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Journal of the European Ceramic Society 26 (2006) 2039–2043

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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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doi:10.1016/j.jeurceramsoc.2005.09.098

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

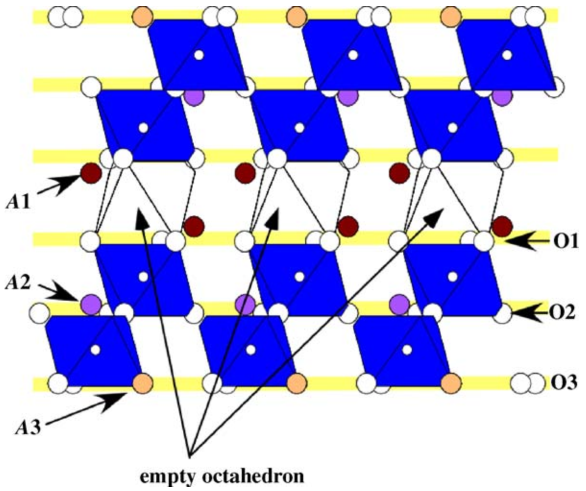

Fig. 1. Schematic representation of the $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) structures as viewed along $(2\bar{1}0)$ plane.

Table 2
Coordinate of $CaLa_4Ti_4O_{15}$ homologous compound

Atom	Site	Occupancy	x	y	z	B_{eq}
Ca (1)	4d	0.24138	1/3	2/3	0.46360 (8)	0.91 (2)
La (1)		0.75862				
Ca (2)	4d	0.11368	1/3	2/3	0.35729 (6)	0.67 (2)
La (2)		0.88632				
Ca (3)	2a	0.28987	0	0	1/4	0.67 (3)
La (3)		0.71013				
Ti (1)	4c	1	0	0	0.4103 (1)	0.42 (2)
Ti (2)	4d	1	1/3	2/3	0.3024 (2)	0.47 (2)
O (1)	12g	1	0.900 (1)	0.236 (1)	0.5536 (2)	0.4 (3)
O (2)	12g	1	0.333 (1)	0.116 (2)	0.3477 (2)	1.2 (4)
O (3)	6f	1	0.563 (1)	0	1/4	0.4 (3)

Original coordinates are sited from Teneze et al.[8]

follows: one is lack of Ti ions of octahedra in the junction slab, and another is the ionic size difference between Ba and Ca ions located in (A, La)O_3 packing layer. In the former, the lack of Ti ions causes the movement because of no repulsion from empty octahedra. In the latter, the difference of ionic size brings differences of ordering on the A_1 and A_2-sites between Ba- and Ca-analogues.

3.2. Relationships between crystal structure and microwave dielectric properties of $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca)

XRPD patterns of the sintered ceramics with $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) compositions are shown in Fig. 3. They were identified as single phase composed by homologous compound with ICDD cards $BaLa_4Ti_4O_{15}$ (No. 89-5557), $SrLa_4Ti_4O_{15}$ (No. 49-0254) and $CaLa_4Ti_4O_{15}$ (No. 36-1278), respectively. According to Fig. 3, these diffraction peaks of Ba-analogy were shifted to low angle compared with those of Sr- and Ca-analogues. It is guessed that the lattice parameters of Ba-analogy are larger than those of Sr- and Ca-analogues.

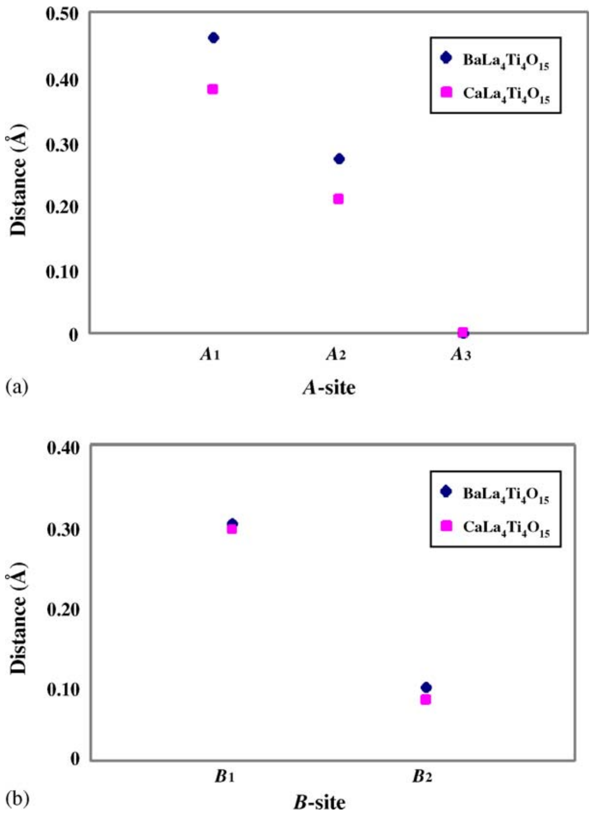

Fig. 2. Distance of A-site ions from oxygen packing layer (a) and B-site ions from center of octahedron (b).

