Research Paper

Changes in Dielectric Properties of Sb, Nb, and Ta-doped BaTiO₃ Systems

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Abstract

Acceptor and donor dopants have a significant effect on the dielectric properties of BaTiO₃. In this paper, Sb, Nb, and Ta were added to BaTiO₃ solid solutions to analyze the specific change of dielectric property based on temperature. First, the crystal stabilization process was analyzed by X-ray diffraction and scanning electron microscopy. Second, the optimum sintering conditions were confirmed according to the results, and specimens were prepared to compare their characteristics. In this experiment, it was found that the calcining condition was ~1100 °C and the sintering condition was ~1300 °C, although the heat treatment conditions were slightly different depending on the additive materials. The dielectric constants of BaTiO₃ doped with 1.0 mole% of Sb, Nb, and Ta reached 4741, 2055, and 2963 at room temperature, and the transition temperatures were ~67, ~116, and ~109 °C, respectively, which shifted to very low temperatures from the transition temperature of pure BaTiO₃ (~125 °C). The results of $1/K$ vs. T and $\ln[(1/K)-(1/K_m)]$ vs. $\ln(T-T_m)$ were partially different from those of pure BaTiO₃, having a temperature slightly higher than the phase transition temperature. This abnormal ferroelectric phase transition property of impurity-substituted BaTiO₃ was confirmed by using the modified Curie-Weiss rule.

Keywords: Sb, Nb, Ta-doped BaTiO₃, Acceptor/donor dopant, Dielectric properties, Modified Curie-Weiss rule

I. Introduction

Ferroelectric BaTiO₃, which has been extensively studied since just before World War II, has since been actively used in industry. The discovery of ferroelectricity in Pb(Mg_{1/3}Nb_{2/3})O₃ and BaTiO₃ is very important, and the BaTiO₃ single crystal and solid solution, unlike Pb(Mg_{1/3}Nb_{2/3})O₃, occupy an important position in lead-free material research. According to the results of several researchers, BaTiO₃ exhibits a Pm3m cubic phase at high temperature and a tetragonal crystal structure at room temperature. In the ferroelectric state below the Curie temperature, spontaneous polarization occurs owing to the non-centrosymmetric displacement of Ti⁴⁺ and O²⁻ ions compared to the Ba²⁺ ions P4mm [1]. Pure BaTiO₃ is well known as a stable dielectric with an energy gap greater than 3.05 eV at room temperature, having large dielectric strength. Addition of appropriate additives to the BaTiO₃ solid

solution can transfer the temperature range of the maximum dielectric constant to room temperature, which is very useful [2,3]. In addition, the sensitivity of the electric field strength and the frequency can be improved in the vicinity of the phase transition temperature from a tetragonal crystal to a cubic crystal [4].

The main purpose of this study is to evaluate the dielectric properties of the BaTiO₃ solid solution prepared by the solid state reaction method with the addition of Sb, Nb, and Ta, which are three potentially useful additives, based on previously published research data [5-7].

II. Experimental details

BaTiO₃ solid solutions containing 1 mole% of Sb, Nb, and Ta were prepared by mixing raw materials (99.9 % or higher purity) of oxides such as BaO, TiO₂, Sb₂O₃, Nb₂O₅, and Ta₂O₅. When BaTiO₃ was doped with Sb, Nb, and Ta, the optimum sintering temperatures were 1320, 1300, and 1320 °C, respectively. As shown

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Figure 1. SEM micrographs of Sb-, Nb-, and Ta-doped BaTiO₃ solid solutions.

Figure 2. (Color online) EDS images of Sb-, Nb-, and Ta-doped BaTiO₃ solid solutions.

in Fig. 1(a), the fracture surface of the sintered body doped with Sb forms a rectangular shape. The sintered bodies doped with Nb and Ta in Figs. 1(b) and 1(c) formed a relatively uniform rounded grain. The difference in grain growth occurs because the donor-type dopants Nb and Ta are expected to penetrate into the body-center of perovskite, but Sb, which is an acceptor-type dopant, is located in the cube corner of perovskite. For example, when donor dopant Nb is doped into BaTiO₃, the result is that the Ti-atom changes to Ti³⁺ from Ti⁴⁺, resulting in a form similar to Ba₂(Ti_{1-2x}⁴⁺+4Nb_x⁵⁺+5Ti_x³⁺)O₃ [8].

