한국표면공학회지
J. Kor. Inst. Surf. Eng.
Vol. 36, No. 5, 2003.
<연구논문>

Dielectric, Pyroelectric, and Piezoelectric Properties of 0.7PMN-0.3PT Ceramics Modified with Cr_2O_3

June Won Hyun*

Department of Applied Physics, Dankook University, Seoul 140-714, Korea

(Received 25 July 2003 ; accepted 15 October 2003)

Abstract

The effect of 0~0.7 mol% addition of Cr_2O_3 on the dielectric, pyroelectric, and piezoelectric properties were studied in the $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$(0.7PMN-0.3PT) ceramics with composition near the morphotropic phase boundary. The dielectric constant and loss of the ceramics samples were measured as a function of temperature at various frequencies (0.1-100 kHz). The pyroelectric coefficient was measured by using the Byer-Roundy method as a function of temperature. Dielectric, pyroelectric, and piezoelectric constant achieved the maximum values of 0.4 mol% Cr_2O_3. The transition temperature is continuously shifted to lower temperature with an increase of a small amount of Cr_2O_3.

Keywords : PMN-PT, perovskite, morphotropic phase boundary, Byer-Roundy method

1. INTRODUCTION

Complex lead-based perovskite oxides with general formula of $Pb(B'B'')O_3$ are characterized by anomalously large and broad dielectric maximas which shifted up in temperature with increasing frequency, where B' is a low valence cation, eg., Mg^{+2}, Ni^{+2}, Fe^{+3}, Zn^{+2}, Sc^{+3} and B'' is a high valence cation, e.g., Nb^{+5}, Ta^{+5}, W^{+6}, Ti^{+4}, Zr^{+4} [1]. These properties have attracted special attention for various device applications, including multilayer capacitors and electrostrictive actuators[2,3]. Relaxor ferroelectric lead magnesium niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$, PMN) has an anomalously high dielectric constant and a broad diffuse phase transition near −15°C[1]. Though the phase transition temperature of PMN is below room temperature, it can be easily shifted upward with an addition of $PbTiO_3$ (PT) because PT is a normal ferroelectric compound with a phase transition at 490°C. It has been reported that a morphotropic phase boundary exists in the solid solution system (1-x)PMN-xPT near x=0.3[4,5]. This composition lying near MPB, which divides the rhombohedral and tetragonal phases, has high dielectric, pyroelectric, and piezoelectric coefficient. Kim *et al.* investigated the electric properties in 0.7PMN-0.3PT ceramics doped with NiO[6] and Ag_2O[7]. In the samples sintered at 1250°C for 2 h, the maximum dielectric (36000) and pyroelectric (0.017 C/m^2K) were obtained at 0.7 mol% Ag_2O. However, the dielectric and pyroelectric constant of the samples doped with NiO were decreased as the amount of NiO content was increased. And, they noted that the diffuseness of phase transition was almost constant because of Ni^{2+} and Ag^+ ions incorporated into A-site. For various device applications, including multilayer capacitors and electrostrictive actuators, the material needs large dielectric, pyroelectric constant, and small dissipation factor. Also, because temperature stability are important, the materials for the applications need the increase of diffuseness of phase transition. We know the improvement of the electric properties $Pb(Mg_{1/3}Ta_{2/3})$-$PbTiO_3$ ceramics doped Cr_2O_3[8]. Thus, in this study, the composition 0.7PMN-0.3PT with composition near the MPB was chosen in (1-x)PMN-xPT solid solution system to investigate the effects of Cr_2O_3 doping in the physical, dielectric, pyroelectric, and piezoelectric properties of a relaxor ceramic material $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ in detail.

*Corresponding author. E-mail : ywhyun@dankook.ac.kr

2. EXPERIMENTAL

Ceramic samples of $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$-x mol% Cr_2O_3(PMN-PT-x mol% Cr_2O_3) ($0.0 \leq x \leq 0.7$) were prepared using the columbite precursor method[9]. Raw materials were $PbCO_3$, MgO, Nb_2O_5, TiO_2, and Cr_2O_3. The process basically involves prereaction of MgO and Nb_2O_5 to form the columbite phase $MgNb_2O_6$ prior to reaction with PbO, TiO_2 and Cr_2O_3. Weighted materials were wet-mixed for 20 h and dried at 80°C for 20 h, then calcined at 850°C for 4 h. After mixing, the various powders were cold pressed to form disks followed by sintering at 1250°C for 2 h in a closed alumina crucibles. The sintered samples were characterized by X-ray diffraction to ensure phase purity. The grain size was determined on fracture surfaces of pellets using scanning electron microscopy (SEM). Opposite faces of the samples were coated with sputtered silver electrodes.

