Research Paper

Changes in Physical Properties of Ta⁵⁺-doped BaTiO₃ Solid Solution

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Abstract

Structural properties for the substitution of Ta⁵⁺ ions in the BaTiO₃ crystal lattice were observed by SEM/EDS. The formation of perovskite phase and the change of (111), (200) and (002) planes of BaTiO₃ solid solution containing a small amount of Ta⁵⁺ were studied. As a result, the relationship between the dielectric properties and the polycrystalline structure of Ta⁵⁺-doped BaTiO₃ was confirmed. It was found that the maximum dielectric constant of the Ta⁵⁺-doped BaTiO₃ solid solution was more than about 8000, and the transition temperature shifted slightly toward the lower temperature as compared with the pure BaTiO₃. The dielectric constants of all the samples measured in the temperature region above the transition temperature showed some diffusivity and satisfied the modified Curie-Weiss law.

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I. Introduction

Nowadays electric and electronic materials are required to be environmentally friendly. Since BaTiO₃ (BT) crystals are ferroelectric materials that are widely used in capacitors, IR sensors, and PTCR fields, the discovery of ferroelectricity in BT crystals is historically very important [1]. The dielectric maximum of BT can move toward room temperature due to composition substitution, and the BT dielectric is sensitive to temperature, electric field strength and frequency, especially around Curie temperature [2].

Powder processing and sintering conditions have a strong influence on the mechanism of doping, the generation of defects, the resulting crystalline structure and finally the properties of the BT. The purpose of this paper is to investigate the effect of donor dopant (Ta⁵⁺) on the microstructure and dielectric properties of BT, and to develop a lead-free environmentally friendly ceramic capacitor composition in the electronics industry.

II. Experimental procedure

Ta⁵⁺-doped BT solid solutions were prepared using raw materials of BaO, TiO₂ and Ta₂O₅ oxides. BT powder was added with 0.5 and 1.0 mole % Ta₂O₅. Finally, compact Ta⁵⁺-doped BT solid solutions was synthesized by firing at

1260~1340 °C for 4 hours. The Ta⁵⁺ ion has a different valence from the valence of Ba²⁺ and Ti⁴⁺, so that if the Ta⁵⁺ is substituted with BT, charge imbalance occurs like a $2\text{BaO} + \text{Ta}_2\text{O}_5 \rightarrow 2\text{Ba}_{\text{Ba}} + 2\text{Ta}_{\text{Ti}} + 6\text{O}_\text{o} + \text{O}_2(\text{g})/2 + 2\text{e}'$. As a result, the titanium atomic valence decreases from Ti⁴⁺ to Ti³⁺, and consequently has the structure of $\text{Ba}^{2+}(\text{Ti}_{1-2x}^{4+} + 4\text{Ta}_x^{5+} + 5\text{Ti}_x^{3+})\text{O}_3$ [3,4]. The formation of the perovskite phase was confirmed by the diffraction pattern obtained by XRD using CuK α radiation. Before measurement, all samples were poled by applying an electric field of 20 kV/cm. After being poled, the polycrystalline dielectrics can exhibit the dielectric effect just as single crystals do. Dielectric properties were measured using an LCR meter (HP4275A), an environmental chamber (Delta Design, Model 2300) and a control unit and interface (HP59500A). The dielectric constant (K) and loss (D) were measured as a function of temperature at various frequencies from 0.1 and 10⁶ Hz at a heating rate of 4 °C/min.

III. Results and discussion

Pure BT crystals exhibit two phases: tetragonal and cubic. Figure 1 shows the X-ray diffraction peaks of (110), (111), (200) and (002) planes of Ta⁵⁺-doped BT solid solutions. The formation of a perovskite phase without any impurities in the X-ray diffraction pattern was confirmed. In other words, the results of this experiment could not detect the evidence of BaO, TiO₂ and Ta₂O₅ precursors by XRD. There was no evidence of coexistence in the XRD diffraction peak, but the diffraction results of the XRD

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Figure 1. XRD patterns of Ta^{5+} -doped BT solid solutions measured at 1 kHz. (a) 0.5 mole % Ta^{5+} , (b) 1.0 mole % Ta^{5+} .

Figure 2. SEM/EDS images of Ta^{5+} -doped BT solid solutions. (a, c) 0.5 mole % Ta^{5+} , (b, d) 1.0 mole % Ta^{5+} .

peak show characteristics of phases different from those of pure BT by adding Ta^{5+} . The XRD measurement results of the small chart inserted in Fig. 1 show two BT phases. Analysis of 002 (tetragonal), 200 (tetragonal) and 200 (cubic) observed at $44.5\sim 45.5^\circ$ confirmed tetragonal and cubic phases.

