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Effects of Atmospheric Powder and Grain Size on Electrical Properties of Lanthanum-modified $PbTiO_3$ Ceramics

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Dielectric and piezoelectric properties of $Pb_{0.9}La_{0.1}TiO_3$ ceramics were investigated as a function of grain size. Sintering atmosphere was controlled with changing the kind of atmospheric powder and its amount. It was confirmed that dielectric and piezoelectric properties of $Pb_{0.9}La_{0.1}TiO_3$ were strongly influenced by the sintering atmosphere. Relative dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$, which was sintered in PbO-deficient atmosphere made by $Pb_{0.9}La_{0.1}TiO_3$ powder, increased with the grain size. However, the dielectric constant of the samples sintered in the PbO-sufficient atmosphere made by $PbZrO_3$ powder was slightly decreased with the grain size. Piezoelectric d_{33} constant of $Pb_{0.9}La_{0.1}TiO_3$ also showed a different trend, depending on the sintering atmosphere. It was almost constant in the range of grain size of 1.3~2.3 μm when the samples were sintered in the PbO-sufficient atmosphere, while it intensively decreased with the grain size in the case of the PbO-deficient condition.

Key words: Dielectric, Piezoelectric, Atmospheric powder, Grain size

I. Introduction

It has been known since the 1950's that the grain size has a significant effect on the dielectric permittivity of $BaTiO_3$ ceramics. This discovery was followed by numerous experimental and theoretical efforts to explain the origin of the anomalously high dielectric permittivity at room temperature in fine grained $BaTiO_3$ ceramics.[1] The concept of internal stress in the fine grain samples appears to be essential for the interpretation of many experimental results al-though some assumptions of the internal stress model[2,3] were proved to be wrong afterward.[4]

There have been also some similar studies in the lead-based ferroelectric ceramics such as PLZT,[5,6] PZT,[7] PMN,[8] and PLT.[9] According to the literature,[5-9] most of them except $Pb_{0.9}La_{0.1}TiO_3$ ceramics showed that the dielectric constant increased with the grain size, which was inconsistent with $BaTiO_3$. Therefore, the internal stress was not concerned in lead based ceramics as an important factor as in $BaTiO_3$ ceramics. Recently, the author reported that the dielectric property of $Pb_{0.9}La_{0.1}TiO_3$ ceramic showed the similar behavior to $BaTiO_3$ in fine-grained region.[10] It was suggested that the grain size effect of the dielectric property of $Pb_{0.9}La_{0.1}TiO_3$ could be explained by modifying the assumption of the internal stress model.

According to the literature,[5-10] the grain size effect of the dielectric property of lead based ferroelectric ceramics is considered to be rather process-dependent. Swarts *et al.* suggested that the effect of PbO weight loss, microcracks, or density can not be perfectly excluded to change the grain size in the lead based ferroelectric ceramics.[8] The sintering atmosphere can be also one of the important experimental variables in the case of La-modified ceramics such as PLT and PLZT. For an instance, the substitution of La^{+3} for Pb^{+2} in oxygen deficient atmosphere changed the chemical state of Ti ions.[11] The atmosphere sintering method using the volatile atmospheric powder at sintering temperature is generally used in the conventional sintering process.[13,14] However, the detailed experimental results between the sintering atmosphere and the electrical property have not been reported yet.

In this study, the dielectric and the piezoelectric properties of $Pb_{0.9}La_{0.1}TiO_3$ were measured at room temperature as a function of grain size. The sintering of the samples was done in two kinds of atmosphere. The one is $PbZrO_3$ powder, which is generally used as an atmospheric powder due to the easy evaporation of PbO, and the other is $Pb_{0.9}La_{0.1}TiO_3$, the same composition as the sample in this experiment, less volatile than the former. The effects of the grain size and the sintering atmosphere on dielectric and piezoelectric properties were investigated in $Pb_{0.9}La_{0.1}TiO_3$ system. The effect of the space charge on the electrical properties was also discussed in $Pb_{0.9}La_{0.1}TiO_3$ system.