The dielectric constant and the dissipation factor of the ceramics were investigated as a function of frequency between 0.1 and 100 kHz at a heating rate of 4°C/min using an Impedence Analyzer (HP4192A). The pyroelectric coefficient was measured by the static Byer-Roundy method as the samples were heated at a rate of 4°C/min[10]. Piezoelectric properties were measured by using resonance-antiresonance method[11] and Berlincourt d_{33} meter. Prior to the dielectric and pyroelectric measurements the specimens were poled by applying a DC field of 20 kV/cm at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1(a) and 1(b) show the microstructures of with small grains and with large grains, respectively. The difference in the composition between these two figures is that Fig. 1(b) contains the Cr_2O_3 component, whereas Fig. 1(b) does not. But, above 0.4 mol% Cr_2O_3 (Fig. 1(c)), the grain sizes decreases. Therefore, it is considered that the small amount the Cr_2O_3 component enhances grain growth. Fig. 2 shows the X-ray diffraction patterns of Cr-doped PMN-PT at room temperature. X-ray diffractometer was used to examine the formation of pyrochlore phase on the component surface. The relative amounts of the pyrochlore phase and perovskite phase were determined by measuring the major X-ray peak intensities for the perovskite and pyrochlore phase [(110) and (222)], respectively. The pyrochlore phase, in addition to other factors such as impurities and intergranular

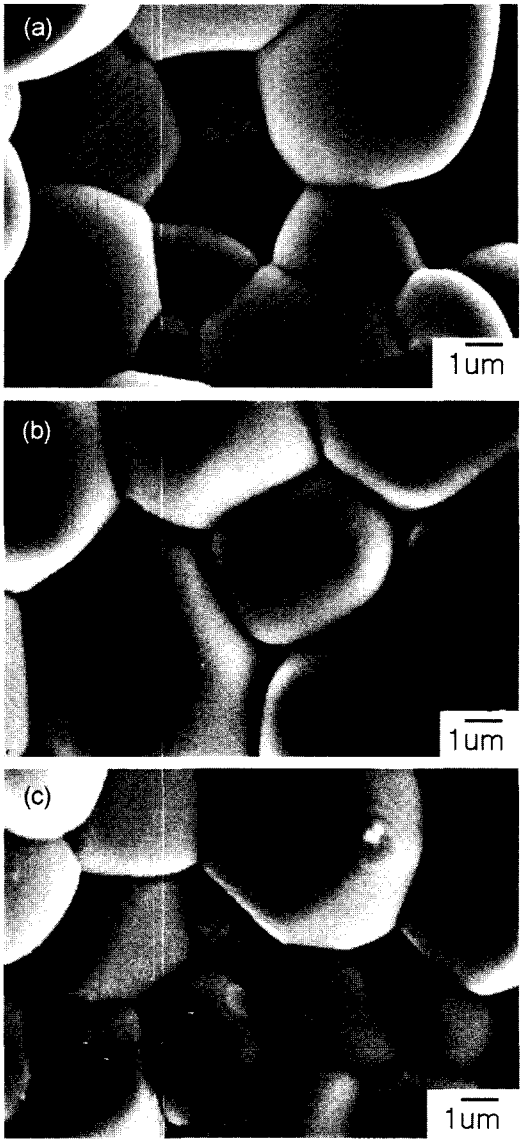

Fig. 1. SEM micrographs of the fracture suface of the composition 0.7PMN-0.3PT-x mol% Cr_2O_3. (a) x=0.0 (b) x=0.4, and (c) x=0.7.

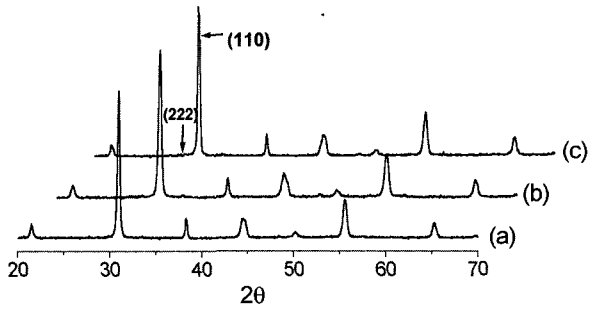

Fig. 2. X-ray diffraction patterns of 0.7PMN-0.3PT-x mol% Cr_2O_3. (a) x=0.0, (b) x=0.4, and (c) x=0.7.

