Formation of solid solutions in wide miscibility-gap perovskite-type oxide system of Ba$_{1-x}$Ca$_x$ZrO$_3$ over the entire Ca composition range

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Formation of solid solutions was examined in a wide miscibility gap system of Ba$_{1-x}$Ca$_x$ZrO$_3$ by preparing film samples having amorphous structures with the help of rf magnetron sputtering and then annealing the amorphous film samples at a moderate temperature condition. Ba$_{1-x}$Ca$_x$ZrO$_3$ solid solutions were successfully formed as monophasic products over the entire Ca composition range, indicating the usefulness of the method for the formation of solid solutions in perovskite-type oxides, and Ca composition dependence of the permittivity was revealed in the solid-solution system.

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1. Introduction

Complex oxides with a perovskite-type structure are important and potential materials as dielectric substances, catalysts, ion conductors and so on,$^{1-5}$ and their physical and chemical properties are often controlled and optimized by varying compositions.$^{1-5}$ The extension of the solubility limit must bring information of value to understand the dependence of their properties on the compositions and open new possibilities for them as functional materials. Sputtering is a convenient way to prepare film samples of oxides, and formed samples on to substrates at low temperatures usually have amorphous structures.$^8$ In the amorphous film sample, the constituent ions are uniformly dispersed so that it can crystallize only by short-distance diffusion of the ions during annealing. Thus the sputtering and subsequent annealing can be a potential method to produce solid solutions of oxides avoiding phase separation. In fact, recently, Ba$_{1-x}$Ca$_x$TiO$_3$ solid solutions with Ca compositions in the miscibility gap have been formed successfully by the annealing of amorphous film samples prepared with the help of rf magnetron sputtering.$^9$ This ‘sputter-anneal’ method is expected to be useful from its simplicity for producing solid solutions in oxide systems widely, and it is indispensable to examine the validity of the method in a system with a narrow solubility limit.

Therefore, in this study, we examined the formation of solid solutions by the method in Ba$_{1-x}$Ca$_x$ZrO$_3$ system, which has been actively studied as an attractive candidate for use in microwave applications$^{2-4}$ and reported to have a quite narrow solubility limit of $x \leq 0.03$ and $x \geq 0.99$ in a conventional solid-state reaction,$^3$ and tried to obtain the information about the composition dependence of their dielectric properties in a wide composition range.

2. Experimental

The powder samples of Ba$_{1-x}$Ca$_x$ZrO$_3$ with the compositions of $x = 0, 0.25, 0.50, 0.75$ and $1$ were prepared from raw materials of ZrO$_2$ (Soekawa Chemicals, 99.9%), BaCO$_3$ (Wako Pure Chemical Industries, 99.9%) and CaCO$_3$ (Kanto Kagaku, 99.99%) by calcining at 1000°C for 12 h. The synthesized samples were pressed into disks and sintered at 1400°C for 6 h. Then the formed disks were polished and shaped into sputtering targets (1 inch$^5$, 2 mm). The depositions of Ba$_{1-x}$Ca$_x$ZrO$_3$ film samples were performed using the targets and an rf magnetron sputtering system (ULVAC, SCOTT-C3-T1) under Ar (1.0 Pa)/O$_2$ (0.4 Pa) mixed gas atmosphere on to quartz glass substrates ($10 \text{ mm} \times 10 \text{ mm} \times 0.8 \text{ mm}$) at ambient temperature. The thicknesses of the film samples were controlled to be ~1μm by setting the sputtering time between 6 and 8 h. Annealing of the film samples was performed under atmospheric condition using an electric furnace. The annealing temperature and duration were set to be 800°C and 3 h, respectively. The annealing temperature of 800°C was decided based on the results of the preliminary experiments; annealing at 600, 800 and 1000°C for 3 h were examined to the Ba$_{1-x}$Ca$_x$ZrO$_3$ film samples with $x = 0, 0.50$ and $1$ prepared by the sputtering, and the samples annealed at 800°C gave the highest area intensity of diffraction peaks in X-ray powder diffraction (XRD) experiments without showing the formation of impurities.
XRD experiments were performed on an X-ray diffractometer (Rigaku, RINT2200VF) using Cu Kα radiation. Morphology observation and elemental analysis of the surfaces of the Ba_{0.50}Ca_{0.50}ZrO_{3} target and the annealed film sample formed from the target by the sputtering were performed on a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer (SHIMADZU, SSX-550 + SEDX-500). The surface of the samples was coated with Au-Pd in ~3-nm thick by using a magnetron sputtering apparatus (VACUUM DEVICE, MSP-1S), and the measurements were done under accelerating voltage of 30 kV. Dielectric measurements were performed using an impedance measurement system (Solartron, SI1260 + SI1287) in the frequency range from 10^{2} to 10^{5} Hz with the electric field of 10 mV_{rms}.

