Contribution of phase stability to dielectric constant of a solid solution (Ba1-xSrx)(Mg1/3Ta2/3)O3 system

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(Ba1-xSrx)(Ma1/3Ta2/3)O3 compounds (BSMT) have been studied in order to clarify a relation between a change in the dielectric constant with increasing temperature and a phase transformation which has been found recently. Raman spectroscopy was done to investigate the crystal structure of BSMT. The Raman peaks signifying the low temperature phase of BSMT have been found. The anomalous change of the dielectric constant of BSMT with temperature has been explained by the phase transformation.

1. INTRODUCTION

Dielectric properties of ordered perovskite compounds with the general formula A(B'1/3B"2/3)O3 have been extensively studied due to their applications as dielectric resonators operated at microwave frequencies. It was reported that the dielectric properties of the (Ba1-xSrx)(B'1/3B"2/3)O3 compounds exhibit a characteristic change with Sr content [1-3]. There is, for instance, a change in a temperature coefficient of a resonant frequency of a dielectric resonator (TCf). With increasing Sr content, the TCf of the (Ba1-xSrx)(B'1/3B"2/3)O3 compounds increases linearly to a peak and then falls off in a fast exponential fashion. In contrast to the non-linear change of the dielectric properties with Sr content, the lattice constants of the compounds indexed on the hexagonal system decrease linearly in the whole range of Sr content. Since the (Ba1-xSrx)(B'1/3B"2/3)O3 compounds are paraelectrics, it is necessary to

clarify the mechanism for the non-linear behavior in the dielectric properties.

Their is a maximum in the dielectric constant of (Ba1-xSrx)(Mg1/3Ta2/3)O3 compounds (BSMT), for x between 0.6 and 0.65, with an increase in temperature. The TCf change of BSMT with Sr content is consistent with this maximum [4]. However, the mechanism of the maximum in the dielectric constant has not been elucidated.

Recently we have found a new phase transformation in BSMT [5]. In alternative compound such as (Ba1-xSrx)(Zn1/3Nb2/3)O3, the phase transformation is also found [6]. These phase transformation are expected to have some effect on the dielectric constant, however, the relation between them have not been clarified.

In the present research, the crystal structure change of BSMT with Sr content or temperature has been studied using Raman spectroscopy. The maximum in the dielectric constant of BSMT with increasing temperature is discussed in terms of the phase transformation.

2. EXPERIMENTAL PROCEDURE

Ceramic pellets of BSMT were prepared according to the procedure described in the previous paper [4]. The compositions of the five samples of $(Ba_{1-x}Sr_x)(Mg_{1/3}Ta_{2/3})O_3$ compounds are expressed by Sr content, $x=0$ (BMT), 0.5, 0.6, 0.65 and 0.7. The density of each sample was greater than 96% of the theoretical one for each composition.

The Raman measurements were performed on 90° geometry with a JASCO-NR1100. The 514.5 nm line of an Ar-ion laser operating at 400 mW was used. The instrumental resolution was 1 cm⁻¹. To measure a change in the Raman spectrum with temperature, a sample stage equipped with a heater unit was used. The temperature of the sample was measured by a thermocouple attached to the sample. Using the same sample, the relative change in the dielectric constant with increasing temperature was examined.

3. RESULTS AND DISCUSSION

In the Raman spectrum of BSMT where $x=0$ (BMT), nine peaks are observed between 100 to 800 cm⁻¹ and three of the nine peaks of BMT are at 162, 212 and 265 cm⁻¹. Since a change in the Raman spectrum with Sr content takes place in the neighborhood of the three peaks, the Stokes-shifted Raman spectra only in the range from 100 to 350 cm⁻¹ are considered in the following.

