MPa into disks of 12 mm diameter and 3 mm thickness. After burning off PVA, The disks were packed with powder of the same composition as that of the disks in an alumina crucible. The crucible was sealed with an alumina cover and then placed in a second alumina crucible. The gap between the inner and outer crucibles was packed with ZrO_2 powder. The disks were then sintered at 1200 °C for 1 h. Using this method of double crucibles, it was possible to suppress the PbO loss.

The relative amounts of pyrochlore and perovskite phases were determined using XRD patterns of powder samples by measuring the major X-ray peak intensities for perovskite and pyrochlore phases, i.e. (1 1 0) and (2 2 2), respectively. The percentage of perovskite phase was calculated by the following equation:

$$\text{Content of perovskite phase (\%)} = \frac{I_{\text{perov}\,(1\,1\,0)}}{I_{\text{perov}\,(1\,1\,0)} + I_{\text{pyro}\,(2\,2\,0)}}$$

where I_{perov} and I_{pyro} stand for the intensities of the major peaks (1 1 0) and (2 2 0) for perovskite and pyrochlore phases, respectively.

The dielectric response was measured at the frequency of 1 kHz using an automatic LCR meter (WK4225) at a temperature range from −60 to 120 °C.

The diffuseness factor δ was obtained from the following formula:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_{\max}} + \frac{1}{2\varepsilon_{\max}\delta^2}(T - T_{\max})^2$$

where, ε and $\varepsilon_{\max}$ are relative dielectric constant and its maximum value, while T and $T_{\max}$ is the temperature corresponding to ε and $\varepsilon_{\max}$, respectively.

The microstructure was observed by scanning electron microscopy (HITACHI S-570).

3. Results and discussion

3.1. Phases analysis

The specimens with 0, 0.5, 1, 3 mol% lead deficiency were numbered MP0, MP1, MP2, and MP3, respectively. According to XRD patterns, the perovskite and pyrochlore phases contents and other physical parameters are shown in Table 1.

Lead deficiency in starting powders was indeed detrimental to phase structure of calcined powders of the four specimens. Though the calcined powder of MP1 with 0.5 mol% lead deficiency was pure perovskite structured, the other three specimens with more than 1 mol% lead deficiency had different content pyrochlore phase, MP2 with 0.7 mol% and MP3 with 1.8 mol% pyrochlore phase, respectively.

The PMN-based ceramics were sintered with non-lead atmosphere, and the effect of lead deficiency on phase structure of the sintered ceramics is very similar to that of calcined powders. Only when lead deficiency was more than 1 mol%, the pyrochlore phase could be detected. The pyrochlore phase resulted from the lead deficiency, and also from lead loss at high sintering temperature. From the above results it was known that minor lead deficiency even did not affect pure perovskite structure, which differs greatly with traditional results. However, with the increasing of lead deficiency, the content of pyrochlore phase was also increased, which agrees with published literature.

3.2. Physical properties and microstructure

The effect of deficient PbO on the physical properties such as density and linear shrinkage was studied. Both these parameters were calculated from the Yoon et al. method [5] and Archimedes' principle, respectively. The density and linear shrinkage values for all samples are given in Table 1. Fig. 1 demonstrates the SEM photos of the three specimens with different lead deficiency.

From Table 2 it was known that with the increasing of lead deficiency, the density and linear shrinkage decreased gradually. Molecular mass of element lead is very large and excess PbO could promote sintering through liquid diffusion, so lead deficiency is certain to result in the decreasing of density and linear shrinkage. It is well known that excess PbO could make grain size increase, so here the deficiency

Table 1
The effect of lead deficiency on density and linear shrinkage of 0.80PMN–0.20PT ceramics

Specimens	Lead deficiency (mol%)	Perovskite phase (%) in calcined powders	Perovskite phase (%) in sintered ceramics	Peak dielectric constant	Diffuseness factor δ (°C)
MP0	0	100	100	25,670	19.7
MP1	0.5	100	100	28,500	18.44
MP2	1	99.4	99.1	34,800	12.79
MP3	3	97.2	96.2	21,150	20.5

