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Relationship between microwave dielectric properties and chemical bonding in R_2BaMO_5 (R = rare earth, M = Cu and Zn) compounds

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Abstract

The relationship between the covalency of cation–oxygen bonds and microwave dielectric properties of the green phase-type R_2BaCuO_5 and R_2BaZnO_5 (R = rare earth) compounds was investigated by using the bond valence theorem. From the calculation results of covalency, it was shown that the covalency of the R─O bond in the R_2BaCuO_5 and R_2BaZnO_5 compounds decreased with increasing ionic radii of the R ions. Comparing the covalency of the R─O bond in the R_2BaZnO_5 compound with that of the R_2BaCuO_5 compound, the former was smaller than the latter; therefore, this result was attributed to the differences in the R─O bonds between the R_2BaCuO_5 and R_2BaZnO_5 compounds. The dielectric constant of both compounds was linearly increased from 14 to 18 with increasing the ionic radii of the R ions. Then, the dielectric constant of the R_2BaZnO_5 compound was large in comparison with that of the R_2BaCuO_5 compound, though the ionic polarizability of Zn was smaller than that of Cu. Thus, it was considered that the difference in the dielectric constant between the R_2BaCuO_5 and R_2BaZnO_5 compounds is related to the covalency of the R─O bonds.

Keywords: Powders-solid state reaction; X-ray methods; Dielectric properties

1. Introduction

Much attention has been paid to the development of new dielectric materials for a substrate of high-temperature superconducting (HTS) devices.[1,2] In the HTS applications, the substrate materials have to fulfil requirements[3] such as the lattice matching, thermal compatibility and chemical compatibility. In addition to these requirements, the dielectric loss (tan δ), which is the inverse of the unloaded Q, must be lower than 10^{-4} at the microwave frequencies ($\sim$10 GHz); a low dielectric constant (ε_r) is also necessary for the integrated circuit designs ($\varepsilon_r < 25$ or ideally less than 10). One of the well known substrates for use in a HTS device is the $LaAlO_3$ compound, which has a good lattice match for $YBa_2Cu_3O_{7-x}$ (YBCO) films and the appropriate dielectric properties; however, it was reported that the $LaAlO_3$ compound is twinned and a ferroelastic phase transition takes also place at a temperature of around 435 °C.[4] In the case of Al_2O_3 compound, although the dielectric constant and dielectric loss are appropriate for use in a HTS device as a substrate, the preparation of a buffer layer is required in order to prevent an interfacial reaction between the Al_2O_3 and YBCO compounds. Thus, the development of a variety of the new substrate materials with the appropriate dielectric and physical properties as mentioned above are especially required.

The Y_2BaCuO_5 so-called “green phase” compound is an insulator phase of the YBCO high-temperature superconductor. The crystal structure of the Y_2BaCuO_5 compound, which is composed of three polyhedra, i.e. Y_2O_{11}, BaO_{11} and CuO_5, is reported and known to be an orthorhombic structure with the space group *Pnma* (No. 62); the crystal structures of R_2BaCuO_5 (R = rare-earth) compounds were investigated by Salinas-Sanchez et al.[5] However, the relationship between the microwave dielectric properties and the R_2O_3–BaO–MO (R = rare earth, M = Cu and Zn) system have not been evaluated to date. Thus, this paper focuses on the relationship between the covalency of the cation–oxygen bond and the microwave dielectric properties of R_2BaMO_5 compounds.