II. Experimental Procedure

PbO, La_2O_3, and TiO_2(Aldrich Chemical Co.) raw powders of which the purity was 99.9% were weighed in stoichiometric amounts. They were milled with zirconia balls in acetone for 24 hours. The mixed powder was calcined in alumina crucible at 900°C for 3 hours. The calcined powder, $Pb_{0.9}La_{0.1}TiO_3$ was then ground with the addition of 0.5 wt% polyvinyl alcohol as a binder in a ball mill for 20 hours and dried in an oven. The pellets of which the diameter was 10 mm were fabricated with uniaxial and then cold isostatic pressing. The samples were sintered at 1250°C for 0.5~30 hours in a closed Al_2O_3 crucible where the sintering atmosphere was controlled with the atmospheric powder. Two kinds of atmospheric powder, $PbZrO_3$ and $Pb_{0.9}La_{0.1}TiO_3$ were chosen to investigate the effect of the sintering atmosphere on dielectric property. $PbZrO_3$ is more volatile than $Pb_{0.9}La_{0.1}TiO_3$ at sintering temperature. The author defined the former as 'PbO-sufficient condition' and the latter as 'PbO-deficient condition' for convenience. The amount of the atmospheric powder was fixed to 5g in each step of sintering process. The author confirmed that 5g of the atmospheric powder is enough for the sintering by doing some pre-experiments.

Their sintering density was relatively constant for all samples in the range of 95-98% regardless of sintering time. The average grain size was measured by linear intercept method.[15] In this experiment, the average grain size of the samples was in the range of 1.3~6.0 μm. X-ray diffractometer was used for phase and structure analysis. Any other phases were not found under the detection limit of the X-ray equipment regardless of the sintering time, which was increased up to 30 hours.

Sintered samples were polished to the thickness of 500 μm. They were all annealed at 900°C for 3 hours in air. Both sides of the samples were electroded with the silver paste and baked at 600°C for 30 minutes for the measurement of dielectric and piezoelectric constant. The relative dielectric constant was measured using HP4194A Impedance/Gain-Phase Analyzer at room temperature. Piezoelectric d_{33} constant was measured with Berlincourt d_{33} piezometer after the samples were poled at 1~6 kV/mm for 30 minutes at 100°C.

III. Results and Discussion

(1) Effect of Atmospheric Powder on Dielectric and Piezoelectric Properties

Fig. 1 shows the variation of relative dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$ measured at 1 kHz as a function of grain size at room temperature. The relative dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$ increases with the grain size when the sintering atmosphere is PbO-deficient condition made with $Pb_{0.9}La_{0.1}TiO_3$ powder, the same composition with the samples, while it slightly decreases with the grain size in the case of PbO-sufficient condition made with $PbZrO_3$ powder. The samples of the PbO-deficient condition have totally higher dielectric constant than those sintered in the PbO-sufficient condition. The relative dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$ reported in the literature is in the range of 400~500, which is similar to those of the PbO-sufficient condition.[9-11] It is also reported that the dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$ ceramics showed the similar tendency to that of $BaTiO_3$ in fine grained region, which is around 1 μm.[1,10] The dielectric property of the samples is considered to deviate from the normal value when they are sintered in the PbO-deficient condition. It also indicates that the dielectric