3. Results and discussion

Figure 1 shows the results of the XRD experiments for Ba_{1-x}Ca_{x}ZrO_{3} targets used in the sputtering along with the XRD patterns of BaZrO_{3} (ICDD No 00-006-0399) and CaZrO_{3} (ICDD No 00-035-0790). The x = 0 (BaZrO_{3}) and x = 1 (CaZrO_{3}) targets gave the diffraction patterns well corresponding to those reported for BaZrO_{3} and CaZrO_{3}, respectively. The targets with the Ca compositions x = 0.25, 0.50 and 0.75 exhibited the patterns by the coexistence of BaZrO_{3}-rich and CaZrO_{3}-rich phases as the result of the phase separation advanced during the preparation process of the targets, i.e., the calcination of the powder samples and the sintering of the pressed disks.

Figure 2 shows the results of the XRD experiments for the film samples prepared by the sputtering and for the samples after the annealing. The as-prepared film samples by the sputtering showed weak halo patterns at around 2θ = 30°, indicating that the samples have amorphous structures produced by the rapid quenching of the sputtered clusters on the substrates. On the other hand, the annealed samples showed diffraction peaks indicating that the amorphous film samples crystallized even at the rather low temperature of 800°C. The x = 0.50 sample showed no change in the diffraction pattern nor diffraction-peak intensities by the additional annealing for 6h at 800°C, and thus the crystallization of the samples is considered to complete within 3h. Although the samples with x = 0.25, 0.50 and 0.75 have compositions exceeding the solubility limit of the Ba_{1-x}Ca_{x}ZrO_{3} system in the ordinary solid-state reaction, the diffraction peaks of the annealed samples showed no splitting by the coexistence of BaZrO_{3}-rich and CaZrO_{3}-rich phases differently from the targets. The enlarged view of the diffractions of the annealed samples, Fig. 3(a), clearly shows the shift of the peak positions with the Ca composition x, and the dependence of the lattice constants, which were estimated from the results of the XRD experiments with assuming cubic structures for the crystallites, on the composition x is shown in Fig. 3(b). The samples with x = 0, 0.25, 0.50 and 0.75 exhibited
XRD patterns assignable to cubic crystalline structures, and their lattice constants were evaluated from the angles of 110, 200 and 211 diffraction peaks in cubic structure by using a unit cell parameter refinement program of CellCalc. In the sample with \( x = 1 \) (BaZrO\(_3\)), which showed the XRD pattern of orthorhombic crystalline structure, the lattice constant was estimated as the cube root of the lattice volume evaluated by using CellCalc from the angles of 101, 200, 121, 002 and 202 diffraction peaks in orthorhombic structure. The lattice constants \( a \) showed continuous and rather linear relation to \( x \). The absence of peak splitting by the phase separation in XRD and the continuity in the relation between the composition \( x \) and the lattice constant \( a \) indicate the formation of single-phase \( \text{Ba}_{x} \text{Ca}_{1-x} \text{ZrO}_3 \) solid solutions without a miscibility gap between \( \text{Ba}^2+ \) and \( \text{Ca}^2+ \) ions. Additionally, the linear relation of the \( a \) to \( x \) according to Vegard’s law signifies that the formed solid-solution samples have the same compositions as the targets used in the sputtering.

