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용융염 합성법에 의한 PLZT 세라믹스의 제작과 그 전기적 · 광학적 특성

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Electrical and Optical Properties of PLZT Ceramics Prepared by Flux Method

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ABSTRACT

$(Pb_{1-x}La_x)(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$ (PLZT X/65/35) powders were prepared by molten salt synthesis using NaCl-KCl and conventional calcining of oxides. The effects of molten salt on formation and charactrization of PLZT powder, and on dielectric, piezolectric and optical properties of PLZT ceramics, were studied.

The completed PLZT powder formation in the presence of fused salt was attained at 50−100°C lower temperature than that in solid state reaction, and the particle size of the powder made by molten salt synthesis was markedly increased with increasing calcining temperature. The substitution of Na and/or K ions in NaCl-KCl for Pb ion in process of molten salt synthesis, was increased with increasing La concentration X. These substituted Na and/or K ions were identified as the origins of decreasing coupling factor and optical transmittance of PLZT ceramics.

1. Introduction

Molten salt synthesis is one of the important preparation methods of ceramic powder such as ferrite and ferroelectric oxide.[1-2] This technique holds out the possibility of producing a more homogeneous and more fully reacted ceramic powder than that of conventional calcination of some oxide powders, because the effective contact area between particles and also the reaction rate are greater than those of conventional powder processing. Furthermore, for the making the grain oriented ceramics, plate- or needle-like particle can be prepared by both controlling the shape anisotropy and selecting the starting materials.[3-4] However, the molten salt solvent has a possibility to act as a medium of the reaction between the constituent oxides.[5]

In present work, PLZT powders were prepared by molten salt synthesis using NaCl-KCl and by conventional calcining of oxides. The characterization of molten salt synthesized PLZT powder, and the dielectric, piezoelectric and optical properties of ceramics were examined, and they were compared to those prepared from the conventional calcining oxides. The influence of La substitution in the composition 65/35 Zr/Ti ratio was also investigated and discussed.

2. Experimentals

2.1. Sample preparation

Highly purified raw materials – PbO, La_2O_3, ZrO_2 and TiO_2 – were used for the composition of $(Pb_{1-x}La_x)(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$ (abbreviated to PLZT x/65/35, x=0–10). Weighed powders were mixed with distilled water for 6 hours using polyethylene pot with alumina balls, and then dried above 100°C.

In case of molten salt synthesis, the dried oxides were mixed again with salts of NaCl-KCl in agate mortal for 30 minutes. Amount of salt, F, was defined by

F = total moles of salts / total moles of oxides

The mixed powders of F=0 (conventional method; CON), F=1 and F=2 (molten salt method; FLUX), were calcined at a temperature range from 650 to 1150°C for 5 hours. The salt was washed after calcination with hot water several times until no Cl^- was detected by $AgNO_3$ test solution.

Both calcined powders (CON and FLUX) were mixed with 8 wt.% of PVA solution, and they were pressed into disk 15 mm in diameter and 3–5 mm in height under a pressure of 1000 Kg/cm^2. The pressed compacts were sintered by both ordinary firing and hot-pressing at a temperature range from 1150 to 1250°C for 2–3 hours.

2.2. Measurements

The particle morphology of PLZT powder was examined using a SEM microscopy. The reaction rate of PLZT formation was determined by X-ray analysis. An atomic absortion spectrophotometer was also used to determine the contents of Na and/or K in PLZT powders.

The grain size of PLZT ceramics sintered was measured by a linear-intercept method using SEM micrographs of the optically polished and thermally etched surfaces, where the thermal etching condition was 1100~1200°C for 1–2 hours. For measurements of the dielectric and piezoelectric constants, gold was sputtered on both sides of the PLZT ceramic specimens with a thickness of 0.8 mm. The relative permittivity was measured using an LCR meter at 1 KHz. Specimens were subsequently poled in a silicon oil bath at 50 to 60°C for 20 minutes under a DC field of 3 KV/mm for measurements of coupling factor. The optical transmittance of PLZT ceramics were measured by a spectrophotometer for the optically polished and thermally depolarized samples, in a wavelength range of 400 to 1400 mμ.