The universal energy-dispersive X-ray spectroscopy measuring device, or energy dispersive spectroscopy (EDS), is commonly used to confirm the presence of many elements in dielectric materials. Figure 2(a) displays an EDS image of a pure BaTiO₃ solid solution. The EDS spectra in Figs. 2(b)-(d) respectively show that the regions rich in Sb, Nb, and Ta ions are closely related to the heterogeneous particles in the perovskite. When BaTiO₃ is doped with Sb, Nb, Ta, or the like, a charge imbalance occurs because of the different oxidation states. This stoichiometric non-uniform distribution and segregation affects the dielectric properties of the material. Addition of isovalent impurities to BaTiO₃ has no significant effect on conductivity, but off-valent impurities have a significant effect on both ferroelectricity and

Figure 3. (Color online) XRD patterns of (111), (200), and (002) planes of Sb-, Nb-, and Ta-doped BaTiO₃.

conductivity. The major carriers can significantly affect the crystallization of the solid solution. The diffusion kinetics are affected by additives and charge-compensating defects in sintering. However, the role of the dopants is very complicated, both physically and chemically. The grain growth of BaTiO₃ doped with Nb and Ta greatly increased, but the BaTiO₃ grains doped with Sb did not change in grain size from that of pure BaTiO₃. The major role of donor cations, such as Nb and Ta, can have an impact on particle boundary mobility, as charge compensation has an important effect. Usually, the energy required to bond the dopant ions to each lattice site of the perovskite is related to distortion, and is also closely related to compensation defects during binding of the aliovalent ions. Therefore, because the doping ions exist at a high concentration in the grain boundaries, abnormal grain growth during sintering is suppressed to form high-density, impure BaTiO₃.

Many studies have shown that pure BaTiO₃ is composed of a mixture of two crystal structures: a tetragonal structure and a cubic structure. The X-ray diffraction (XRD) pattern obtained in a diffractometer using CuK α radiation confirmed the formation of the perovskite phase without a pyrochlore phase. Figure 3 shows XRD peaks of the (111), (200), (002), and (210) planes of BaTiO₃ doped with Sb, Nb, and Ta. In particular, the (222) plane around 31 degrees was not observed, and the (110) plane was clearly visible, indicating that a BO₆ structure was stably obtained.

The XRD pattern showed a distinct tetragonal perovskite structure for the BaTiO₃ doped with Nb⁵⁺ and Ta⁵⁺, unlike the case of doping with Sb³⁺. Analysis of the small XRD data in Fig. 3 revealed that

the (200) and (002) planes coexisted at ~ 45 degrees for BaTiO₃ doped with Nb and Ta. However, in the case of BaTiO₃ doped with Sb, only the (200) plane was observed. The 002 (tetragonal), 200 (tetragonal), and 200 (cubic) planes observed at ~ 45 degrees confirm that a coexistence region of tetragonal and cubic crystals was present.

Capacitance was measured at a temperature heating rate of 4 °C/min in a temperature range of 20 °C to 300 °C, and the frequency range was 10 to 10⁶ Hz. Dielectric constant and dielectric loss were calculated from the obtained capacitance, and the differences in dielectric properties among the three BaTiO₃ systems doped with Sb, Nb, and Ta were analyzed.

III. Results and discussion

Through the dielectric constant versus temperature curve, the physical effects of additives on the dielectric properties of BaTiO₃ doped with Sb, Nb, and Ta can be analyzed in detail. As shown in Fig. 4, BaTiO₃ doped with Sb is completely different from BaTiO₃ doped with Nb and Ta. The grain sizes and the degree of densification in the scanning electron microscope (SEM) images of Fig. 1 are reflected as they are, and BaTiO₃ with Nb and Ta doping shows a relatively large dielectric constant value of 8000 or more. Many researchers have reported that the dielectric constant of pure BaTiO₃ ceramics is approximately 7000, and can be as high as 15,000 in a narrow temperature range. However, the dielectric constant of BaTiO₃ doped with Sb was approximately 5000. Figure 4 clearly demonstrates that the phase transition temperature

of BaTiO₃ doped with Sb is shifted to room temperature to a greater extent than in the case of doping with Nb or Ta, thus improving the former's temperature stability. The phase transition temperatures of BaTiO₃ doped with Sb, Nb, and Ta were found to be 67, 116, and 109 °C, respectively, as a result of measuring the dielectric constant and pyroelectric current, which are functions of temperature.