Figure 2 shows SEM/EDS images of BT doped with 0.5 and 1.0 mole % of Ta^{5+} composed of spherical particles with a visually rounded grain size distribution in the SEM image. Often EDS is commonly used to discover the abundance of certain elements present in a material. In this experiment, Ta^{5+} -doped BT crystals caused charge imbalance due to different oxidation states. In the EDS spectra, it was found that the Ta^{5+} ion is related to a part of the sample having a long and needle shaped particle. In addition, the EDS spectra were associated with non-homogeneous particles in the region with a large amount of

Figure 3. SEM micrographs of fracture surfaces at sintered 1300°C . (a) 0.5 mole % Ta^{5+} , (b) 1.0 mole % Ta^{5+} .

Figure 4. Frequency dependence of dielectric constant and loss of Ta^{5+} -doped BT solution solutions. (a) 0.5 mole % Ta^{5+} , (b) 1.0 mole % Ta^{5+} .

Ta^{5+} ions. The corresponding EDS spectrum indicates that the regions rich in Ta^{5+} ions were associated with non-homogeneous grains. Thus, the dielectric constant was slightly reduced due to the non-uniform distribution of Ta^{5+} and segregation. In the EDS image, the influence on the microstructure uniformity was negligible because there was almost no region rich in Ta^{5+} .

Figure 3 shows a SEM micrograph of the fracture surfaces of the Ta^{5+} -doped BT solid solution. In the case of the solid solution, it is a common phenomenon that during the sintering, the crystal grains of the specimen composed of the powder increase with the decrease of the amount of pores. The grain size of the sintered Ta^{5+} -doped BT was about $3.5\sim 4.5\ \mu\text{m}$ and formed into relatively dense grains.

Figure 4 shows the frequency dependence of the dielectric constant of Ta^{5+} -doped BT. Dielectric constants were measured in the frequency range of 10 Hz to 10^6 Hz. As shown in the 0.5 mole % Ta^{5+} -doped BT, the dielectric constant decreased markedly to $\sim 10^3$ Hz, but it slowly decreased in the high frequency range. On the other hand, the dielectric constant of 1.0 mole % Ta^{5+} -doped BT abruptly decreased to $\sim 10^2$ Hz and gradually decreased in the high frequency region. Thus, a significant change in the dielectric constant is due to the higher energy required for the orientation of the dipoles as the frequency increases. These results were similar to those reported by other researchers. As shown in the small chart in Fig. 4, the frequency dependence of the dielectric loss is similar to the

Figure 5. Dielectric properties of Ta⁵⁺-doped BT solutions measured at 1 kHz. (a) 0.5 mole % Ta⁵⁺, (b) 1.0 mole % Ta⁵⁺.

frequency dependence of the dielectric constant. The addition of Ta⁵⁺ to pure BT increased the dielectric constant at the phase transition temperature, but the dielectric constant at room temperature did not find a relatively large change. These results show that BT with added BT has more crystal defects in crystal structure and Ta⁵⁺ ion exchanges Ti⁴⁺ ions at B site (higher coordination number) of ABO₃. Therefore, it is considered that adding Ta⁵⁺ optimally to pure BT reduces the local disorder around the Ba²⁺ atom and also has some effect on the local structure of Ti⁴⁺. At 1 kHz frequency, the maximum dielectric constants of BT doped with 0.5 mole % Ta and 1.0 mole % Ta were measured to be 7161 at 105 °C and 9940 at 118 °C, respectively. However, the dielectric loss at room temperature for both compositions was relatively large as shown in Fig. 4. The dielectric constants of BT doped with 0.5 mole % Ta⁵⁺ and 1.0 mole % Ta⁵⁺ at room temperature were measured to be 3490 and 2513, respectively. In Ta⁵⁺-doped BT, chemically heterogeneous systems can be formed. The Ta⁵⁺ ions lead to the formation of core-shell structure, with BT core and Ti⁴⁺ modified BT shell. Ta⁵⁺ ions also segregating at grain boundaries, act as grain growth inhibitors. Since the Ta⁵⁺-doped BT samples exhibit a different dielectric behavior it is for expected that the Curie constant would be very sensitive to the type and concentration of additive. Therefore, the dielectric constant of Ta⁵⁺-doped BT solid solution can vary greatly because it is governed by two different microstructural regions. It was judged that non-ferroelectric behavior was observed in a part of the sample due to the composition fluctuation. In all investigated samples dielectric constant after initially large value at low frequency attains a constant value at $f \geq 10$ kHz. Pure BT undergoes a sharp phase transition from ferroelectric to paraelectric phase at Curie temperature. However, in this experiment, the phase transition of Ta⁵⁺-doped BT was slightly different from that of pure BT.