3. Result and discussion

3.1 Effect of flux on PLZT formation

Figure 1 shows the SEM micrographs of typical CON and FLUX PLZT 8/65/35 powders calcined at various temperatures for 5 hours. As can be seen, the powders obtained do not have shape-anisotropy. We can observe some of the primary powders which are not reacted in a sample calcined at 750°C by conventional method. The remarkable result is that the average particle size of PLZT powder prepared by flux method [FLUX] increases radically with increasing of calcining temperature. In case of calcining at 1150°C, the particle size of FLUX (3.8 μm in diameter) was 2.6 times larger than that of CON.

Figure 2 illustrates the effect of molten salt on formation of PLZT 8/65/35 powder, where the fraction reacted (α) is plotted against the calcining temperature for F=0, F=1 and F=2 respectively. The fraction reacted is defined by

$$\alpha = I_{PLZT} / (I_{PLZT} + I_{ZrO_2})$$

where I_{PLZT} and I_{ZrO_2} are relative X-ray diffraction intensity of PLZT and ZrO_2 respectively. As can be seen, the fraction reacted is promoted by fused salt, and PLZT formation of FLUX is completed at 50–100°C lower compared to that of CON. It is also shown in Fig. 2 that the

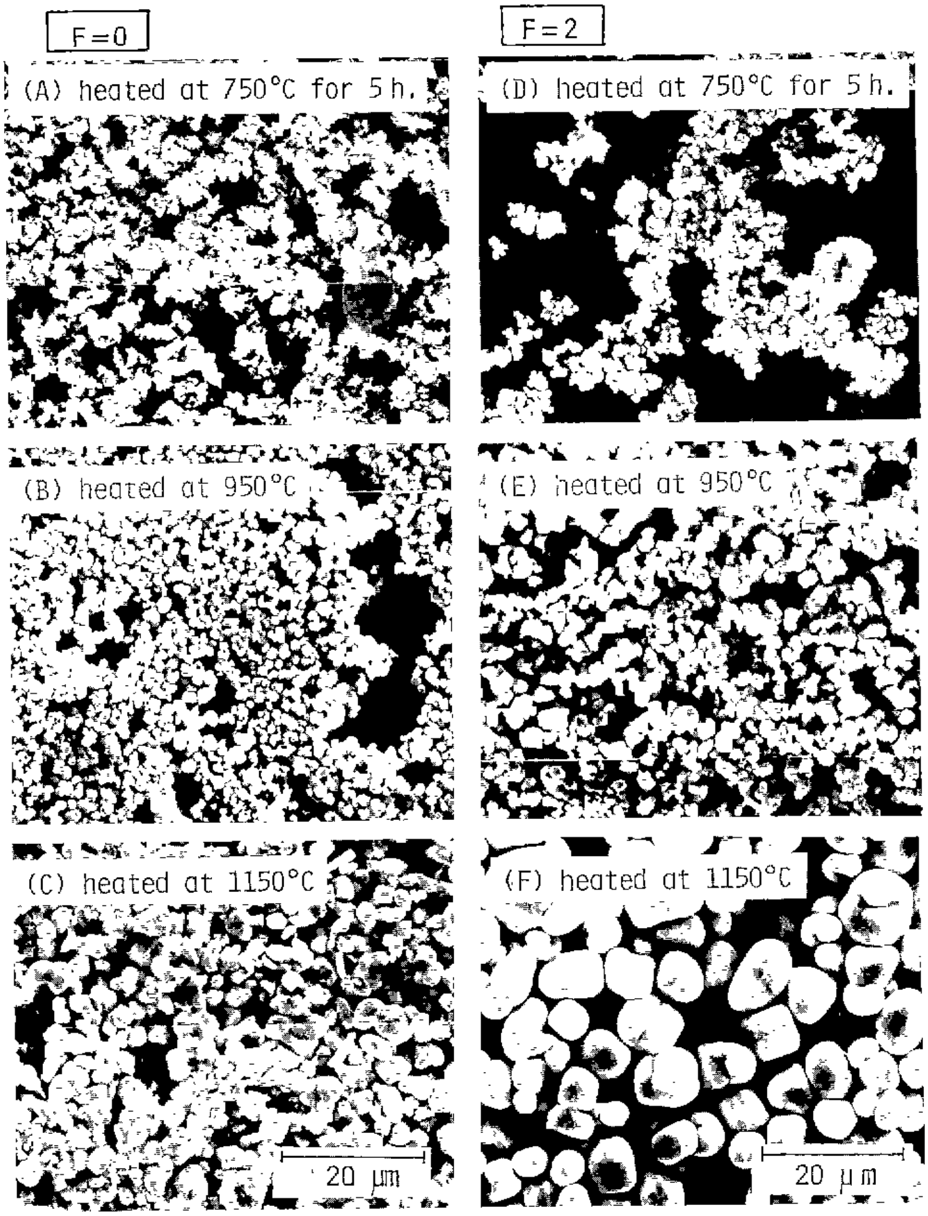

Fig. 1. SEM of PLZT 8/65/35 powder after heat-treatment at various temperature.

reaction rate of F=2 is slightly higher than that of F=1.

