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Electrical properties of grain and grain boundary in PFW ceramics

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Anomalous rise in dielectric constant above room temperature was observed on PFW dielectrics prepared by a conventional solid state reaction using PbO, Fe_2O_3 and WO_3 powders. From a complex impedance analysis at higher temperature, the equivalent electrical circuits were constructed from a series connection of two RC parallel circuits. They were related to grain and grain boundary, respectively. The anomalous rises in dielectric constants of specimens were suppressed by reduction in N_2 atmosphere, slow cooling from sintering temperature and addition insulating additives. It was clear that the anomalous rise in the dielectric constant was due to the decreasing of the resistivity of grain in PFW ceramics.

1. INTRODUCTION

$Pb(Fe_{1/3}W_{2/3})O_3$ (hereafter designated PFW) is one of the most sinterable lead-based perovskite ferroelectric compound at lower temperature. The dielectric properties and diffuse phase transition for PFW have been reported in the brief note[1]. However, there are few reports on the anomalous steep risein dielectric constant and dissipation factor above the Curie temperature. The rising temperature of dielectric constant was shifted toward higher temperature with increasing frequency. In several recent studies, it has been tried to demonstrate the anomalous rise in dielectric constant using a complex impedance analysis method [2,3].

In this study, ac measurement and equivalent circuit representation were used to evaluate the properties of the grain and the grain boundary. Furthermore, the relation ship between anomalous dielectric phenomena and the grain and the grain boundary characteristics were tried to clarify.

2. EXPERIMENTAL

2.1. Sample preparation

All samples were prepared by a conventional solid state reaction using reagent grade PbO, Fe_2O_3 and WO_3 powders at elevated temperature. The powder mixtures were ball-milled for 12 hours, dried and calcined at 750°C for 2 hours and pressed into a disc 10mm in diameter and 3mm thick using cellulose binder. The binder was burned out in air at 400°C.The discs were sintered in a closed magnesia crucible at 870°C for 2 hours in O_2 or air. The magnesia crucible was pre-coated on its inside by the PFW powder for suppressing the vaporization of PbO from the discs. A weight loss on sintering was kept less than 3wt% for all the samples. Relative densities were approximately 90-95%. The samples were heated in O_2,N_2 and air at 878°C for 2 hours.

2.2. Electric measurement

In-Ga alloy electrodes were employed to measure the electrical properties on their polished surfaces of specimens. An impedance analyzer (HP4192A;Hewlette Packard Ltd.) was used from 1 to 1000KHz to measure the dielectric constant. A dc multimeter was used for resistance measurement. Applied voltage was 0.1 V/mm across the sample.

3. RESULTS AND DISCUSSION

3.1. Anomalous rises in the dielectric constant

Figure 1 shows the typical temperature dependence of dielectric constant of PFW prepared in O_2 at various frequencies.

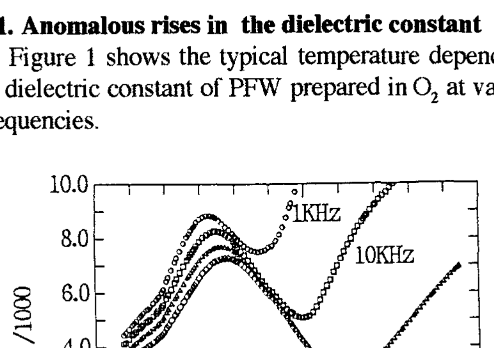


Figure 1. Temperature dependence of dielectric constants of PFW.

The temperature-dielectric constant curves revealed a broad maximum around -60°C related to disperse phase transition(DPT) and anomalous rise above the DPT. The anomalous rise in dielectrics constant was shifted to higher temperature with increasing frequency.

3.2. Impedance analysis

An impedance analysis was carried out to find out the origin of the abnormal dielectrics. Figure 2 shows a Cole-Cole plot of PFW measured at various temperatures. The samples were prepared in O_2.

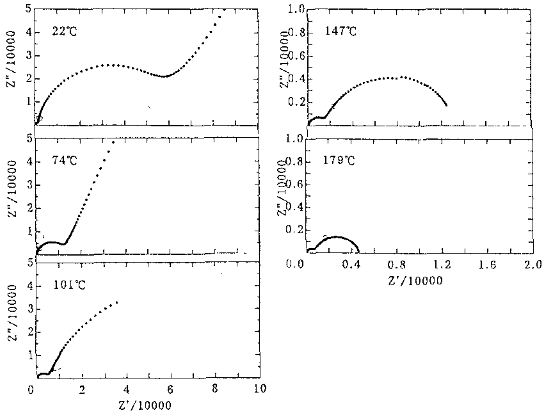
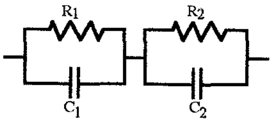


Figure 2. Cole-Cole plot at various temperature

All the plots are consist of two semicircles. Each semicircle was related to three regions, such as grain, grain boundary and interface between electrode and PFW sintered bodies. Nevertheless, the effect of this interface could be ignore, because of no difference in the Cole-Cole plot for different electrode materials. Therefore, properties of grain and grain boundary were appeared on the Cole-Cole plots. Those plots can be analyzed using an equivalent circuit with a series connection of two resistance and capacitance parallel circuits as following.



