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The Effect of Annealing Conditions on $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$ - $0.3PbTiO_3$ Ceramics Fabricated by Spark Plasma Sintering

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The effect of annealing conditions on $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$ - $0.3PbTiO_3$ ceramics fabricated by spark plasma sintering (SPS) method were investigated. As-sintered samples were required a post annealing treatment for recovering their insulation from the conductive behavior caused by a partial reduction during SPS process. The treatment was necessary in a PbO-rich atmosphere for avoiding the decomposition of samples, and it not only removed oxygen vacancies but also promoted the crystal grain growth as well as the dielectric properties of samples. The higher anneal temperature and longer anneal duration were effective in the increase of the dielectric properties of samples.

Key words: spark plasma sintering, post annealing treatment, dielectric property, PMN-PT

1. INTRODUCTION

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), is a well-known relaxor ferroelectric. It exhibits a diffuse phase transition that is characterized by anomalously large dielectric maxima with strong frequency dependences. The solid solution system of $(1\text{-}x)$PMN-$x$$PbTiO_3$(PT) shows an exceptionally high dielectric constant near room temperature at $x \sim 0.4$[1-3] and excellent piezoelectric properties, $d_{33} = 800$ pC/N as well as $k_{33} = 78\%$ at $x = 0.3$[4], which is in the composition region of morphotropic phase boundary (MPB)($0.25< x <0.35$)[5-7]. The much research was carried out on the PMN-PT system for applications in multi layer ceramic capacitors, piezoelectric transducers and actuators due to their wonderful ferroelectric and piezoelectric properties. Generally, high-density samples are necessary for these applications, therefore a high sintering temperature, ~ 1200°C, is usually required. However, some impurity phases are formed by lead volatilization at the high temperature. Consequently, there is always a problem that is difficult to get a both high dense and stoichiometric sample.

Recently, a new sintering method, spark plasma sintering (SPS) was applied to the fabrication of dielectric materials at low temperature. Naturally, it was also used to PMN-PT system because it was hard to sinter in stoichiometry. Park *et al.* reported 0.65PMN-0.35PT sintered by SPS at 900°C under a pressure of 30 MPa, and showed that post annealing at 1200°C was more effective for developing enhanced dielectric properties than annealing at 800°C[8]. Chen *et al.* also reported the sintering of 0.7PMN-0.3PT was through the SPS method at 800°C under a pressure of 20 MPa with an annealing at 700°C for 4h[9]. Although these reports indicated that the SPS technique was an alternative sintering technique for PMN-PT at rather low temperatures in short times, they did not study details of post annealing and its effect on the dielectric properties.

The SPS process is characterized by charging between powder particles with electrical energy and uniaxial sintering pressure. An advantage of SPS is the ability to densify samples at low temperature with a super-high sintering speed as compared to conventional sintering methods. On the other hand, a disadvantage of SPS for oxides ceramics is that it requires a post annealing treatment to recover from partial reduction during processing. Consequently, the post annealing treatment is an indispensable and important procedure in fabricating dielectric materials by the SPS method, but few details of post annealing treatment were indicated. In this work, 0.7PMN-0.3PT ceramics have been prepared by SPS method at an ultra-low temperature, 700°C. We investigated some phenomena during the post annealing treatment with different conditions, such as atmosphere, temperature and processing time, and reported the effect of post annealing treatment on the grain size and dielectric properties of the sample.

2. EXPERIMENTAL

The 0.7PMN-0.3PT powder used in this study was made by Cerone Inc. The powder was sintered by SPS technique at 700 °C for 5 minutes with a heating rate of 400 °C/min under an uniaxial pressure of 500 MPa in vacuum. A graphite sheet was taken to prevent direct contact between the powder and the die.

The obtained as-sintered pellets were annealed under a PbO-rich atmosphere at different temperatures (700, 850, 1000 and 1200°C) for 12h and at 850°C for different durations (12, 30, 45, 72 and 156h). The PbO-rich atmosphere was created by $PbZrO_3$ powder that was separated from sample with a platinum foil. The same 0.7PMN-0.3PT powder also was sintered with a conventional method at 1200°C for 2h under the atmosphere which was similar to the annealing.

