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Microwave dielectric properties and crystal structure of homologous compounds $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) for base station applications

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Abstract

Homologous compounds $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) with high dielectric constant ϵ_r and quality factor $Q \times f$ are candidate materials for dielectric resonators in base station of telecommunication systems. We have investigated the relationship between the microwave dielectric properties and crystal structure of these new materials. Single crystals of $CaLa_4Ti_4O_{15}$ were synthesized to analyze the crystal structure precisely. The ceramic discs of the $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) were also synthesized and the microwave dielectric properties were measured. Ba-analogy showed the highest ϵ_r of 44.4 due to the large cationic movement. Ca-analogy showed the highest $Q \times f$ of 50,246 GHz due to resemblance in ionic radius between Ca^{2+} ($r = 1.34$ Å: 12-coordination) and La^{3+} ($r = 1.36$ Å: 12-coordination) ions. Sr-analogy showed near zero temperature coefficient of resonant frequency τ_f of -8.4 ppm/°C compared with the others. The relationships between their crystal structures and properties were discussed.

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

1. Introduction

Recently, microwave dielectric ceramics have been used in mobile telecommunication devices as resonance elements. The important characteristics required for dielectric resonators are high dielectric constant ϵ_r, high quality factor $Q \times f$ and near zero temperature coefficient of resonant frequency τ_f. In particular, the microwave dielectric materials used in the base stations of portable telephones are required to have high $Q \times f$ for high power and high ϵ_r for miniaturization. It is difficult to obtain microwave dielectric materials with high ϵ_r and high $Q \times f$ because ϵ_r and $Q \times f$ has generally negative correlation. Some of the reported candidate systems with high ϵ_r and $Q \times f$ for base station resonators are $BaO–TiO_2–ZnO$: $\epsilon_r = 36$, $Q \times f = 42{,}000$ GHz[1] and $ZnNb_2O_8–TiO_2$: $\epsilon_r = 37$, $Q \times f = 29{,}000$ GHz.[2] Recently, $Ba_nLa_4Ti_{3+n}O_{12+3n}$ ($n = 0$, 1 and 2) homologous compounds in the $BaO–La_2O_3–TiO_2$ ternary system have been reported[3] as a very useful material for base station applications. In our previous studies,[4] we have found $BaLa_4Ti_4O_{15}$ had high ϵ_r of 44 and high $Q \times f$ of 47,000 GHz. The microwave dielectric properties of $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) have been investigated by Jawahar et al.[5] According to their reports, $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) ceramics showed high ϵ_r in the range 42–54, high quality factors with in the range 16,222–50,215 GHz.

These homologous compounds of $Ba_nLa_4Ti_{3+n}O_{12+3n}$ ($n = 0$, 1 and 2) are located on the $BaTiO_3–La_4Ti_3O_{12}$ binary phase diagram presented by Saltykova et al.[6] and hexagonal perovskite-like layer structure as fundamental crystal structures are also presented by them. Harre et al.[7] analyzed crystal structure of $BaLa_4Ti_4O_{15}$ without distinguishing Ba/La by X-ray diffraction. This structure stacking with $(Ba, La)O_3$ close-packed layer is constructed with two kind of slabs: one is perovskite slab with cubic closed packing and another is junction slab with hexagonal closed packing. The crystal structure with Ba/La ordering is analyzed using Rietveld full profile analysis of neutron powder diffraction patterns by Teneze et al.[8] We also successfully distinguished the sites of Ba^{2+} and La^{3+} in $BaLa_4Ti_4O_{15}$ compound by X-ray single crystal analysis regardless of similarity for atomic scattering factors.[9] But in our knowledge, crystal structures of the compounds in Sr- and Ca-analogies have not been clarified yet.

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In the present study, the crystal structure of $CaLa_4Ti_4O_{15}$ is refined by X-ray single crystal analysis, and the microwave dielectric properties of $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) ceramics are observed. We discuss the relationships between their crystal structures and microwave dielectric properties.

2. Experimental procedure

The single crystals of $CaLa_4Ti_4O_{15}$ were grown by self-flux method. The crystal obtained was ground to the shape of sphere by the Bond method. Intensity data were collected at room temperature on an X-ray single-crystal Wissenberg-type diffractometer with imaging plate using Mo Kα radiation (Rigaku: R-AXIS RAPID). The initial atomic parameters of $CaLa_4Ti_4O_{15}$ were referred from the work of Teneze et al.[8] with Ba/La ordering. The crystal structures of these single crystals were analyzed by full-matrix least-squares refinements program RADY.[10]

The ceramic discs of $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) were prepared by solid-state reaction method. According to the stoichiometric of $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca), $BaCO_3$ (99.0%), $SrCO_3$ (99.0%), $CaCO_3$ (98.0%), La_2O_3 (99.9%) and TiO_2 (99.8%) were weighed, and ball-milled in a polyethylene jar using zirconia balls and ethanol media for 24 h. The mixtures were dried and calcined at 1000 °C for 2 h in air. The calcined powders were ground and mixed with polyvinyl alcohol as a binder. The powders were passed through a 300 mesh and pressed into discs at a pressure of 98 MPa. The conditions of sintering treatment in air are as follows; Ba-analogy (at 1600 °C for 2 h), Sr-analogy (at 1550 °C for 48 h) and C-analogy (at 1550 °C for 24 h). The crystalline phases of sintered samples were identified by X-ray powder diffraction (XRPD). The dielectric constant ϵ_r, unloaded Q values and temperature coefficients of the resonant frequency τ_f between 20 and 80 °C were measured using a pair of parallel conducting Ag plates under the TE_{011} mode by Hakki and Coleman's method.[11,12] The bulk density was measured by Archimedes' method.