phases, is considered to be determined to by the dielectric properties of ferroelectric relaxor materials[12,13]. The percentage of perovskite phase is calculated

from the XRD pattern using the following equation (1)[8]. Fig. 2 shows that all of the samples sintered at 1250°C for 2 h resulted in almost complete formation of perovskite phase (98%).

$$\text{Perovskite}(\%) = \frac{I_{perov.}}{(I_{perov.} + I_{pyro.})} \times 100 \quad (1)$$

Fig. 3 shows the dielectric constant and dissipation factor as a function of temperature at various frequencies from 0.1 to 100 kHz in the compositions PMN-PT-x mol% Cr_2O_3 (x=0.1, 0.3, and 0.7). The phase transition temperature occurs within a broad temperature range. Also, the shift of dielectric and tanδ loss maxima to higher temperatures at increasing frequency was observed. The diffuseness of the phase transition slightly increases with the increasing Cr content. Therefore, the dielectric properties exhibited by this composition are characteristic of a relaxor material. This may be due to the fact that Cr ions prefer to enter B-sites with equal valence and similar radii. Complex perovskite-type ferroelectric compounds $Pb(B'B'')O_3$ with disordered cation (B'B'') arrangements show diffuse phase transitions characterized by a broad maximum for the temperature dependence of the dielectric constant and dielectric dispersion in the transition region[14,15]. The dopant can go either to the A or to the B site in ABO_3-type perovskite structure. Its distribution on the two sites is the dependent on the valence and ionic radius of the dopant[16]. The dopant ions, with appropriate valencies, create lattice vacancies which strongly affect the electrical and structural properties of the matterial[17]. The radius of Cr^{3+} ion (0.062 nm) is nearly the same as that of B-site cations (Mg^{2+}; 0.072, Nb^{5+};0.064, Ti^{4+}; 0.060 nm)[18]. Owing to the principle of crystal chemistry, metalic ions prefer to enter sites with equal valence and similar radii. Therefore, it was inferred that Cr^{3+} ion would be incorporated into a B-site sublattice and Cr^{3+} ions would be affected as acceptor.

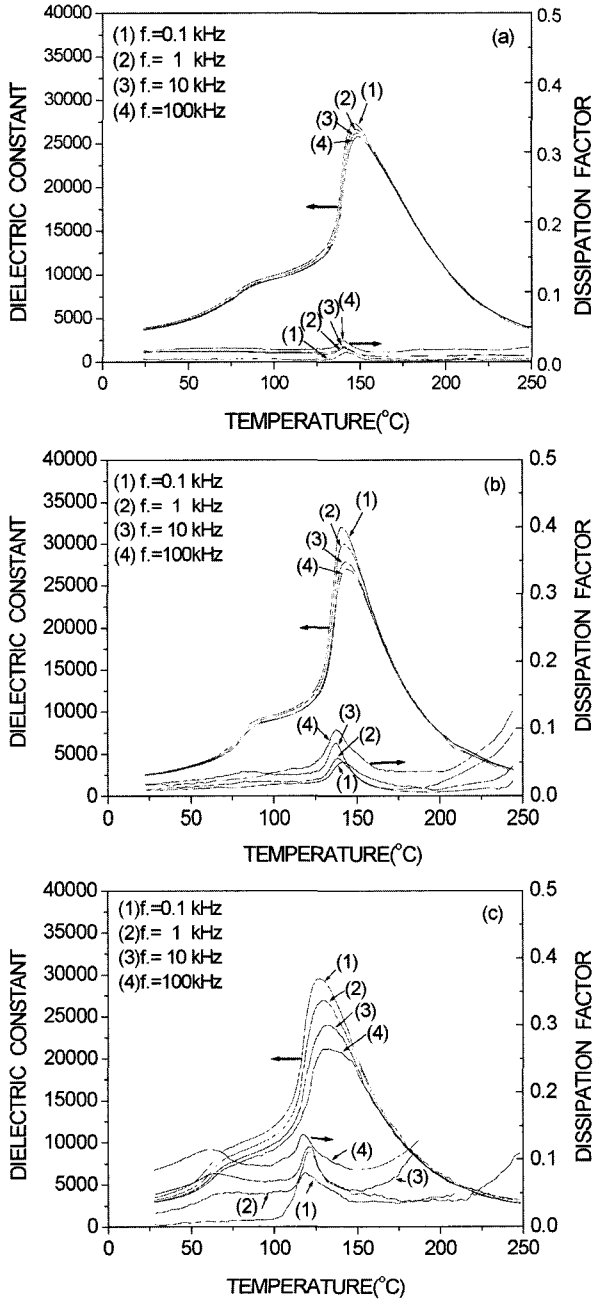

Fig. 3. Temperature dependence of the dielectric constant and dissipation factor at various frequencies. (a) x=0.1, (b) x=0.3, and (c) x=0.7.