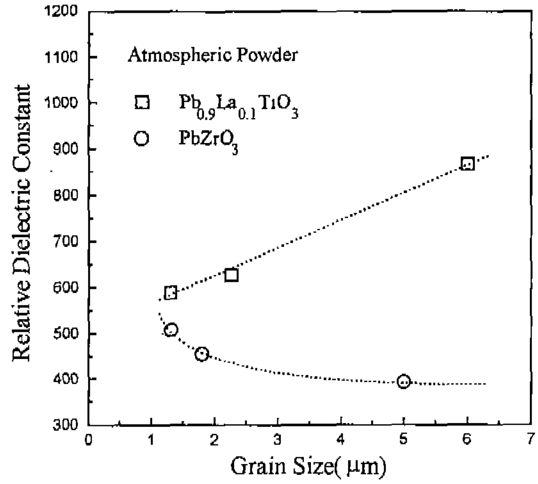
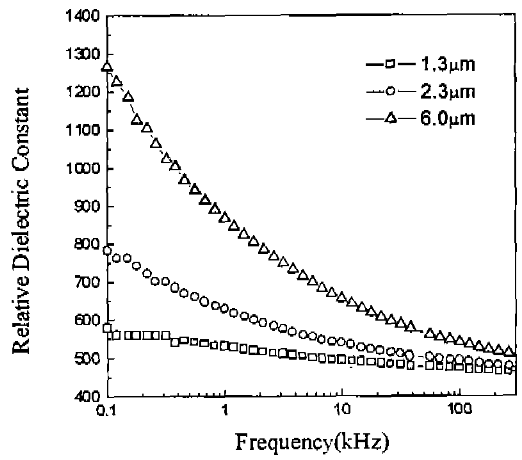
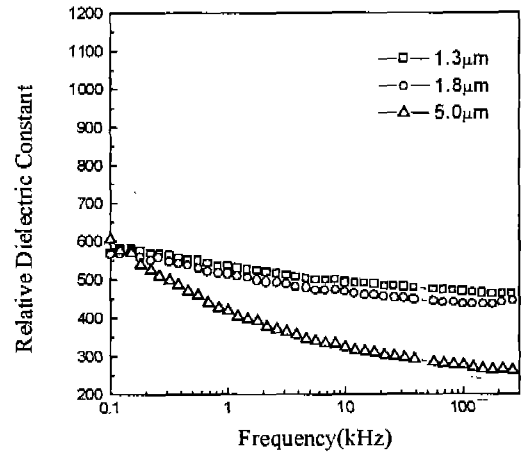


Fig. 1. Variation of relative dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$ ceramic measured at 1kHz as a function of grain size. (a) PbO-deficient condition($Pb_{0.9}La_{0.1}TiO_3$ powder) and (b) PbO-sufficient condition($PbZrO_3$ powder).



(a) PbO-deficient condition($Pb_{0.9}La_{0.1}TiO_3$ powder)



(b) PbO-sufficient condition($PbZrO_3$ powder)

Fig. 2. Frequency dependence of dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$.

property is more influenced by the sintering atmosphere as the sintering time gets longer, considering that the 6.0 μm-samples which were sintered for 30 hours in the PbO-deficient condition show almost two times higher value than those sintered in PbO-sufficient condition.

Fig. 2 shows the frequency dependence of the dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$ as a function of grain size. As the grain size increases, the dielectric constant is intensively relaxed with the frequency in the case of the samples sintered in PbO-deficient condition as shown in Fig. 2(a). However, Fig. 2(b) indicates that the dielectric constant of the samples sintered in PbO-sufficient condition does not almost depend on the frequency. The 5.0 μm-sample is only decreased slightly with the frequency. Fig. 2(a) represents that the region where the relaxation of the dielectric property occurs is located in the range of a low frequency. It is known that the polarization mechanism which makes a dominant contribution to the dielectric property in a low frequency region results from the space charge.[16] The space charge is defined as the mobile charges which are present because they are impeded by interfaces, because they are not supplied at an electrode or discharged at an electrode, or because they are trapped in the material.[16] Above results confirm that the space charge affects the dielectric property in $Pb_{0.9}La_{0.1}TiO_3$ system when they are sintered in PbO-deficient condition.

Fig. 3 represents the variation of piezoelectric d_{33} constant of $Pb_{0.9}La_{0.1}TiO_3$ ceramic of which the grain size is in the range of 1.3~2.7 μm. The poling condition was 6 kV/mm at 100°C for 10 min. All the samples showed the saturation behavior of d_{33} over 2 kV/mm. The value of d_{33} intensively decreases with the grain size in the case of the sample sintered in PbO-deficient condition, while there is almost no change in PbO-sufficient condition. The piezoelectric property of $Pb_{0.9}La_{0.1}TiO_3$ ceramic is not affected by the grain size in the range of 1.3~2.7 μm, considering that the piezoelectric constants of the samples sintered in PbO-sufficient condition are almost the same. It also means that the poling treatment was effectively done because it is needed to induce the piezoelectric property. However, the poling treatment became less successful in the case of PbO-deficient condition as the grain size increased as shown in Fig. 3. High leakage current was released during poling process in the case of the samples sintered in PbO-deficient condition. It is considered that the samples sintered in PbO-deficient condition do not have enough resistivity to be poled. It confirms that the samples should be sintered in PbO-sufficient condition, which means that the atmospheric powder should be more volatile than the samples to be sintered in $Pb_{0.9}La_{0.1}TiO_3$ system.