Figure 3 shows SEM micrographs of the polished and thermally etched surfaces of PLZT 8/65/35 ceramics sintered at 1200°C for 2 hours. Figure 4 shows dependence of calcining temperature on the particle size of PLZT 8/65/35 powder and grain size of PLZT 8/65/35 ceramics. As shown in Fig. 3 and 4, the grain size of PLZT ceramics from CON calcined at below 950°C is almost the same as that from FLUX. However, in sample calcined at 1150°C, the grain size of FLUX is 1.5 times larger than that of CON.

From the facts described above, it may be

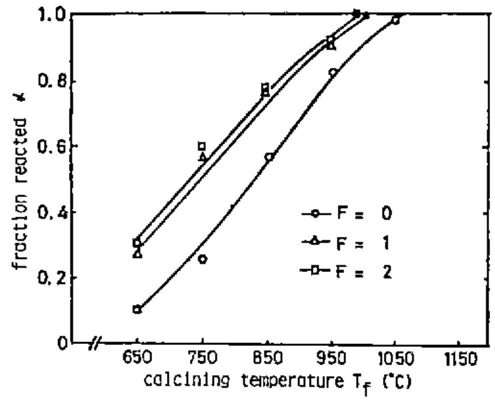

Fig. 2. Fraction reacted of PLZT 8 / 65 / 35 powder as a function of calcining temperature.

concluded that the paticle size of PLZT powder and grain size of PLZT ceramics are more promoted in sample produced by molten salt synthesis.

3.2 Piezoelectric and optical properties

Figure 5 shows the electromechanical coupling factor k_p of PLZT 8/65/35 ceramics for radial mode vibration as a function of calcining temperature, for samples sintered at 1150 and 1200°C respectively. For samples sintered at 1150°C, the coupling factor of FLUX is larger in sample calcined below 750°C, but smaller in sample calcined above 850°C compared to that of CON. While in the samples sintered at 1200°C, the coupling factor of CON is larger than that of FLUX in all range of calcining temperature.

Figure 6 shows the wavelength dependence of optical transmittance for samples prepared by both conventional method and molten salt method. As can be seen, the optical transmittance of FLUX is 55% for wavelength above 1200 mμ, but that of CON is 64% for the same wavelength range.

As described above, the coupling factor and optical transmittance of molten salt synthesized PLZT 8/65/35 ceramics were smaller compared to those of conventional method. To explain