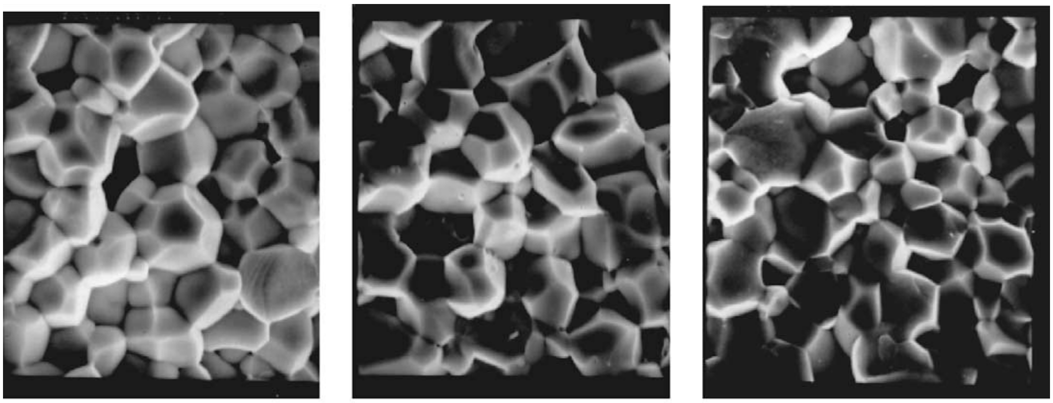
(a) (b) (c)

Fig. 1. SEM photos of 0.80PMN–0.20PT specimens with different lead deficiency.

Table 2
The effect of lead deficiency on density and linear shrinkage of 0.80PMN–0.20PT ceramics

Specimens	Lead deficiency (mol%)	Density (g/cm^3)	Linear shrinkage (%)	Grain size (μm)
MP0	0	7.89	15.17	4.52
MP1	0.5	7.81	15.15	4.24
MP2	1	7.73	14.17	3.58
MP3	3	7.34	12.53	–

of PbO must decrease grain size, as shown in Fig. 1, where (a), (b), and (c) correspond with the specimens contained 0, 0.5, and 1 mol% lead deficiency, respectively.

3.3. Dielectric properties

Dielectric constant and dissipation factor were measured for the samples at 0.1, 1, and 10 kHz frequencies during cooling, over a range of temperature from +120 to −60 °C. All the specimens with different PbO deficiency show broad maxima in the dielectric constant versus temperature plot and negligible dissipation factor at room temperature, as shown in Figs. 2 and 3.

In Figs. 2 and 3, it demonstrated the effect of lead deficiency on dielectric constant and loss for 0.80PMN–0.20PT ceramics. When lead deficiency content is very little, for example, less than 1 mol%, the dielectric constant increased rapidly with the increase of lead deficiency. Especially the peak dielectric constant for the specimens with 1 mol% lead deficiency reached almost 35,000. This high peak dielectric constant for 0.80PMN–0.20PT ceramics has never been reported. Usually peak dielectric constants were around 25,000 in published literature.

The reasons why minor PbO deficiency could rapidly increase the dielectric constant for PMN-based ceramics can be concluded as follows: lead deficiency effectively eliminates low-permittivity PbO-rich inter-granular layers.

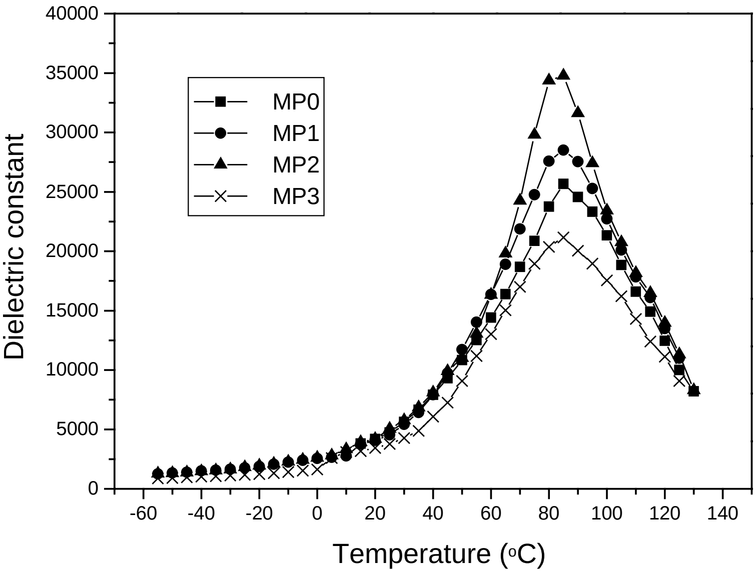

Fig. 2. The temperature dependence of dielectric constants (1 kHz) for 0.80PMN–0.20PT ceramics with different lead deficiency.