The dielectric constant by the effect of Cr_2O_3 doping as a function of temperature behavior at 1 kHz is shown in Fig. 4. The dielectric constant slightly rises up to 0.4 mol% Cr_2O_3 and the decreases with further addition of Cr_2O_3. Though no pyrochlore phase was found to be present, the decrease in the maximum value of the dielectric constant was appeared

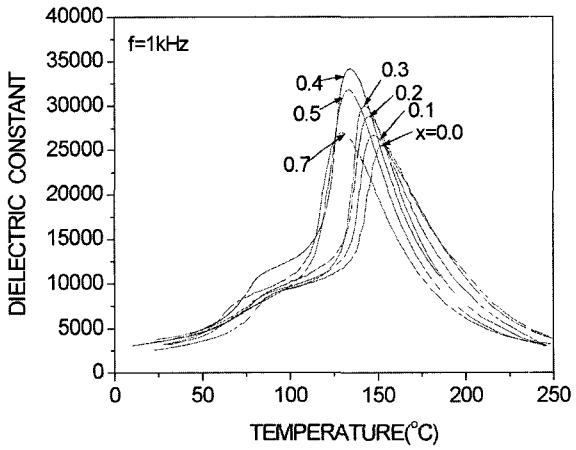

Fig. 4. Dielectric constant vs. temperature behavior at 1 kHz for 0.7PMN-0.3PT-x mol% Cr_2O_3.

in the composition with higher than 0.4 mol% Cr_2O_3. This result occurs probably because of the lattice impurities and integranular phase[16].

Fig. 5 shows the temperature dependence of the pyroelectric coefficient for the base composition doped with Cr_2O_3 as a function of temperature. The maximum value of pyroelectric coefficient was obtained at 0.4 mol% Cr_2O_3. The peak temperature of pyroelectric coefficient was continuously shifted to lower temperature with the increasing Cr_2O_3 content. The variation of the dielectric and pyroelectric peak temperature as a function of the amount of Cr_2O_3 was shown in Fig. 6. The decrease in the dielectric and pyroelectric peak temperatures indicate that Cr_2O_3 is incorporated into PMN-PT sublattice. The reason for these phenomena is not yet clear and further investigations are in progress[19]. The difference between the dielectric and pyroelectric peak temperature increases as the Cr_2O_3 content increases. This may be due to the diffuseness of phase transition increases as the amount of Cr_2O_3 increases.

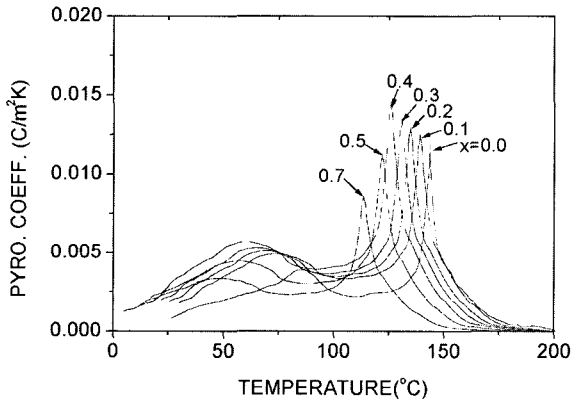

Fig. 5. Pyroelectric coefficient vs. temperature behavior for 0.7PMN-0.3PT-x mol% Cr_2O_3.

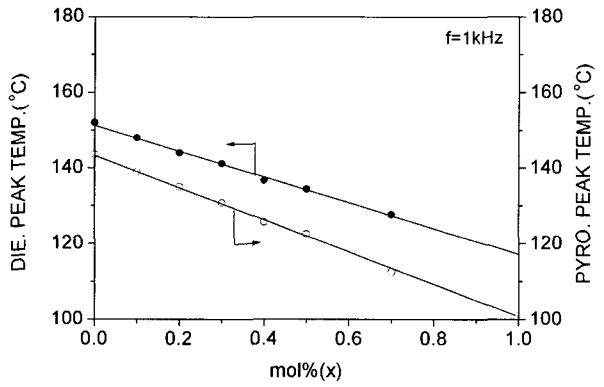

Fig. 6. Dielectric and pyroelectric peak temperatures of 0.7PMN-0.3PT-x mol% Cr_2O_3.