Figures 1 (a)-(e) show a series of Raman spectra measured at room temperature. In the spectrum of BSMT where $x=0.6$, the peaks are located at 142, 218 and 254, respectively. Two peaks shift to lower frequencies and one peak
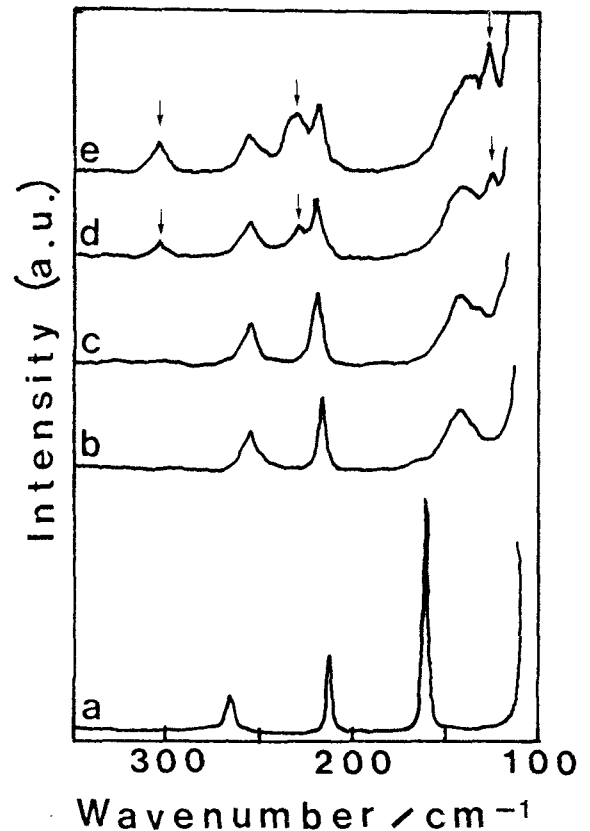

Fig. 1 The Raman spectrum of $(Ba_{1-x}Sr_x)(Mg_{1/3}Ta_{2/3})O_3$ compounds. (a) $x=0$ (BMT), (b) $x=0.5$, (c) $x=0.6$, (d) $x=0.65$, (e) $x=0.7$.

shifts to a higher frequency with increasing Sr content where $x=0$, $x=0.5$ and $x=0.6$. Since BSMT where $0 \le x \le 0.6$ have the hexagonal ordered perovskite structure, their change in the Raman spectrum with Sr content is explained by the substitutional effect in a Ba site.

In the spectrum of the sample where $x=0.65$, on the other hand, three new peaks appear. The additional peaks are indicated by arrows in Fig. 1

(d). The three peaks appear also in the spectrum of BSMT where x=0.7. The new peaks are attributed to Raman scattering of optical phonons because all of the three new peaks appear also in the anti-Stokes-shifted spectra.

Since it has been already reported that BSMT where x≥0.7 exhibits a low temperature phase at room temperature [5], the three additional peaks originate from a low symmetry structure of the low temperature phase.

It must be noted here that the low temperature phase in BSMT where x=0.65 is not confirmed at room temperature by transmission electron microscopy (TEM) [5]. The difference in the results of the Raman spectroscopy and TEM is probably explained by the nature of the phase transformation, which is considered as a tilt of the oxygen-octahedra: Raman spectroscopy is more sensitive to a displacement of oxygen.