The density was given using the Archimedes method and the microstructure on the surface of the sample was observed using the scanning electron microscopy (SEM; JEOL Ltd., JSM-5500). X-ray diffractometry (XRD; Philips Co. Ltd., X'pert PRO) was used to identify the crystalline phase. The pellet branded the silver paste on both sides was used for the measurement of the dielectric characteristic. The dielectric constant was measured at 100 kHz in the temperature range from 300°C to room temperature using an impedance analyzer (Agilent, 4294A).

3. RESULTS AND DISCUSSIONS

Densification of 0.7PMN-0.3PT was successful using the SPS technique. The result of density measurement showed a relative density over 98% which was little higher than that of the sample sintered by conventional method (96%). Due to the reductive atmosphere by the graphite sheet and vacuum conditions, the as-sintered pellet was slightly reduced and became black. Therefore an additional oxidization process was necessary. Figure 1 shows XRD patterns in different annealing conditions. Annealing in air, the XRD pattern presents almost a single pyrochlore phase, while annealing with $PbZrO_3$ powder that reveals single perovskite phase. It is considered that $PbZrO_3$ powder made PbO-rich atmosphere and avoid the decomposition of sample during annealing. The resistivity of the as-sintered sample is 10^5 - 10^6 Ωcm and this value indicates that partial reduction occurred in the SPS

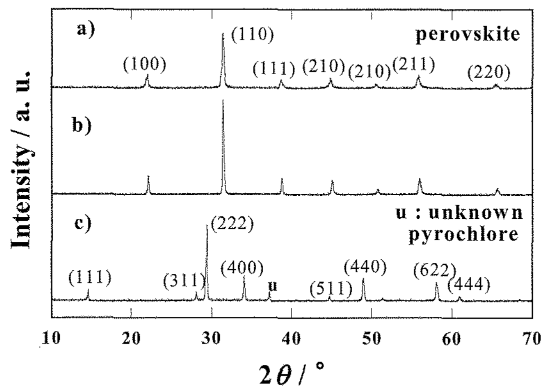

Figure 1 XRD pattern of the sample surface before sintering (a), annealed at 1000°C with $PbZrO_3$ powder (b) and without $PbZrO_3$ powder (c)

process. On the other hand, the tanδ of the annealed sample is 0.03-0.05 that means oxygen vacancies in sample were compensated well through the annealing process.

The temperature dependence of the dielectric constant of samples annealed at different temperatures (700-1200°C) for different duration times (12-156h) are shown in Fig. 2. For comparison, the data of sample sintered by conventional method is also shown in Fig. 2. With increasing annealing temperature, the broad dielectric constant-temperature curve turned to sharp and approached to the response of conventionally prepared sample. As the results, the temperature of the maximum dielectric constant (T_m) shifted toward the higher temperature side, and the maximum dielectric constant (ε_m) became larger. However, the effect of long-time annealing at low temperature is almost equal to that of the annealing at high temperature in the short time.

The microstructures of the samples annealed at different conditions were observed by scanning electron microscopy(SEM). Grain growth is highly dependent on the annealing temperature. The grain size of the sample annealed at 700°C for 12h was about 0.2 μm and that of the sample annealed at 1200°C for 12h was 8-12 μm (Fig. 3). Similar to the temperature dependence of the grain growth, the grain growth is also affected to

