

Dielectric Properties of Layered $Ba_{1-x}Sr_xTiO_3$ Ceramics

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1. Introduction

Pure $BaTiO_3$ shows a paraelectric to ferroelectric phase transition at 120°C , which is accompanied by a sharp peak in the dielectric permittivity. Partial substitution of either Ba ions or Ti ions is often employed to modify the nature and temperature of the paraelectric-ferroelectric transition for particular applications. $SrTiO_3$ is usually added as a shifter in order to move the T_C to lower temperatures because it is well established that the Curie point of $BaTiO_3$ decreases linearly with a solid solution of Sr^{+2} in place of Ba^{+2} . It is not fully understood yet, however, how $SrTiO_3$ effects on the peak value of dielectric constant at the Curie temperature of $Ba_{1-x}Sr_xTiO_3$ solid solutions. This paper reports the variation of the dielectric constant of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions at the Curie temperature in the range of $x=0\sim 0.6$. Specimens were sintered between $1350^\circ\sim 1450^\circ\text{C}$ in order to investigate the microstructure dependence of the dielectric constant of the material.

A number of additives have been associated with the ability to flatten the dielectric constant versus temperature characteristic of $BaTiO_3$. A sharp peak of dielectric constant at T_C can be easily flattened, and therefore the temperature coefficient of dielectric constant can be reduced, by adding the depressor material, such as $CaTiO_3$ and $MgTiO_3$. However, one of the most important characteristics of $BaTiO_3$, a very high dielectric constant at T_C , should be sacrificed. If the Curie point can be changed as a function of position by grading its composition, the transition from the paraelectric to the ferroelectric phase would be broadened with respect to the temperature. Consequently, the temperature coefficient of the dielectric constant could be lowered. In the present investigation, multi-layered $Ba_{1-x}Sr_xTiO_3$ composites were fabricated by using the concept of FGMs in order to reduce the temperature coefficient of the dielectric constant without depressors.

2. Experimental

Specimens were prepared from commercial $BaTiO_3$ (Fuji Titanium Industry Co., Japan) and $SrTiO_3$ (Ferro Corp., Penn Yan, NY, USA) powders. According to the data provided by the producers, the purity and average grain size of $BaTiO_3$ were 99.8% and $0.63\mu\text{m}$, respectively, and those of $SrTiO_3$ were 99.8% and $1.3\mu\text{m}$. Powder slurries were made by mixing $(BaTiO_3)_{1-x}(SrTiO_3)_x$ (in unit of mol%) powder mixtures (where $x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6$) for 24 h in polyethylene bottle with ethyl alcohol and zirconia balls. The dried slurry was crushed in an agate bowl and sieved to $125\mu\text{m}$. The pure $BaTiO_3$ and mixed powders were slightly pressed into disks 10mm in diameter and 2mm in thickness and then isostatically pressed again under 150MPa. The compacts were sintered $1350^\circ, 1400^\circ, 1450^\circ\text{C}$, respectively for 1 hour in air. In the case of multi-layered compaction, the prepared powders were stacked sequentially with stepwise changes in mixing ratio and pressed into $10\times 10\times 10$ mm. The compacts were isostatically pressed again under 150 MPa and then sintered at 1400°C for 1 h in air.

The microstructures of the sintered specimens were observed by an optical and a scanning electron microscope after etching polished sections. The dielectric constant of the single- and multi-layered specimens with silver electrodes were measured by an impedance/gain-phase analyzer (HP4194) at 1 kHz from -150°C to $+150^\circ\text{C}$.

3. Results and Discussion

In the case of $Ba_{1-x}Sr_xTiO_3$ specimens sintered $1350^\circ C$, the Curie temperature and the peak value of the dielectric constant decreased with increasing $SrTiO_3$ contents. When the sintering temperature was increased to $1400^\circ C$, however, the dielectric constant maximum increased with an increase in the x value, reaching highest value at $x=0.4$ and then decreased. The dielectric constant maximum of $Ba_{1-x}Sr_xTiO_3$ specimens sintered $1450^\circ C$ monotonically increased with increasing $SrTiO_3$ contents up to $x=0.6$.

$BaTiO_3$ is well known to grow by abnormal grain growth mode during sintering. In the case of sintering pure $BaTiO_3$ and $Ba_{0.9}Sr_{0.1}TiO_3$, $1350^\circ C$ for 1 hour is enough to finish abnormal grain growth. In the composition of $x>0.2$, abnormal grain growth is still on going and the microstructure shows a bimodal structure consisting of abnormally growing grains and fine matrix grains. The average grain size and total volume fraction of abnormally growing grains were decreased with increasing $SrTiO_3$ contents. When sintering temperature was increased to $1400^\circ C$, almost all the fine matrix grains were disappeared up to $x=0.3$ but they still present in the composition of $x>0.4$. Under the sintering condition of $1450^\circ C$ for 1 hour, however, fine matrix grains were not observed even $x=0.6$.

The dielectric constant vs temperature of layered $Ba_{1-x}Sr_xTiO_3$ ($x=0\sim 0.4$, step of 0.02, each layer has the same thickness) sintered at $1400^\circ C$ showed a linear characteristic in the temperature range between 20° and $120^\circ C$. But there is a slope of the linear dielectric constant vs temperature due to a difference of the dielectric constant between individual layers. When the thickness of individual layers were controlled in inverse proportion to the value of the dielectric constant maximum at T_C of each layers (i.e. $\epsilon_i t_i = \text{constant}$), the slope of the dielectric constant decreased remarkably.

4. Conclusions

From this study, the peak value of dielectric constant at the Curie temperature of $Ba_{1-x}Sr_xTiO_3$ ceramics was found to be dependent on $SrTiO_3$ contents and the microstructure. The $SrTiO_3$ affects contrarily on the peak value of the dielectric constant when it is incorporated into $BaTiO_3$. On the one hand, the intrinsic dielectric constant maximum of $Ba_{1-x}Sr_xTiO_3$ increases with increasing $SrTiO_3$ contents. On the other hand, the addition of $SrTiO_3$ reduces the maximum dielectric constant of $Ba_{1-x}Sr_xTiO_3$ ceramics by decreasing their average grain size. Based on these results, functionally graded $Ba_{1-x}Sr_xTiO_3$ materials were fabricated by a conventional powder processing. A layered $Ba_{1-x}Sr_xTiO_3$ composite with controlled thickness of individual layers shows a flat characteristic of the dielectric constant in a wide temperature range.