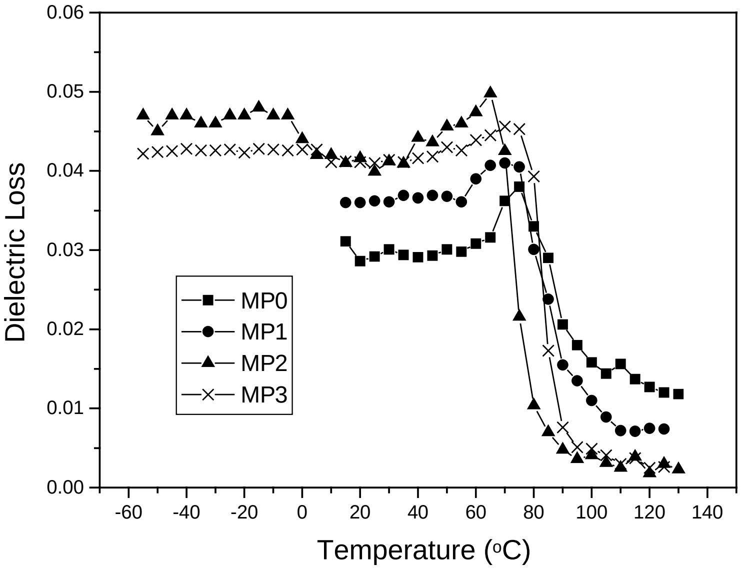

Fig. 3. The temperature dependence of dielectric loss (1 kHz) for 0.80PMN–0.20PT ceramics with different lead deficiency.

Though excess PbO is easy to form into a PbO-rich liquid phase and thus could promote sintering, the surplus non-reacted PbO would form a PbO-rich layer that is detrimental to dielectric properties. Jang and Lee [4] proved that the elimination of PbO-rich inter-granular layers by annealing increased dielectric constant about 10%, but our results demonstrated that deficient PbO could increase dielectric constant as much as almost 40%, which is similar to that of Cho et al.'s results [6].

When lead deficiency is more than 1 mol%, the dielectric constant for PMN-based specimens also began to decrease. At last, it must be mentioned that pyrochlore phase is less harmful to dielectric properties than PbO-rich inter-granular layers. For example, the maximum dielectric constant for MP2 is the highest among the four specimens, but it contained 0.9 mol% pyrochlore phase.

4. Conclusions

The results of this investigation for 0.80PMN–0.20PT ceramics with different PbO deficiency in starting raw powders are as follows:

(1) With the increase of lead deficiency, the amount of perovskite phases of both of the calcined powders and sintered ceramics decreased. Because of the evaporation of lead, perovskite phase content of the sintered ceramics decrease slightly quickly than that of the calcined powders. However, both the specimens of the calcined powder and sintered ceramics with 0.5 mol% lead deficiency are still 100% perovskite-structured.

(2) Lead deficiency in starting raw powders affected density, microstructure, and linear shrinkage rather greatly, especially when lead deficiency is more than 1 mol%. When the content of lead deficiency varied from 0 to 1 mol%, the density, linear shrinkage during sintering, and grain size decreased from 7.89 g/cm^3, 15.17%, and 4.52 μm to 7.73 g/cm^3, 14.17%, and 3.58 μm, respectively.

(3) With the increase of lead deficiency, the dielectric constant increased rapidly, especially when lead deficiency reached 1 mol%, the specimen's maximum dielectric constant jumped to amazing 35,000, which has never been reported before. However, when lead deficiency is more than 1 mol%, with the increase of lead deficiency the dielectric constant began to decrease. The increase of dielectric constant with increase of lead deficiency ascribed for the elimination of low-permittivity PbO-rich inter-granular layers.

(4) Pyrochlore phase is less harmful to dielectric properties than PbO-rich inter-granular layers.

Acknowledgements

This work was supported by the Ministry of Sciences and Technology of China through 973-project under grant 2002CB613305 as well as International Cooperation Research Project of China–Israel (time 2002–2003).

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