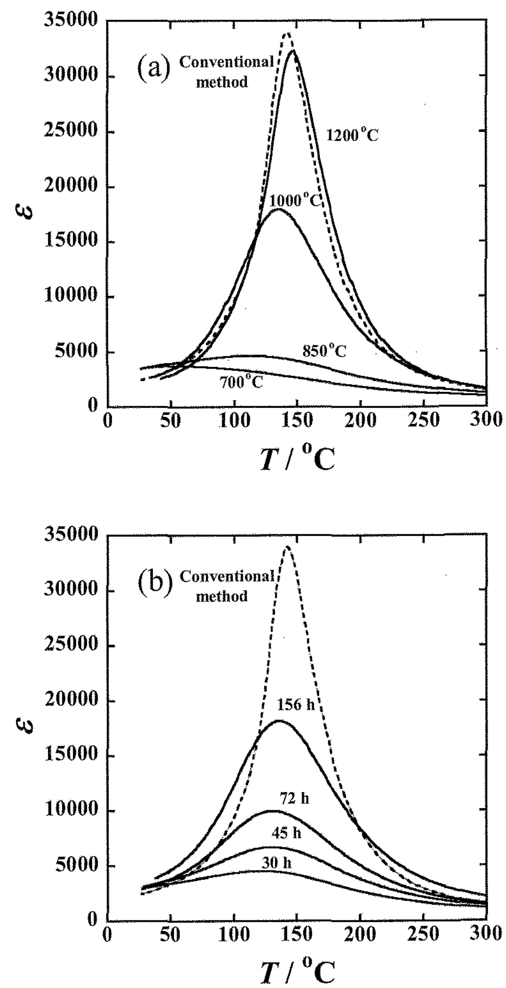

Figure 2 Temperature dependence of dielectric constant of the samples annealed at different temperatures for 12 hours (a) and in different durations at 850°C (b).

some degree by the annealing duration, but the effect is lower than that of temperature. The grain size of the sample annealed at 850°C for 12h was about 0.3 μm and that annealed at 850°C for 156h was about 1 μm.

Compared the sample annealed at 1000°C for 12h with the sample annealed at 850°C for 156h, we can found their dielectric constant-temperature curve was almost the same but the grain size was different greatly. It is suggested that dielectric characteristic depends not on the grain size but on another factor, such as oxygen vacancy or residual stress etc, which in general broaden the dielectric constant peak and lower the dielectric constant value. Higher temperature or longer duration anneals can eliminate both oxygen vacancies and residual stress,

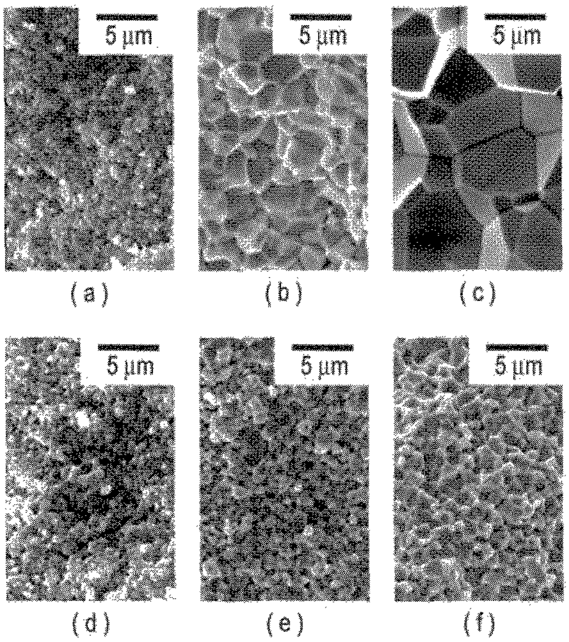

Figure 3 SEM images of fractured surface for samples after annealing (a) 700°C-12h, (b) 1000°C-12h, (c) 1200°C-12h, (d) 850°C-30h, (e) 850°C-72h and (f) 850°C-156h.

and realizes recovery to "normal ferroelectric" behavior, like that of conventionally sintered sample. In case of annealing in insufficient condition, the oxygen vacancies or residual stress cannot be eliminated completely and therefore samples still have a lower value of T_m and ε_m.

4. CONCLUSION

0.7PMN-0.3PT ceramics with densities over 98% were successfully fabricated by the SPS method. The dielectric properties showed a strong dependence on post-annealing conditions. Lower temperature or shorter duration anneals resulted in a downward shift in the T_m and a smaller ε_m as compared to samples sintered by the conventional method. Higher temperature or longer duration anneals resulted in normal ferroelectric properties approximating the conventionally sintered samples.

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