Figure 4 shows SEM images of the \( x = 0.50 \) target and the annealed film sample formed by using the target along with the two-dimensional elemental mappings corresponding to the SEM images for Ba and Ca by the EDX analyses. In the target, the existence of Ba-rich and Ca-rich phases was observed clearly. On the other hand, the results of the EDX analysis exhibited homogeneous distributions of Ba and Ca in the annealed film sample, supporting the formation of \( \text{Ba}_{0.50} \text{Ca}_{0.50} \text{ZrO}_3 \) solid solution.

Annealing at a much lower temperature of 800°C than that applied in an ordinary solid-state reaction allows only short-distance diffusion of the constituent ions in the amorphous samples. However, such diffusion is sufficient for the amorphous sample to crystallize due to the uniform dispersion of the constituent ions and the continuous structure as the characteristic property of amorphous. The \( \text{Ba}_{1-x} \text{Ca}_x \text{ZrO}_3 \) solid solutions are considered to be formed in such a way without phase separation, which occurs through long-distance diffusion of the ions.

To obtain the information about the dielectric responses of \( \text{Ba}_{1-x} \text{Ca}_x \text{ZrO}_3 \) solid solutions, preparation of the solid-solution film samples was examined on an electrically conductive substrate of Nb(1.0 wt%)-doped SrTiO\(_3\) single crystal (SrTiO\(_3\):Nb, Furuuchi Chemical, 10 mm \( \times \) 10 mm \( \times \) 0.5 mm) by the same procedure as on to the quartz glass substrate. The formation of solid solutions was confirmed also on the SrTiO\(_3\):Nb substrates by XRD experiments, and dielectric measurements were performed by using the substrate as an electrode and preparing a Pt counter electrode on the surface of the sample by sputtering. No significant change was observed in the dielectric constants \( \varepsilon \) with frequency in each sample in the measured frequency range of \( 10^2 \)–\( 10^6 \) Hz as shown in Fig. 5, and the evaluated \( \varepsilon \) for the \( x = 0 \) (BaZrO\(_3\)) sample agreed with the reported value within the estimated experimental error.  

The Ca composition dependence of \( \varepsilon \) at 1 kHz is shown in Fig. 6. The constants \( \varepsilon \) decreased linearly with the Ca
The peculiar Ca composition dependence of the permittivity in Ba$_{1-x}$TiO$_3$ solid solutions has been understood in terms of the mixing of Ba$^{2+}$ and Ca$^{2+}$ ions, which allow larger displacement of Ti$^{4+}$ ions responding to the applied electric field. Thus the difference in the Ca composition dependence of the permittivities between BaTiO$_3$ and ZrO$_2$ is considered to be due to the larger size of Zr$^{4+}$ + than Ti$^{4+}$, which restricts the displacement of Zr$^{4+}$ ions in the crystalline lattice.

4. Conclusions

In this study, Ba$_{1-x}$Ca$_x$ZrO$_3$ solid solutions were successfully formed over the entire Ca composition range, despite the narrow solubility limits in the system. The formation of the solid solutions demonstrates the usefulness and validity of the sputter-anneal method for the formation of solid solutions in perovskite-type oxides. It should be noted that the attempts to form CaZrO$_3$ film samples by rf magnetron sputtering and laser ablation on to heated substrates have been reported to result in the formation of calcia-stabilized zirconia besides CaZrO$_3$. Nevertheless, CaZrO$_3$ crystalline film sample was obtained here without the formation of byproducts by the sputter-anneal method, indicating the usefulness of the method also for the preparation of the crystalline film samples in perovskite-type compounds.

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