3. Results and discussion

3.1. Single crystal structure analysis of $CaLa_4Ti_4O_{15}$

The crystal data of $CaLa_4Ti_4O_{15}$ are shown in Table 1. The possible space groups are $P\bar{3}c1$ (No. 165) and $P3c1$ (No. 158) including in trigonal crystal system based on the extinction rule of $l = 2n + 1$ on $000l$. The crystal structure refined with the $P\bar{3}c1$ the same space group as Ba-analogy was converged to reliability factor of $R = 3.66$ and $R_w = 3.92\%$. The $P3c1$ space group without centrosymmetry was applied for Ba-analogy by Harre et al.,[7] but reliability factor was not converged. The refined unit-cell parameters obtained by R-AXIS RAPID (RIGAKU) diffractometer were $a = 5.531(7)$ Å, $c = 22.03(2)$ Å, and the number of formula unit in unit cell is $Z = 2$.

The coordinates of Ca-analogy converged with $P\bar{3}c1$ are shown in Table 2. This compound has a sequence of five (A, La)O_3 close packed layers like *hccch* of the $Ba_5Nb_4O_{15}$ type.[13] Here, A is cation located in cuboctahedron in the perovskite structure, *h* means hexagonal close packing and *c* is cubic close packing. The perovskite slab with cubic close packing composed four TiO_6 octahedral layers and the junction slab with hexagonal close packing between perovskite slabs composed of a three-octahedron string shared face with an empty octahedron in center.

Table 1
Crystal data of the $CaLa_4Ti_4O_{15}$ homologous compound with $n = 1$

Composition	$CaLa_4Ti_4O_{15}$
Formula weight (g/mol)	1027.305
Crystal system	Trigonal
Space group	$P\bar{3}c1$ (No. 165)
Point group	$\bar{3}m1$
Lattice parameter (Å)	
a	5.531(7)
c	22.03(2)
Unit cell volume (Å^3)	584(4)
Formula number (Z)	2
Calculated density (D_x) (g/cm^3)	5.845
Linear absorption coefficient (cm^{-1})	177.157
Reliability factors (%)	
R	3.66
R_w	3.92

It was clarified that Ba- and Ca-analogies have difference of ordering form for A-site cations. In the case of Ca-analogy, Ca^{2+} ions ($r = 1.34$ Å) are occupied in all A-sites: A_1, A_2 and A_3 including La ($r = 1.36$ Å) ions as shown in Fig. 1 although Ba^{2+} ($r = 1.61$ Å) ions in Ba-analogy are predominantly occupied in A_1-sites as reported by Teneze et al.[8] and in our previous paper.[9] As the space of A_1-sites is larger than those of A_2- and A_3-sites, Ba^{2+} ions with large ionic radius occupy A_1-sites predominantly. On the other hand, as the ionic radius of Ca^{2+} ($r = 1.34$ Å) is close to that of La^{3+} ions, Ca ions of Ca-analogy are randomly occupied A-sites.

Fig. 2(a) and (b) show the displacement values of cations in A-site from oxygen packing layer and Ti ions in B-site from the center of TiO_6 octahedron for Ba and Ca-analogies, respectively. These displacements of cations are caused by two reasons as

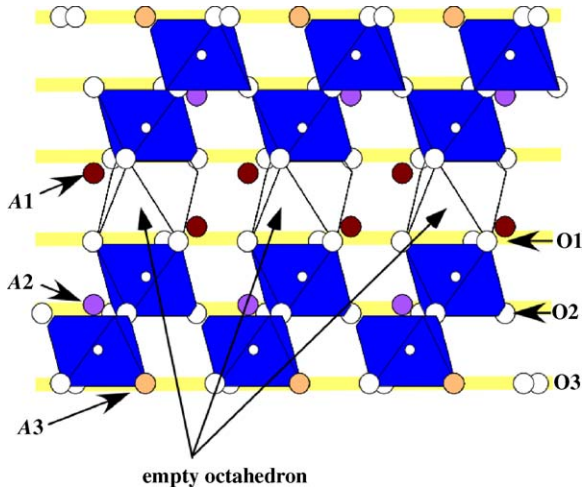

Fig. 1. Schematic representation of the $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) structures as viewed along $(2\bar{1}0)$ plane.