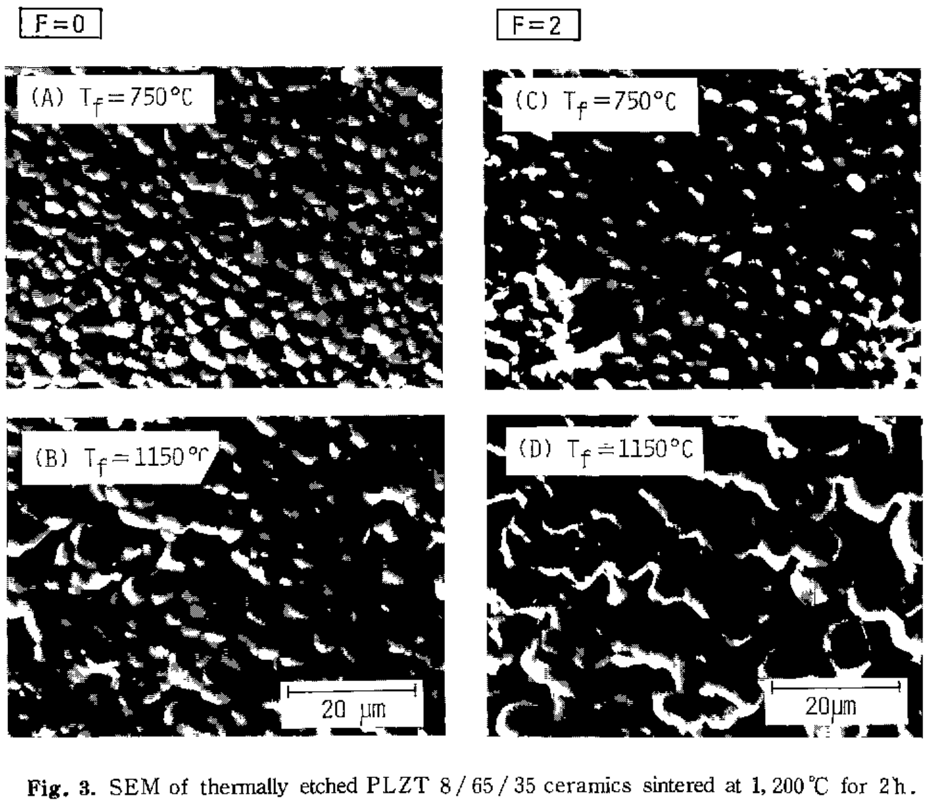

Fig. 3. SEM of thermally etched PLZT 8 / 65 / 35 ceramics sintered at 1,200℃ for 2h.

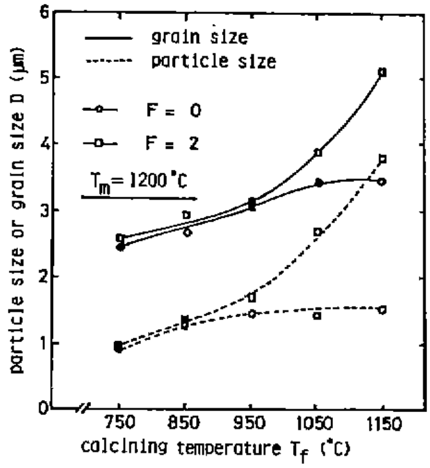

Fig. 4. Particle size of PLZT 8/65/35 powder and grain size of PLZT 8/65/35 ceramics as a function of calcining temperature.

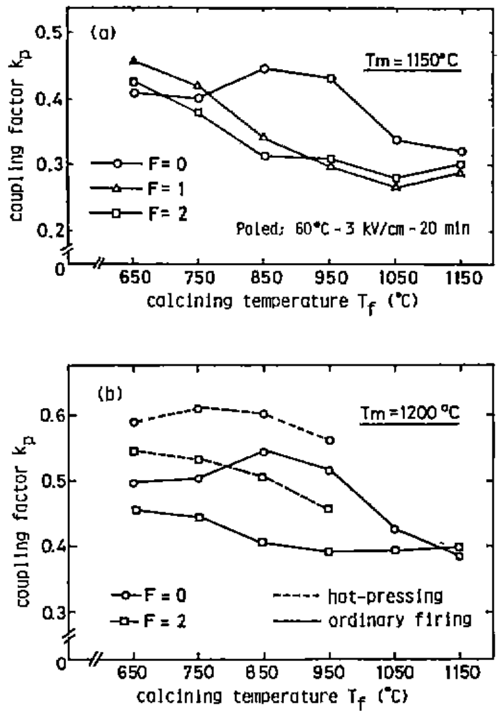

Fig. 5. Coupling factor of PLZT 8/65/35 ceramics as a function of calcining temperature.

this fact, the content of Na and/or K in molten salt synthesized PLZT x/65/35 (x=0–10) powders was determined by an atomic absorption spectrophotometer. As shown in figure 7, 0.38 wt. % of

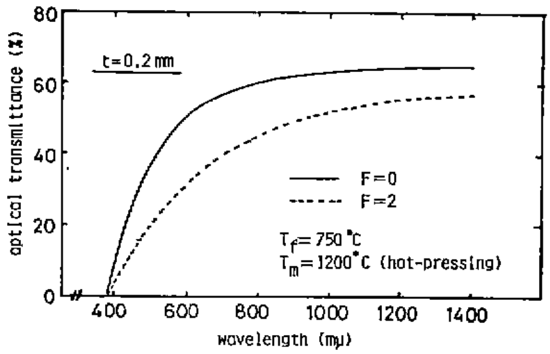

Fig. 6. Optical transmittance of hot-pressed PLZT 8/65/35 ceramics as a function of wavelength.