(2) Effect of Grain Size on Dielectric Property in PbO-sufficient condition

Fig. 4 shows the variation of relative dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$ as a function of grain size. They were sintered for 0.5~20 hours in PbO-sufficient condition made by $PbZrO_3$ powder. The amount of $PbZrO_3$ was fixed to 1g and 5g, respectively. 1g of $PbZrO_3$ powder is expected to make the sintering atmosphere less PbO-sufficient than 5g as the sintering time becomes longer. When the sintering time is short enough, the variation of the dielectric constant shows no change regardless of the amount of $PbZrO_3$. However, the difference of the dielectric constant between both kinds of samples gets larger as the sintering time increases though they are of the same grain size. The samples sintered in 1g of $PbZrO_3$ shows a similar trend to those sintered in PbO-deficient condition as shown in Fig. 1, when the sintering time is too long. It indicates that the contribution of the space charge to the dielectric property becomes larger when the sintering atmosphere remains PbO-deficient for a long time during the sintering process.

Meanwhile, the dielectric constant of the samples sintered in 5g of $PbZrO_3$ monotonously decreases with the grain size. It is confirmed that the space charge effect on the dielectric property is perfectly excluded in this case. When the sinter-

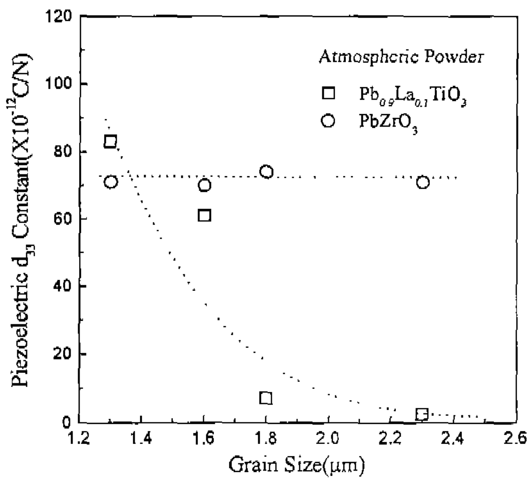


Fig. 3. Variation of Piezoelectric d_{33} constant as a function of grain size.

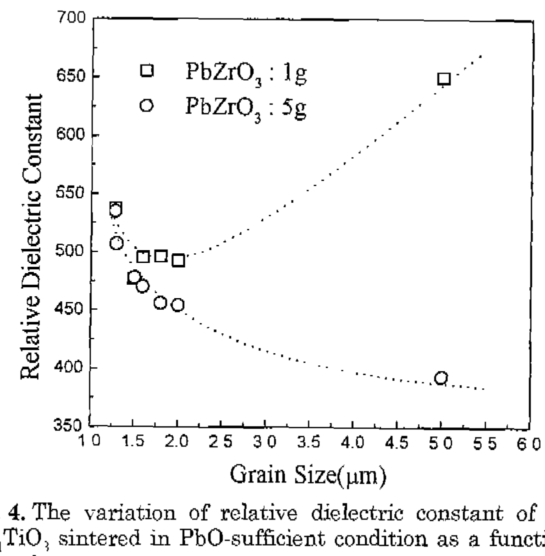


Fig. 4. The variation of relative dielectric constant of $Pb_{0.9}La_{0.1}TiO_3$ sintered in PbO-sufficient condition as a function of grain size.

ing time is long enough, for example, such as the case of 5 μm-samples, other factors, the evaporation of PbO, or micro-cracks, or the second phase should be also concerned in lead based ferroelectric ceramics although the sintering atmosphere can be sustained PbO-sufficient. How-ever, it is considered that the internal stress can be an important factor to explain the grain size effect of dielectric property when the sintering time is short enough for example, 0.5~2 hours, and the grain size is in the range of 1.3~2.7 μm. The author reported that the internal stress model could be applied to $Pb_{0.9}La_{0.1}TiO_3$ system by modifying the assumption that there are no 90° domains in the fine grained ceramic.[10] Each 90° domain wall was assumed to be a stressed particle, which Buessem *et al.*[2,3] proposed at that time. Therefore, the contribution of 90° domain wall to the increase of dielectric constant is expected in the fine grained region as the grain size decreases. Instead, such a result may be covered with other effects such as the case of PbO-deficient condition, where the space charge makes more contribution to the dielectric property. It means that the dielectric property as a function of grain size is rather a process dependent property in the lead based ferroelectric ceramics.