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2. Experimental method

Polycrystalline samples of the R_2BaMO_5 series (R = Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb; M = Cu and Zn) were prepared by a standard solid-state reaction method, using high purity (99.9%) R_2O_3, $BaCO_3$, CuO and ZnO powders. The powders weighted on the basis of stoichiometric composition were mixed with acetone. After calcining at 950 °C for 20 h in air, these calcined powders were ground with polyvinyl alcohol. Subsequently, the powders were uniaxially pressed into pellets (12 mm in diameter and 7 mm in thickness) and sintered at the various temperatures for each composition for 10 h until the highest density was obtained. The sintered pellets were polished and annealed at 850 °C for 2 h in air. The microwave dielectric properties of the sintered specimens were evaluated by using Hakki and Coleman method.[6,7] X-ray powder diffraction (XRPD) with the Cu Kα radiation was extensively used to characterize the crystallographic phases of the sintered samples; the crystal structures of each compound were refined by using the Rietveld analysis.[8,9] The XRPD data for the Rietveld analysis were obtained in terms of a step scanning method in the range of $10° \leq 2\theta \leq 90°$ with a step size of 0.03°/step and a counting time of 3.0 s. The bond length and volume of the polyhedra were determined from the refined crystal structure parameters. Moreover, the covalency of the cation–oxygen bonds was estimated on the basis of the bond valence theorem reported by Brown and co-worker[10,11] and the relationship between the covalency and bond length was given by the following equations:

$$s = \left(\frac{R_{ij}}{R_0}\right)^{-N} \tag{1}$$

$$f_c = as^M \tag{2}$$

where the R_0 and N represent the fitted constants, respectively; R_{ij} is the bond length between cation i and anion j which is obtained by the Rietveld analysis. Moreover, a and M in Eq. (2) are the empirically determined parameters in order to estimate the covalency of cation–oxygen bond[11]; f_c is covalence of cation–oxygen bond.

3. Results and discussion

From the XRPD profiles, the samples were determined to have an orthorhombic structure (S.G. *Pmna*); however, in the case of the Yb_2O_3–BaO–ZnO system, the presence of three phases, i.e. Yb_2O_3, $Yb_2Ba_2O_5$ and ZnO, was recognized in these profiles; a single phase of Yb_2BaZrO_5 compound was not obtained. The influence of rare-earth substitution for Y on the lattice parameters of the R_2BaCuO_5 and R_2BaZnO_5 compounds are shown in Fig. 1 as a function of the ionic radii of the rare-earth ions. All the lattice parameters of the R_2BaCuO_5 and R_2BaZnO_5 compounds linearly increased, depending on the differences in the ionic radii of the R ions. When comparing the lattice parameters of the R_2BaCuO_5 compounds with those of the R_2BaZnO_5 compounds, the lattice parameters, a and b, of the R_2BaZnO_5 compounds were larger than those of the R_2BaCuO_5 compounds, whereas the lattice parameter c of the R_2BaZnO_5 compounds was smaller than that of the R_2BaCuO_5 compounds. In this crystal structure, it is known that the Zn substitution for Cu especially exerts an influence on the M–O (M = Cu and Zn) bond lengths in the MO_5 pyramid[12] where the O(3) and M are located at the top and bottom of the pyramid, respectively; the bottom plane of the pyramid is composed of O(1) and O(2). With the Zn substitution for Cu, the expansion of bottom plane in the MO_5 pyramid was recognized; this expansion led to the increase in the lattice parameters a and b because the bottom plane of the MO_5 pyramid was nearly parallel to the ab plane. In addition, the M–O(3) bond length was decreased by the Zn substitution for Cu; it was considered that the decrease in the M–O(3) bond length exerts an influence on the variation in the lattice parameter c.