Next, the change in the crystal structure of BSMT with temperature is examined. The Raman spectrum of the compound where x=0.65 was measured at various temperature. The results are shown in Figs. 2 (a)-(f). The additional peaks above-mentioned are indicated by arrows and their intensity gradually decreases with increasing temperature. They disappear at a temperature between 77 to 88°C. On cooling down to room temperature, the peaks corresponding to the low temperature phase appear again. The change in the intensity of the three peaks is reversible for a heating and cooling treatment. The phase transformation temperature of BSMT where x=0.65 is
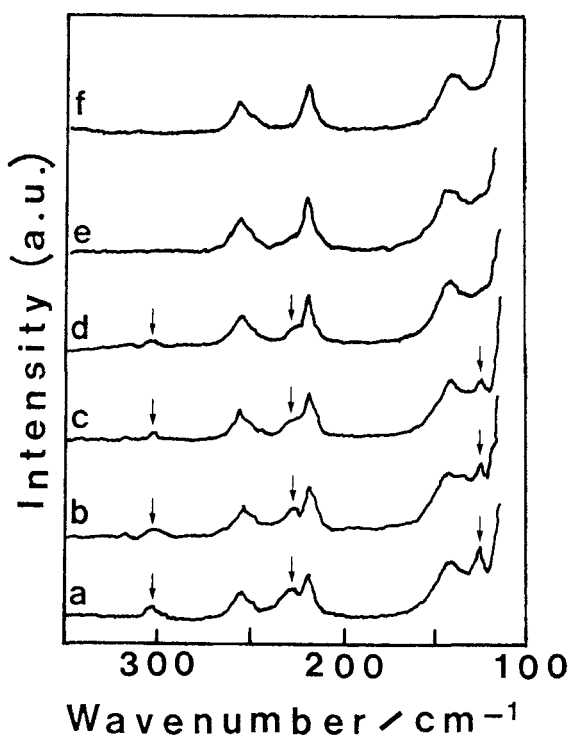

Fig.2 The Raman spectrum of (Ba₀.₃₅Sr₀.₆₅)(Mg₁/₃Ta₂/₃)O₃ compound measured at various temperature. (a) at room temperature, (b) at 47°C, (c) at 60°C, (d) at 77°C, (e) at 88°C, (f) at 104°C.

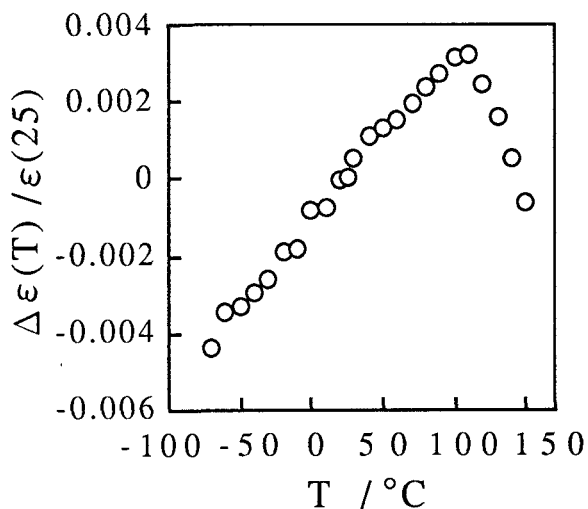Fig. 3 The relative change in the dielectric constant of (Ba₀.₃₅Sr₀.₆₅)(Mg₁/₃Ta₂/₃)O₃ compound.

determined to be at about 80°C by Raman spectroscopy. In a similar way, the transformation temperature of BSMT where x=0.7 is estimated to be 160°C.

Finally, the change in the dielectric constant of BSMT with temperature is discussed in connection with the phase transformation. The relative change in the dielectric constant of BSMT where x=0.65 was determined by the procedure described in the previous paper [4]. The result is shown in Fig. 3. The dielectric constant reaches the maximum value in the vicinity of 100°C. The phase transformation of BSMT where x=0.65 occurs at about 80°C, thus, the maximum is about 20°C higher than the transformation temperature. The difference is thought to be partly attributable to a heating effect for the sample by the laser irradiation during the Raman measurement. It is concluded that the dielectric constant of BSMT reaches the maximum at the phase transformation temperature. Since the maximum of the dielectric constant with temperature is the origin of the non-linear change of TCf with Sr content, the phase transformation is the key to understanding the mechanism of the non-linearity of the dielectric properties of BSMT.

4. CONCLUSIONS

The conclusions are summarized as follows.
1. The low temperature phase of the $(Ba_{1-x}Sr_x)(Mg_{1/3}Ta_{2/3})O_3$ compound is able to be identified by the appearance of additional peaks in the Raman spectrum.
2. The maximum in the dielectric constant with increasing temperature takes place at the phase transformation temperature in the $(Ba_{1-x}Sr_x)(Mg_{1/3}Ta_{2/3})O_3$ compound.

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