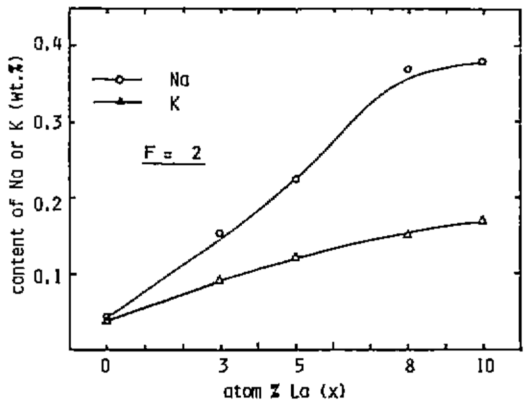

Fig. 7. Content of Na and/or K as a function of La composition x, in molten salt synthesized PLZT x/65/35 powder.

Na and 0.17 wt. % of K are included in sample x=10. An interesting result is that the content of Na and/or K in PLZT powder is increased with increasing La concentration x. It can be considered that Na and/or K ions in NaCl and/or KCl may be coupled with La and they are substituted for Pb ion in PLZT powder, in process of molten salt synthesis. These substituted ions Na and/or K cause decreasing coupling factor and optical transmittance.

3.3 Influence of La concentration

The influence of La concentration on relative permittivity of PLZT ceramics is shown in figure 8, where the relative permittivity is plotted against temperature for PLZT x/65/35 ceramics

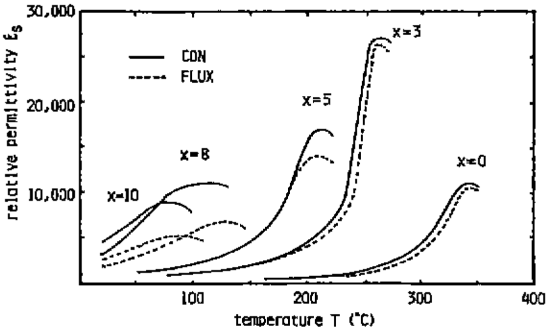

Fig. 8. Temperature dependence of relative permittivity for PLZT x/65/35 ceramics.

with x=0–10. As can be seen, the peaks in relative permittivities were reduced in temperature and in height as La content increased. These results are in good agreement with the curves reported by Haertling et al.[6] But the relative permittivities of FLUX were lower than those of CON in all range of x. The remarkable result is that Curie temperature of FLUX is 15–20°C higher compared to that of CON, especially in samples of x=8 and x=10. This result also seems to be caused by the fact that the substitution of Na and/or K ions for Pb ion in PLZT increases with increasing La content.

Figure 9 illustrates the coupling factor as a function of La concentration x for PLZT x/65/35 samples prepared by both conventional method and molten salt synthesis. As shown in this figure, the coupling factor of CON increases with increasing La content x going through a maximum at x=8. While the coupling factor of FLUX is maximized at x=5, and the values are smaller compared to that of CON in all range of x, especially at x=8.

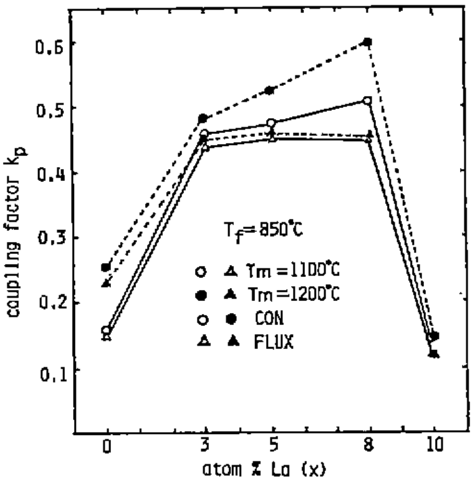

Fig. 9. Coupling factor of PLZT x/65/35 ceramics as a function of La composition x.

4. Conclusion

The results obtained in this study are summarized as follows;

1. The completed PLZT formation in the presence of fused salt was attained at lower temperature than that in solid state reaction.
2. The particle size of PLZT powder and grain size of PLZT ceramics prepared by molten salt synthesis increased with increasing calcining temperature.
3. The substitution of Na and/or K ions for Pb ion in molten salt synthesized PLZT powder increased with increasing La concentration and these substituted Na and/or K caused decreasing of the coupling factor and optical transmittance.

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