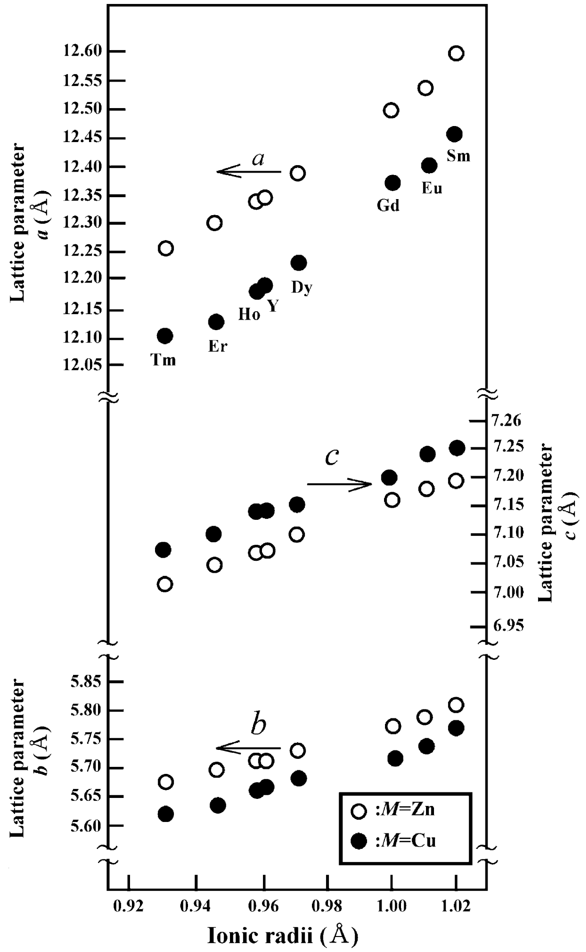

Fig. 1. Lattice parameters of R_2BaMO_5 (M = Zn and Cu) compounds as a function of ionic radii of R ions.

Fig. 2 shows the relationship between the volume of the R_2O_{11}, BaO_{11} and MO_5 polyhedra and the ionic radii of the rare-earth ions. The volume of the MO_5 pyramid is almost constant in both R_2BaCuO_5 and R_2BaZnO_5 compounds; on

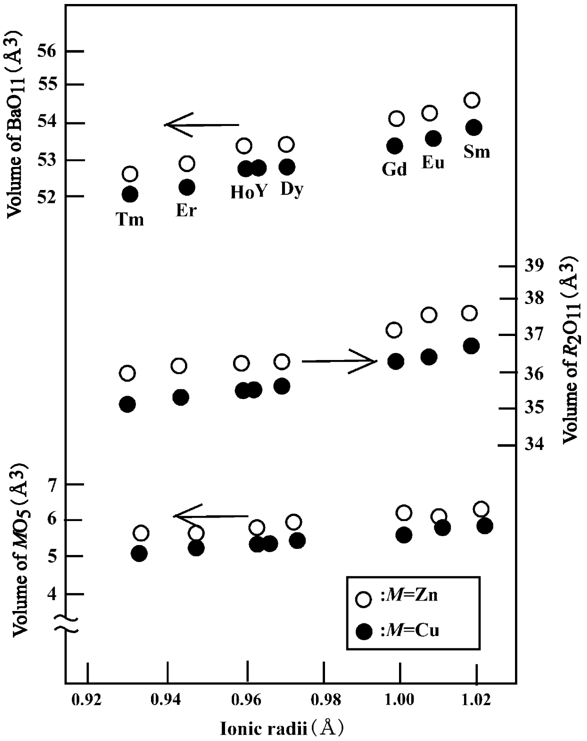

Fig. 2. Relationship between ionic radii of R ions and volume of three polyhedra in R_2BaMO_5 (M = Zn and Cu) compounds.

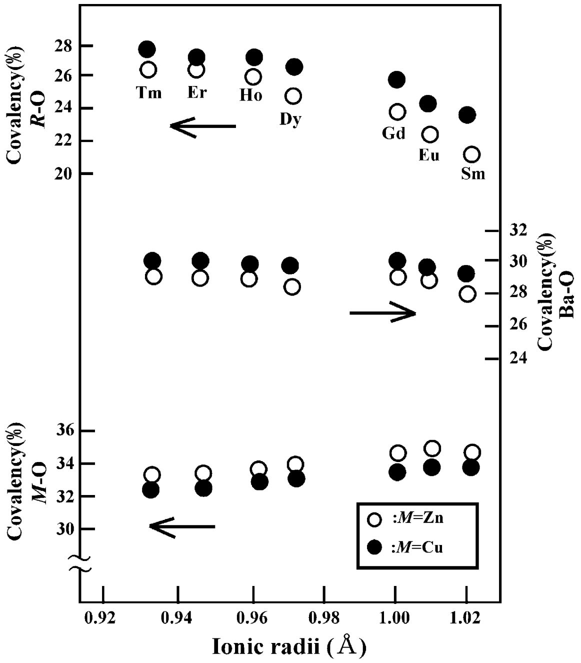

Fig. 3. Covalency of cation–oxygen bond in R_2BaMO_5 (M = Zn and Cu).

the other hand, the volume of the R_2O_{11} polyhedra exhibits a linear increase, depending on the differences in the ionic radii of the R ions. Moreover, the variations in the volume of the BaO_{11} polyhedra were slightly increased by the R substitution for Y. Thus, it is considered that the differences in the ionic radii of R ions predominantly exert an influence on the expansion of volume in R_2O_{11} polyhedra, resulting in the increase in the R–O bonds.

