Changes in Physical Properties of Ta$^{5+}$-doped BaTiO$_3$ Solid Solution

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Received September 27, 2018; accepted October 10, 2018

Abstract

Structural properties for the substitution of Ta$^{5+}$ ions in the BaTiO$_3$ crystal lattice were observed by SEM/EDS. The formation of perovskite phase and the change of (111), (200) and (002) planes of BaTiO$_3$ solid solution containing a small amount of Ta$^{5+}$ were studied. As a result, the relationship between the dielectric properties and the polycrystalline structure of Ta$^{5+}$-doped BaTiO$_3$ was confirmed. It was found that the maximum dielectric constant of the Ta$^{5+}$-doped BaTiO$_3$ solid solution was more than about 8000, and the transition temperature shifted slightly toward the lower temperature as compared with the pure BaTiO$_3$. 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.

PACS numbers: 77.12, 77.64, 77.81
Keywords: Ta$^{5+}$-doped BaTiO$_3$, Dielectric properties, Modified Curie-Weiss law

I. Introduction

Nowadays electric and electronic materials are required to be environmentally friendly. Since BaTiO$_3$ (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 (Ta$^{5+}$) 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

Ta$^{5+}$-doped BT solid solutions were prepared using raw materials of BaO, TiO$_2$ and Ta$_2$O$_5$ oxides. BT powder was added with 0.5 and 1.0 mole % Ta$_2$O$_5$. Finally, compact Ta$^{5+}$-doped BT solid solutions was synthesized by firing at 1260–1340 °C for 4 hours. The Ta$^{5+}$ ion has a different valence from the valence of Ba$^{2+}$ and Ti$^{4+}$, so that if the Ta$^{5+}$ is substituted with BT, charge imbalance occurs like a 2BaO+Ta$_2$O$_5$→2BaTiO$_3$+2Ta$^{5+}$+5Ti$^{3+}$+5O$_2$(g)/2+2e'. As a result, the titanium atomic valence decreases from Ti$^{4+}$ to Ti$^{3+}$, and consequently has the structure of Ba$^{2+}$(Ti$_{1-2x}$$^{4+}$+4Ta$^{5+}$+5Ti$^{3+}$)O$_3$ [3,4]. The formation of the perovskite phase was confirmed by the diffraction pattern obtained by XRD using CuKα 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 10$^6$ 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 Ta$^{5+}$-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, TiO$_2$ and Ta$_2$O$_5$ precursors by XRD. There was no evidence of coexistence in the XRD diffraction peak, but the diffraction results of the XRD...
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 44.5~45.5° 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 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 3.5~4.5 μm 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 ~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 ~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
of Ta concentration of additive. Therefore, the dielectric constant exhibit a different dielectric behavior it is for expected that grain growth inhibitors. Since the Ta 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 Ta. It is clear that the degree of diffuse phase transition change will change as the addition of Ta increases, which can be analyzed by diffuseness parameter in $\frac{1}{K} - \frac{1}{K_m}$. In this equation, C is the Curie constant, $\gamma$ 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 $\frac{1}{K} = \frac{1}{K_m} + \frac{(T - T_m)}{2K_m\delta}$. 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, $\delta$ and $\gamma$ 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 Ta-doped BT can be displayed and analyzed as shown in Fig. 4. The change in diffuseness parameter in Ta-doped BT can be analyzed from the slope of the graph using modified Curie-Weiss law. In the case of Ta-doped BT, the $\gamma$ value decreased slightly when the Ta concentration increased from 0.5 mole % Ta to 1.0 mole % Ta. This can be attributed to the increase of the particle size of the sample in proportion to the increase of the Ta 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 Ta-doped BT, unlike pure BT. For more confirmation the diffuse with Ta 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 % Ta-doped BT solid solutions. Since the two compositions doped with Ta are not uniformly distributed, they have a small effect on inherent dielectric parameters such as Curie temperature. For Ta-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 $\text{Ta}^{5+}$ 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 % $\text{Ta}^{5+}$ to 1.0 mole % $\text{Ta}^{5+}$. In addition, the fine-grain and high density of BT ceramic result in its excellent dielectric properties. The dielectric behavior of $\text{Ta}^{5+}$-doped BT is in agreement with the presence of the tetragonal structure observed by XRD. The dielectric constant of 0.5 mole % $\text{Ta}^{5+}$-doped BT reaches to 3490 at room temperature. These results show that the additives such as $\text{Ta}^{5+}$ did not cause a significant change in the local structure around the $\text{Ti}^{4+}$ atom, and that the local structure is similar to the pseudo-cubic crystal in comparison with other references. The crystal structure of $\text{Ta}^{5+}$-doped BaTiO$_3$ is considered to show some tetragonality. The BT added with $\text{Ta}^{5+}$ showed a characteristic of a relatively uniform microstructure having a homogeneous additive distribution in the formation of the crystal structure. Therefore, BT with $\text{Ta}^{5+}$ 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 $\text{Ta}^{5+}$ was well satisfied with the modified Curie-Weiss law.

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