Microwave dielectric properties of the Ba-, Sr- and Ca-analogues ceramics are shown in Table 3. These samples showed excellent microwave dielectric properties such as ϵ_r greater than 40, $Q \times f$ greater than 40,000 GHz and τ_f within −30 ppm/°C. The highest ϵ_r of 44.4 was observed in the case of Ba-analogue, and the values are decreased to 41.1 for Ca. The highest $Q \times f$ of 50,246 GHz was observed in the case of Ca-analogue, and the values are decreased to 46,220 for Sr and to 41,008 GHz for Ba. These values are much higher than that of an earlier report.[5]

We would like to consider that the reason of large ϵ_r and high $Q \times f$ based on the crystal structure. There are three characteristic points on the crystal structure: one is size of cation sites another is shift of cation positions and different divalent cations distribution. Table 4 shows site volumes of each cationic polyhedra for Ba- and Ca-analogues. Large volume of cation sites brings large ϵ_r. The divalent cation with large ionic radius such as Ba, Ca and Sr expands the lattice and brings enlargement of

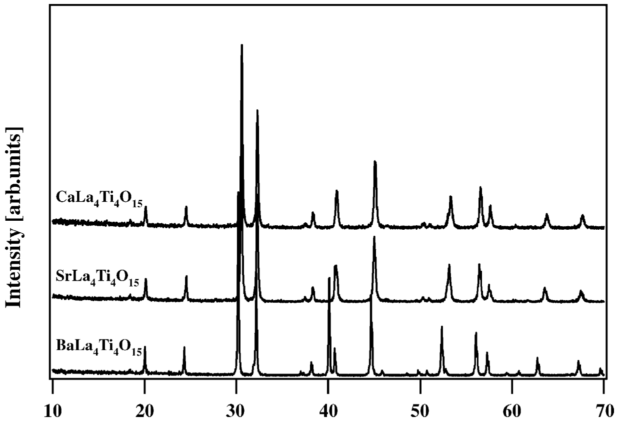

Fig. 3. X-ray powder diffraction patterns of homologous compounds $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca).

Table 3
Relative density and microwave dielectric properties of $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) ceramics

Composition	Sintering condition	d_r (%)	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
$BaLa_4Ti_4O_{15}$	1600 °C, 2 h	98.4	44.4	41,008	−26.0
$SrLa_4Ti_4O_{15}$	1550 °C, 48 h	98.9	43.7	46,220	−8.4
$CaLa_4Ti_4O_{15}$	1550 °C, 24 h	94.8	41.1	50,246	−25.5

Table 4
Volume of cationic polyhedra for $ALa_4Ti_4O_{15}$ (A = Ba and Ca)

Site	Cation	Position	C.N.	Volume (Å^3)
(a) $BaLa_4Ti_4O_{15}$				
A_1	Ba, La	4d	12	54.045
A_2	La	4d	12	49.294
A_3	La	2a	12	48.638
B_1	Ti	4c	6	10.377
B_2	Ti	4d	6	10.188
(b) $CaLa_4Ti_4O_{15}$				
A_1	Ca, La	4d	12	49.682
A_2	Ca, La	4d	12	47.898
A_3	Ca, La	2a	12	47.420
B_1	Ti	4c	6	10.073
B_2	Ti	4d	6	9.889

cation sites. Especially, expansion of B-site volume effects Ti ion movement based on the rattling effect. In the case of Ba-analogue with highest ϵ_r value, the volume is larger than that of Ca-analogue. Ba ion with large ionic radius of 1.61 Å is more effective than Ca ion with $r = 1.34$ Å as shown in Table 2. In the second case of shift of cation positions, the ϵ_r of Ba-analogy with large shift larger than that of Ca-analogy. This shift might brings movability of La-ion with small ionic radius. So, ϵ_r of Ba-analogy with large shift is greater than that of Ca-analogue. High $Q \times f$ value might come from cation distribution and volume of cation sites. In the case of Ca-analogue, as the shift of cations from close packed layer of oxygen is smaller than Ba-analogue, $Q \times f$ value becomes high due to small movement of cations. Moreover, the Ca ions occupied widely A-sites might be distributed periodically with La-ions to bring high $Q \times f$. ϵ_r values are depend on the ionic polarization in turn Ba ($P = 6.4$), Sr ($P = 4.24$) and Ca ($P = 3.16$).[14] These homologous compounds show characteristic near zero τ_f ppm/°C. τ_f of Sr-analogy is near zero ppm/°C compared with the others. This reason might come from analogue of $SrTiO_3$ having a large positive τ_f of 1200 ppm/°C.[15]

4. Conclusions

Crystal structure of a homologous compound $CaLa_4Ti_4O_{15}$ with $P\bar{3}c1$ was analyzed by X-ray single crystal analysis converged to $R = 3.66\%$. The Ca ions are distributed in all A-positions though Ba ions of Ba-analogue ordered in A_1-position. The $ALa_4Ti_4O_{15}$ (A = Ba, Sr and Ca) compounds have good dielectric properties useful for base station of mobile phone: highest $Q \times f$ value is 50,246 GHz, the highest ϵ_r is 44.4 and near zero τ_f is −8.4 ppm/°C. The relationship between crystal structure and properties are presented. These good dielectric properties come from crystal structure of cation displacement with different ionic size.

It was found that the crystal structure of homologous compounds has close correlation with their microwave dielectric properties. $BaLa_4Ti_4O_{15}$ ceramics showed the highest ϵ_r of 44.4 because of the large cationic movement. $CaLa_4Ti_4O_{15}$ ceramics indicated the highest $Q \times f$ of 50,246 GHz due to the decrease of layer gap between A-site ions and oxygen. On the other hand, $SrLa_4Ti_4O_{15}$ ceramics showed near zero τ_f of −8.4 ppm/°C compared with others.

Acknowledgments

The authors would like to thank Dr. M. T. Sebastian (Regional Research Laboratory, Council of Scientific and Industrial Research) for discussion in this study. This work was supported by a grant from the NITECH 21st Century COE Program “World Ceramics Center for Environmental Harmony”. We would also like to thank Mr. A. Harada, President of Daiken Chemical Co., Ltd. for his arrangement in the measurement of microwave dielectric properties.

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