The effects of R substitutions for Y on the variations in the covalency of cation–oxygen bond of the R_2BaCuO_5 and R_2BaZnO_5 compounds were calculated from the bond valence theorem; the results are shown in Fig. 3. The decrease in the covalency of the R–O bond was observed in both of the compounds with increasing the ionic radii of R ions; these variations in the covalency of the R ions substantially related to the increase in the R–O bond caused by the R substitution for Y because the bond strength of the R–O bond was proportional to the variations in the R–O bond. Moreover, the covalency of the M–O bond in the R_2BaZnO_5 compounds is larger than that of the R_2BaCuO_5 compounds, whereas those of the R–O and Ba–O bonds in the R_2BaZnO_5 compounds are smaller than those of the R_2BaCuO_5 compounds as shown in Fig. 3. The variations in the covalency of M–O bonds in the R_2BaCuO_5 and R_2BaZnO_5 compounds are due to the decrease in the M–O(3) bonds caused by the Zn substitution for Cu.

The normalized covalencies of the R–O, Ba–O and M–O bonds are shown in Figs. 4–6 as a function of the ionic radii of the R ions. The normalized covalency of the R–O bond in the R_2BaCuO_5 and R_2BaZnO_5 compounds linearly decreased, depending on the ionic radii of R ions because of the expansion of the R_2O_{11} polyhedron as mentioned above. Moreover, comparing the normalized covalency of the R_2BaZnO_5 compounds with that of the R_2BaCuO_5 compounds, the normalized covalency of the R_2BaZnO_5 compounds is smaller than that of the R_2BaCuO_5 compounds. This result closely relates to the increase in the R–O bond length caused by the expansion of the bottom plane of the MO_5 pyramid by the Zn substitution for Cu.

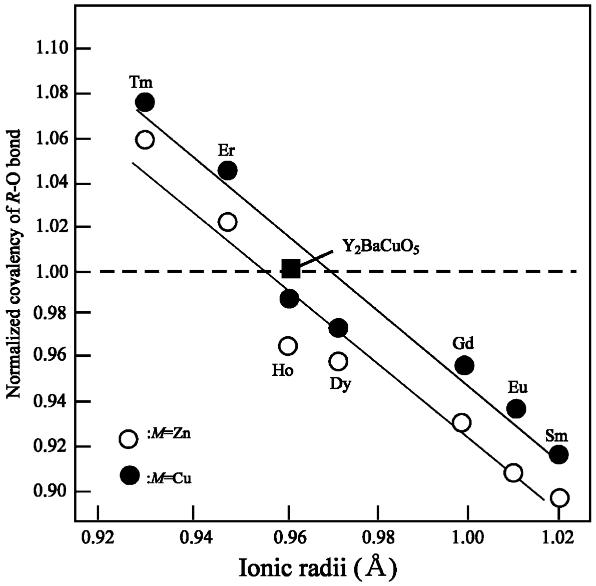

Fig. 4. Variations in normalized covalency of R–O bond in R_2BaMO_5 (M = Zn and Cu).