(3) Origin of Space Charge in $Pb_{0.9}La_{0.1}TiO_3$ Ceramic

There exist many vacancies in $Pb_{0.9}La_{0.1}TiO_3$ system because the substitution of La^{+3} for Pb^{+2} creates Pb vacancies to satisfy the electrical neutrality condition. According to Hennings *et al.*,[11-12] the formation of Ti^{+3} at B-site in $Pb_{1-x}La_xTiO_3$ system is possible in the oxygen deficient sintering condition to compensate the additional positive charge introduced at A-site by the La^{+3} ions. It is also reported that the Pb or Ti vacancies are generally formed instead of Ti^{+3} for the charge compensation when La^{+3} is doped over 5 mol%.[11,12] However, they did not describe in detail on other cases that the valence state of Ti^{+4} ions can change to +3. In PLZT system, which is expected to have a similar vacancy structure to $Pb_{0.9}La_{0.1}TiO_3$ ceramics, Ti^{+4} ions can change to Ti^{+3} to compensate the extra positive charge, which is called induced valency phenomenon.[17]

In this experiment, the samples, which have abnormally high dielectric constant and low piezoelectric constant showed a blackened yellow though they were annealed in air after sintering, while those in PbO-sufficient condition still have a yellow-lemon color. Therefore, it is considered that the Ti^{+3} ions are formed in PbO-deficient sintering atmosphere. If Ti^{+3} ions are assumed to exist in the case of PbO-deficient condition, they will act as donor centers or make couplings with other ions or vacancies in the lattice. According to Laguta's report,[18] Ti^{+3} which has a coupling with oxygen and Pb vacancies was appeared in pure $PbTiO_3$ single crystal. It is more possible in La-doped $PbTiO_3$ because La^{+3} ions are expected to create more vacancies in the lattice. That is, they have a role of the space charge to make contribution to the dielectric property in a low frequency region. It is reported that Fe-doped $BaTiO_3$ ceramic showed a dielectric dispersion in a low frequency region, which was resulted from the space charge formed by the doping of Fe.[19] Therefore, Ti^{+3} ions is expect to operates as the space charge center, considering the valence state of Fe ion is +2 or +3 in the lattice different from Ti^{+4}.

Meanwhile, T^{+3} ions in the lattice will also make the poling treatment less effective. The ceramics should have low resistivity compared with that of insulators for the effective poling. In the case of 180° domain during poling treatment, Ti^{+4} ions move toward the poling direction by the applied electric field. However, Ti^{+3} ions existing in the lattice is expected to release an electron, disturbing the switching of Ti ions. It may appear as a form of leakage current during the poling treatment. Therefore, it is considered that the samples sintered in PbO-deficient condition were not effectively poled, discharging the leakage current during poling, and decreasing the piezoelectric constant after poling as the grain size increases.

IV. Conclusions

Dielectric property of $Pb_{0.9}La_{0.1}TiO_3$ ceramic which was sintered in a different sintering atmosphere was investigated as a function of grain size in the range of 1.3~6.0 μm. The dielectric constant increased with the grain size in the case of PbO-deficient atmosphere, which was made by $Pb_{0.9}La_{0.1}TiO_3$ powder. The frequency dependence became larger as the grain size increased in the PbO-deficient condition, which was due to the space charge polarization. The dielectric constant monotonously decreased with the increase of grain size in the case of PbO-sufficient atmosphere, which was made by $PbZrO_3$ powder. The variation of dielectric constant was explained by the internal stress model in a fine grained region. However, the dielectric constant increased again with the grain size over 2 μm when the amount of the atmospheric powder, $PbZrO_3$ was changed from 5 g to 1 g.

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