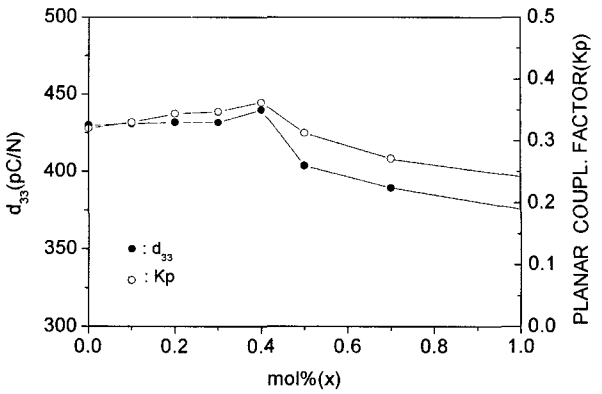

Fig. 7. Room-temperature piezoelectric d_{33} constant and electromechanical coupling factor kp for 0.7PMN-0.3PT-x mol% Cr_2O_3.

Fig. 7 shows the room-temperature values of piezoelectric d_{33} and electromechanical coupling factor kp of the composition 0.7PMN-0.3PT-x mol% Cr_2O_3 as a function of mole fraction of Cr_2O_3. The maximum piezoelectric d_{33} and electromechanical coupling factor kp are observed at 0.4 mol% Cr_2O_3. The composition with the maximum dielectric and pyroelectric coefficient exhibits relatively superior piezoelectric properties.

4. CONCLUSIONS

All compositions 0.7PMN-0.3PT-x mol% Cr_2O_3 sintered at 1250°C for 2 h resulted in an almost complete formation of perovskite structure. The dielectric, pyroelectric and piezoelectric properties of the 0.7PMN-0.3PT ceramics were improved with the addition of small amounts of Cr_2O_3 up to 0.4 mol%. The frequency dispersion and diffuseness of the phase transition increases with the addition of small amount of Cr_2O_3. The dielectric and pyroelectric peak temperatures are continuously shifted to lower temperature with the addition of small amount of Cr_2O_3. An improvement of the these properties by doping Cr_2O_3 are important results for achieving various device applications.

ACKNOWLEDGMENT

The present research was conducted by the research fund of Dankook University in 2003.

REFERENCES

1. G. A. Smolenskii and A. I. Agranovskaya, Sov. Phys.-Tech. Phys., 3 (1958) 1380.

2. K. Uchino, Am. Ceram., 65 (1986) 647.
3. Y. Tsuchiyz, K. Uchino and S. Nomura, J. J. Appl. Phys., 20 (1981) 1841.
4. S. W. Choi, T. R. Shrout, S. J. Jang and A. S. Bhalla, Ferroelectrics 100 (1989) 29.
5. S. W. Choi, S. J. Jang and A. J. Bhalla, J. Koreans Phys. Soc., 22 (1989) 91.
6. G. B. Kim, and S. W. Choi, J. J. Appl. Phys., 39 (2000) 5552.
7. G. B. Kim, J. M. Jung, and S. W. Choi, J. J. Appl. Phys., 38 (1999) 5470.
8. G. B. Kim, and S. W. Choi, J. Koreans Phys. Soc., 35 (1999) S1267.
9. S. L. Swartz and T. R. Shrout, Mat. Res. Bull., 17 (1982) 1245.
10. R. L. Byer and C. R. Roundy, Ferroelectrics, 3 (1972) 333.
11. Proc. IRE. Inst. Radio Engrs., 49 (1961) 1161.
12. J. Chen, and M. P. Harmer, J. Am. Ceram. Soc., 73 (1990) 68.
13. G. B. Kim, Y. J. Kim, and S. W. Choi, J. Korean Phys. Soc., 32 (1998) S1010.
14. G. A. Smolensky, J. Phys. Soc. Jpn. Suppl. 28 (1970) 26.
15. L. E. Cross, Ferroelectrics 76 (1987) 241.
16. P. Gonnard and M. Troccaz, J. Solid State Chem., 23 (1978) 32.
17. G. H. Dai, P. W. Lu, X. Y. Huang, A. S. Liu and W. R. Xue, J. Mat. Sci., 26 (1991) 167.
18. R. D. Shannon and C. T. Prewitt, Acta Crystallogr., B26 (1970) 1046.
19. G. A. Smolenskii, and A. I. Agranovskaya, Sov. Phys. Solid State, 1 (1960) 729.