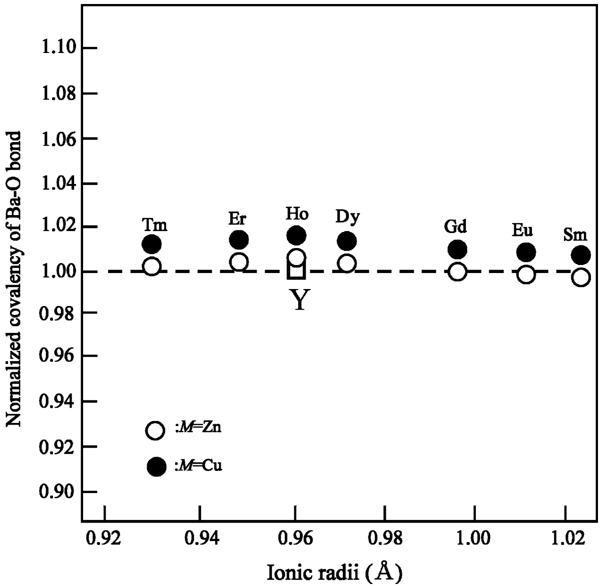

Fig. 5. Normalized covalency of Ba—O bond in R_2BaMO_5 (M = Zn and Cu) compounds.

On the other hand, the normalized covalency of the Zn–O bond in the R_2BaZnO_5 compounds is higher than those of the R_2BaCuO_5 compounds. Moreover, in the case of Ba–O bond, the significant variations in the normalized covalency of Ba–O bond were not recognized in both the R_2BaCuO_5 and R_2BaZnO_5 compounds as shown in Fig. 5. From these results, it was found that the rare earth substitutions for Y exert an influence on the decrease in the covalency of the R–O bond in the crystal structure as shown in Fig. 4.

The dielectric constants of the R_2BaCuO_5 and R_2BaZnO_5 compounds are shown in Fig. 7 as a function of the ionic radii of R ions. In both of the R_2BaCuO_5 and R_2BaZnO_5 compounds, the dielectric constant linearly increased as the increase of ionic radii of R ions ranged from 12 to 18; these values were similar to those of the $RAlO_3$ ceramics,[2] which are known to be one of the appropriate substrates for a HTS filter. In general, it is known that the dielectric constant of the dielectric ceramics at a microwave frequency is effected by the ionic polarizability of cations and anions in the compound, and this behavior can be interpreted by considering the Clausius-Mosotti equation which relates with the dielectric constant of a macroscopic sphere having the volume of V_m to the macroscopic polarizability, α_m. The relationship between the dielectric constant and α_m is given by the following equation:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{4\pi\alpha_m}{3V_m}. \quad (3)$$

The macroscopic polarizabilites of the R_2BaCuO_5 and R_2BaZnO_5 compounds calculated from the measured value of the dielectric constant are shown in Fig. 8. Such poralizabilities of both compounds linearly increased; these variations in the macroscopic polarizabilities exhibited a similar tendency to those of the dielectric constant. Moreover, the ionic polarizability of R ions was reported by Shannon.[13]

Thus, it is considered that the decrease in the covalency of R–O bonds enhances the increase in the macroscopic polarizabilities. Thus, from these results, it is considered that the variations in the covalency of R–O bond exert an influence on the dielectric constant in this system.

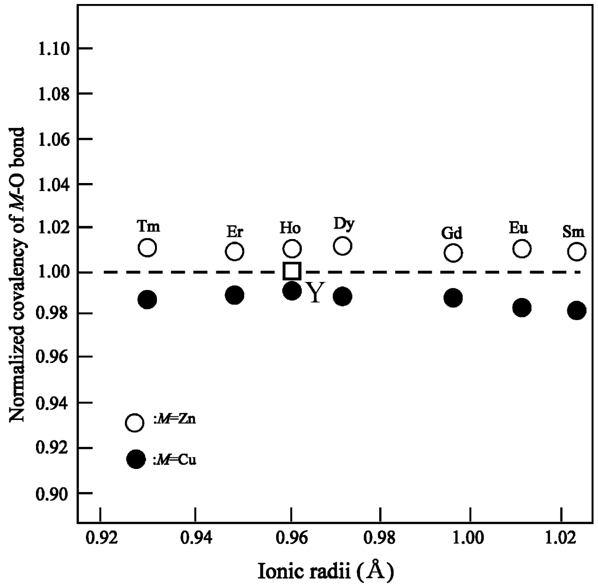

Fig. 6. Normalized covalency of M—O bond versus ionic radii of R ions for R_2BaMO_5 (M = Zn and Cu).