As shown in Fig. 5, the frequency dependence of the dielectric constant and dielectric loss for Sb, Nb, and Ta doped BaTiO₃ is clear. In all three compositions, the dielectric constant and dielectric loss decreased sharply to the 10³ Hz point, and then continued to gradually decrease in the high frequency range above 10⁴ Hz. This dielectric relaxation means that as the frequency increases, higher amounts of energy are needed for the electric dipole to rotate.

Figure 6 shows the change of the reciprocal dielectric constant vs. temperature and the $\ln[(1/K)-(1/K_m)]$ vs. $\ln(T-T_m)$ curves of BaTiO₃ doped with Sb, Nb, and Ta. Perovskite compositions doped with an acceptor or donor material have a small effect on the Curie temperature, which is an intrinsic dielectric parameter, because it is difficult to uniformly distribute the dopant. As shown in Fig. 4, when Sb, Nb, and Ta were poured into the BaTiO₃ solid solution, a continuous dielectric response was observed in the transition region where the dielectric constant phase region significantly reduced the dielectric constant. The diffusion characteristics of the partial relaxor BaTiO₃ can be analyzed qualitatively by the Curie-Weiss rule $[\frac{1}{K} = \frac{1}{K_m} + (\frac{T - T_m}{C})^Y]$, where K is the

Figure 4. (Color online) Temperature dependence of dielectric constant and loss of Sb-, Nb-, and Ta-doped BaTiO₃.

Figure 5. (Color online) Frequency dependence of dielectric constant and loss of Sb-, Nb-, and Ta-doped BaTiO₃.

Figure 6. (Color online) Plot of reciprocal dielectric constant vs. temperature and $\ln[(1/K)-(1/K_m)]$ vs. $\ln(T-T_m)$ for Sb-, Nb-, and Ta-doped BaTiO₃.

dielectric constant, K_m is the maximum dielectric constant, T is the temperature, T_m is the dielectric constant maxima temperature, C is the Curie constant, and γ is the critical exponent. The value of the critical exponent γ can be obtained from the slope of the fitting curve by applying this equation [9-11]. As shown in Fig. 6, when BaTiO₃ is doped with Nb and Ta, the degree of the diffusivity index changes and can be expressed as a critical exponent γ . Sb-doped BaTiO₃ also differs slightly from the perovskite diffusivity of the Pb(A,B)O₃-type, but it can be analyzed by applying a diffusion phase transition mechanism. That is, by calculating the critical exponent γ , it is possible to analyze the diffusivity of the ferroelectric. The critical exponent γ of the normal ferroelectric is 1, while the critical exponent γ of the relaxor has a value close to 2. The dielectric constant of the relaxor is determined by the modified Curie-Weiss quadratic equation, $\frac{1}{K} = \frac{1}{K_m} + \frac{(T-T_m)^\gamma}{2K_m\delta^2}$, where δ is the diffuseness parameter. As the Nb and Ta contents increased, the critical exponent γ of the samples decreased. However, the critical exponent slightly increased when doped with Sb. Many researchers have reported that these diffusion phenomena are explained by the change of the local composition according to different micro-regions, and each micro-region has slightly different phase transition temperatures. These results are due to the increase of the grain size resulting from Nb

and Ta doping, which is consistent with the results confirmed by the SEM/EDS data in Figs. 1 and 2.

IV. Conclusions

In this paper, the microstructure and dielectric properties of BaTiO₃ polycrystalline samples doped with Sb, Nb, and Ta were compared. BaTiO₃ doped with Nb and Ta confirmed the distinct growth of crystal grains, and the crystal structure showed a lower degree of tetragonality. Meanwhile, Sb-doped BaTiO₃ exhibited very limited grain growth, and the dielectric phase transition temperature shifted sharply toward a lower temperature. Abnormal grain growth was suppressed by doping with Sb. The dielectric constants of BaTiO₃ doped with 1.0 mole% of Sb, Nb, and Ta were 4741, 2055, and 2963 at room temperature, respectively. The Curie temperatures of the three irradiated compositions were lower than those of the pure BaTiO₃ solid solution and single crystals. The phase transition temperatures of BaTiO₃ doped with Sb, Nb, and Ta were 67, 116, and 109 °C, respectively. A linear reduction of the dielectric constant was observed at frequencies up to 10³ Hz in all three compositions. As a result of the analysis of the three compositions based on $1/K$ vs. T and $\ln[(1/K)-(1/K_m)]$ vs. $\ln(T-T_m)$, the diffusivity of their ferroelectricity at temperatures above the Curie temperature is slightly different from pure BaTiO₃.

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