The modified Curie-Weiss law was used to investigate the diffusional phase transition properties of the BT solid solution with the addition of Ta⁵⁺. It is clear that the degree of diffuse phase transition change will change as the addition of Ta⁵⁺ increases, which can be analyzed by diffuseness parameter in $\frac{1}{K} = \frac{1}{K_m} + \left(\frac{T-T_m}{C}\right)^\gamma$ [5-8]. In this equation, C is the Curie constant, γ is the diffuseness parameter, K_m is the maximum dielectric constant and T_m is the corresponding temperature of maximum dielectric constant at Curie temperature. In particular, the diffuseness parameter provides information about the nature of the transition. In the case of normal Curie-Weiss law, the diffuseness parameter is almost equal to 1, but the diffuseness parameter of the ideal diffuse phase transition is approximately 2. The dielectric constant of the relaxor ferroelectric near the Curie temperature can be analyzed by the modified Curie-Weiss quadratic law $\left[\frac{1}{K} = \frac{1}{K_m} + \left(\frac{T-T_m}{2K_m\delta^2}\right)^\gamma\right]$. Where K is the dielectric constant, K_m is the maximum dielectric constant, and T_m is the dielectric constant maxima temperature. Unlike modified Curie-Weiss law, δ and γ in Curie-Weiss law are defined as a diffuseness parameter and a critical exponent, respectively. Based on modified Curie-Weiss law, a plot of $\ln(1/K-1/K_m)$ versus $\ln(T-T_m)$ of Ta⁵⁺-doped BT can be displayed and analyzed as shown in Fig. 4. The change in diffuseness parameter in Ta⁵⁺-doped BT can be analyzed from the slope of the graph using modified Curie-Weiss law. In the case of Ta⁵⁺-doped BT, the γ value decreased slightly when the Ta⁵⁺ concentration increased from 0.5 mole % Ta⁵⁺ to 1.0 mole % Ta⁵⁺. This can be attributed to the increase of the particle size of the sample in proportion to the increase of the Ta⁵⁺ content. The deviation from the Curie-Weiss law can also be observed in Fig. 5. In this experiment, this deviation represents the temperature fluctuation of the maximum dielectric constant temperature. This result can be evidence of some diffuse phase transition in Ta⁵⁺-doped BT, unlike pure BT. For more confirmation the diffuse with Ta⁵⁺ addition, the normalized dielectric constant is plotted against the normalized temperature, which leads to the same conclusion that the diffusivity is increased with increase in frequency. According to reports, the occurrence of this diffuseness is caused by the change of the local composition including the different micro-regions, and the phase transition temperature in each region is known to have slightly different temperature [9]. Dielectric behavior above the Curie temperature in the two compositions satisfies the modified Curie-Weiss law. Also, Fig. 5 shows the change of the reciprocal dielectric constant with temperature of 0.5 and 1.0 mole % Ta⁵⁺-doped BT solid solutions. Since the two compositions doped with Ta⁵⁺ are not uniformly distributed, they have a small effect on inherent dielectric parameters such as Curie temperature. For Ta⁵⁺-doped BT, a continuous dielectric response is

observed in the transition region where the paraelectric phase region significantly reduces the dielectric constant.

IV. Conclusions

In this paper, the microstructure and dielectric properties of BT solid solution doped with Ta^{5+} were analyzed. According to the results, the grain size increased slightly from 3.5 μm to 4.5 μm when the addition amount was increased from 0.5 mole % Ta^{5+} to 1.0 mole % Ta^{5+} . In addition, the fine-grain and high density of BT ceramic result in its excellent dielectric properties. The dielectric behavior of Ta^{5+} -doped BT is in agreement with the presence of the tetragonal structure observed by XRD. The dielectric constant of 0.5 mole % Ta^{5+} -doped BT reaches to 3490 at room temperature. These results show that the additives such as Ta^{5+} did not cause a significant change in the local structure around the Ti^{4+} atom, and that the local structure is similar to the pseudo-cubic crystal in comparison with other references. The crystal structure of Ta^{5+} -doped BaTiO_3 is considered to show some tetragonality. The BT added with Ta^{5+} showed a characteristic of a relatively uniform microstructure having a homogeneous additive distribution in the formation of the crystal structure.

Therefore, BT with Ta^{5+} was analyzed for a large change in dielectric constant, which is a function of temperature. The phase transition temperature of all samples analyzed by the experimental results is lower than that of pure BT solid solution. The dielectric behavior in the transition temperature range above the Curie temperature in both compositions with Ta^{5+} was well satisfied with the modified Curie-Weiss law.

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