The equivalent circuit in Figure 2 was given as following equation.

$$Z=\frac{R_1}{1+\tau_1{}^2w^2}+\frac{R_2}{1+\tau_2{}^2w^2}-j\left[\frac{R_1\tau_1 w}{1+\tau_1{}^2w^2}+\frac{R_2\tau_2 w}{1+\tau_2{}^2w^2}\right] \quad (2)$$

Here τ_1 is $R_1 \cdot C_2$ and τ_2 is $R_2 \cdot C_2$. R_1 and C_1 parallel circuit represent the left smaller semicircle and R_2 and C_2 parallel circuit represent larger one in the figure. The calculations of R_1, R_2, C_1 and C_2 were carried out by following the previous study [4].

Figure 3(a) shows the temperature dependence of capacitance on grain and grain boundary regions and Figure 3(b) shows the logarithmic resistance of both regions. Since C_2 value was too large compared with the typical PFW ceramics, both R_1 and C_1 were related to the grain, and both R_2 and C_2 were related to the grain boundary.

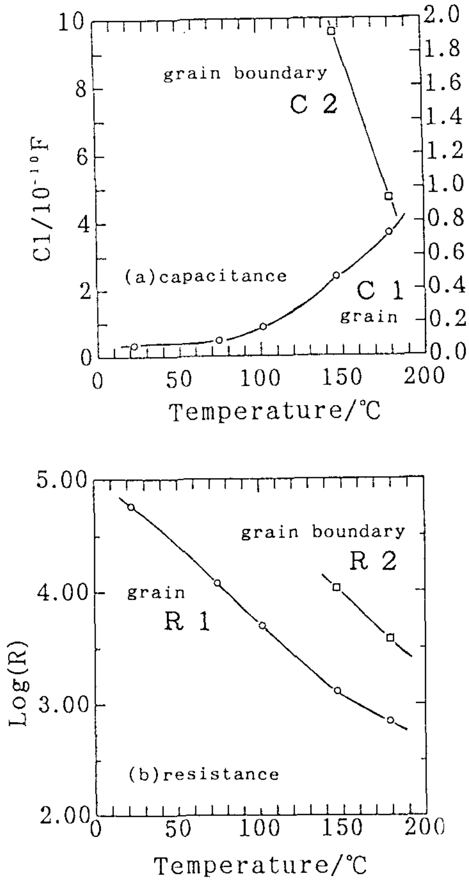


Figure 3. Temperature dependence of grain and grain boundary of (a)capacitance and (b)logarithmic resistance.

The capacitance of grain, C_1 ,slightly increased with the temperature, while, C_2 decreased with the temperature and was larger than C_1 about 2 or 3 orders of magnitude. The resistances of both grain and grain boundary decreased with the temperature up to 200°C.

In the equation (1), if C_2 is much larger than C_1 and R_1 is smaller than R_2, the apparent capacitance is approached to C_2. Therefore, as the temperature increased, the apparent capacitance became larger than that of grain C_1. Consequently, the anomalous rise in dielectric constant was observed at higher temperature.

3.3. Resistivity of sample

To suppress the anomalous rise in dielectric constant, the resistivity of grain should be large. There are some ways to make the grain and the grain boundary with high electrical resistivity. Figure 4 shows the change of the resistivity with reciprocal temperature. The samples were heated in O_2 and N_2 at 878°C. The resistivity of the sample prepared in N_2 was large about one to two orders of magnitude over that of the sample prepared in O_2 atmosphere. The carrier of electrical conductivity in the sample prepared in O_2 was determined to be hole by a seebeck measurement. The holes were made from Pb vacancy[5], which existed in the sample prior to the reduction. The reduction of the sample in N_2 reduced the carrier concentration. No anomalous dielectric phenomena were observed in the reduced sample in N_2.

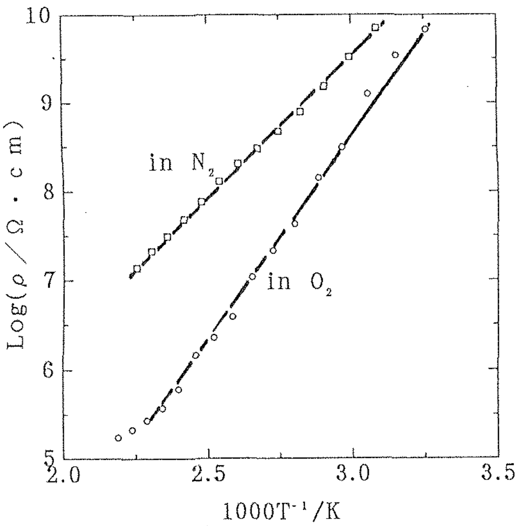


Figure 4. Reciprocal temperature dependence of logarithmic resistivity.