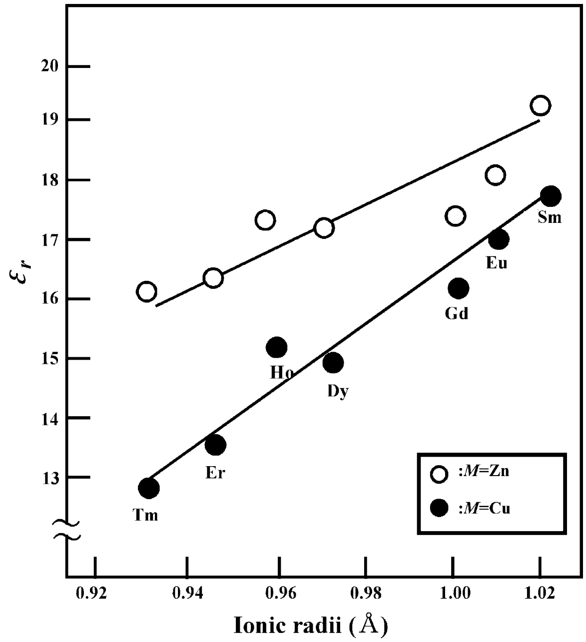

Fig. 7. Variation of dielectric constant with ionic radii of R ions for R_2BaMO_5 (M = Zn and Cu).

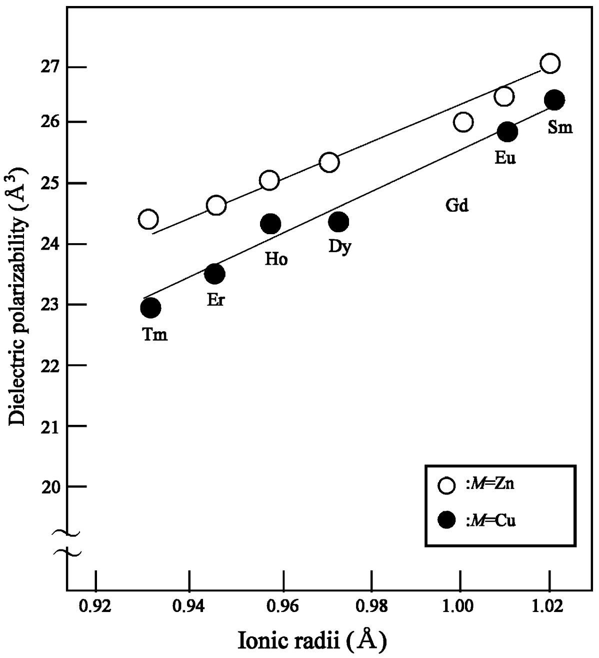

Fig. 8. Variations in dielectric polarizability of R_2BaMO_5 (M = Zn and Cu) as a function of ionic radii of R ions.

4. Conclusions

The influences of R substitution for Y on the covalency of cation–oxygen bonds and the microwave dielectric properties of the R_2BaCuO_5 and R_2BaZnO_5 (R = rare earth) compounds were investigated; from the calculation of covalency of cation–oxygen bonds, it was found that the covalency of the R–O bond in the R_2BaCuO_5 and R_2BaZnO_5 compounds decreases with increasing the ionic radii of R ions because of the increase in the R–O bond length. When comparing the covalency of the R–O bond in the R_2BaZnO_5 compound with that of the R_2BaCuO_5 compound, the covalency of the R–O bond in the R_2BaZnO_5 compound was smaller than that of R_2BaCuO_5 compound; this result is closely related to the differences in the R–O bond distances between the R_2BaCuO_5 and R_2BaZnO_5 compounds. The dielectric constant of both compounds was linearly increased from 14 to 18 with the increase of the ionic radii of R ions. Also, the dielectric constant of the R_2BaZnO_5 compound was large in comparison with that of the R_2BaCuO_5 compound, though the ionic polarizability of Zn was smaller than that of Cu. Thus, it is considered that the difference in the dielectric constant between the compounds R_2BaCuO_5 and R_2BaZnO_5 is related to the covalency of the R–O bonds.

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