Another methods were tried to increase the resistance in PFW ceramics. Figure 5 shows the SEM photographs of fracture surface of (a)rapid cooling and (b)slow cooling samples from 880°C in air.

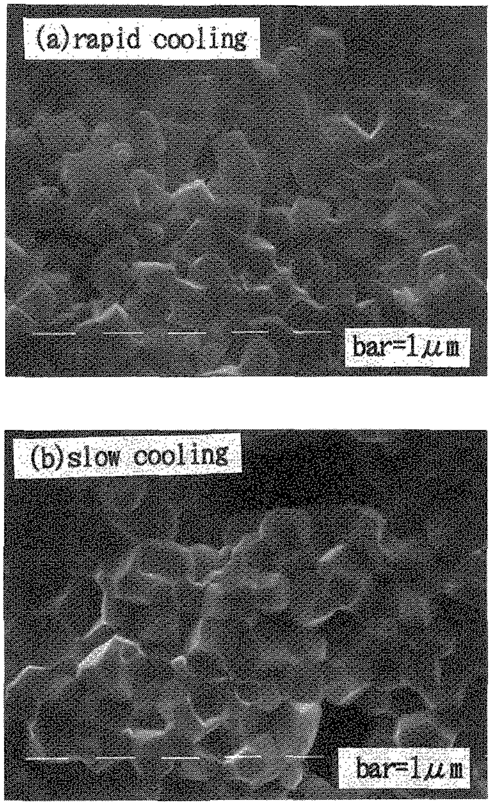


Figure 5. SEM photograph of fracture surfaces of PFW prepared (a)rapid cooling and (b)slow cooling.

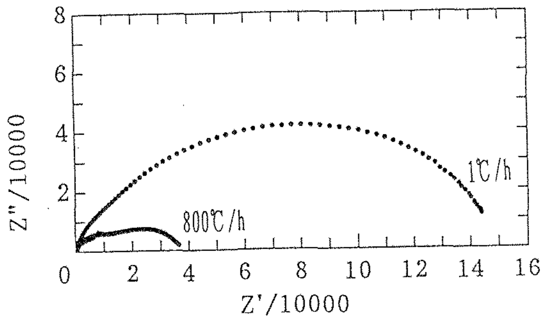


Figure 6. Cole-Cole plots of PFW prepared by rapid and slow cooling.

The grain sizes of each sample were almost the same. Second phases or grain boundary phases were observed in a quenched sample but not observed in slow cooled sample. The Cole-Cole plots of both sample are shown in Figure 6. The quick cooled sample showed the pattern consisted of two small semicircles. This shows the resistivities in both grain and grain boundary. On the other hand, the slow cooled sample had only one semicircle and its resistance was large. In the slow cooled sample, the grain boundary phenomena could be neglected and no abnormal dielectric phenomena were observed.

Figure 7 shows the temperature dependence of the resistivity of the grain R_1 estimated from the Cole-Cole plots of various samples. The samples were diffused MnO_2 and CuO into grain and grain boundary from the surface. The heat treated samples in various atmospheres were also shown as a reference.

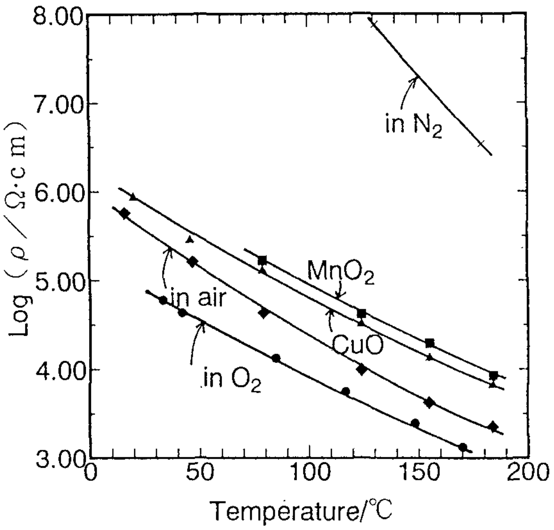


Figure 7. Temperature dependence of resistivity of PFW prepared by various conditions.

MnO_2 was usually used to make high insulating resistivity in lead-based perovskite dielectrics. CuO was used as an insulating additive for semi-conducting $BaTiO_3$ or $SrTiO_3$. Both MnO_2 and CuO diffused samples were increased in resistivity and disappeared abnormal dielectric phenomena.

4. CONCLUSIONS

Abnormal dielectric phenomena were observed over the Curie temperature in PFW ceramics. From the impedance analysis of sample, grain and grain boundary properties were observed independently. The abnormal dielectric phenomena were carried out by decreasing the resistivity of grain and emphasized grain boundary capacitance. To prevent anomalous phenomena, resistibilities were tried to make large by different three methods. The reduction by N_2, slow cooling from sintering temperature and using to insulating additives were effective way to improve the electrical properties for PFW ceramics.

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