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Rietveld Refinement and Dielectric Properties of $CaLa_4Ti_5O_{17}$ and $SrLa_4Ti_5O_{17}$ Ceramics

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Dedicated to the memory of Professor Ljubo Golič

Abstract

The ceramic materials of $CaLa_4Ti_5O_{17}$ and $SrLa_4Ti_5O_{17}$ were synthesized using the solid-state reaction method. Rietveld refinements of XRD data were carried out using different models obtained from the structural database and the orthorhombic structure (*Pmnn* space group) proved to be most suitable for both compounds. Like in similar compounds of the general formula $A_nB_nO_{3n+2}$, where perovskite-like slabs are separated by oxygen-rich layers, Ca or La and Sr or La occupy the A site. The refined occupancies indicate that Ca preferably occupies the A sites within the perovskite slabs, while Sr is preferably found within the oxygen-rich layers. The characterization of microwave dielectric properties revealed that ceramics based on these compounds exhibit permittivity in the range of 39–51, high quality factor (Qxf) in the range of 13140–14200 and negative value of temperature coefficient of resonant frequency τ_f = –29 ppm/K for $CaLa_4Ti_5O_{17}$ and positive value of τ_f = 58 ppm/K for the Sr-analog.

Keywords: Powder diffraction, Rietveld refinement, Microwave ceramics

1. Introduction

In the past two decades a lot of effort was put into investigations of new dielectric ceramic materials due to specific demands. The most important and constant interest has been focused on miniaturization, which imposes higher permittivity (ε), high quality factor (Qxf) and temperature stable resonant frequencies (τ_f), of the new materials.

Compounds in the La_2O_3–TiO_2-based system were also examined as microwave frequency dielectric ceramics.[1] The addition of selected oxides, for example Al_2O_3,[1] Ga_2O_3,[2] CaO[3] causes formation of an A-site deficient perovskite $La_{2/3}TiO_3$ compound. Solid solutions $(1–x)La_{2/3}TiO_3$(stab)-$xLaAlO_3$ stable over the range $0.04 \leq x \leq 1$ and $(1–x)La_{2/3}TiO_3$(stab)-$xCaTiO_3$ stable for $0.1 \leq x \leq 0.96$ were identified in the systems La_2O_3–TiO_2–Al_2O_3 and La_2O_3–TiO_2–CaO, respectively. Single phase ceramics based on these solid solutions exhibit excellent microwave dielectric properties, which can be simply tuned by changing the $La_{2/3}TiO_3$/($LaAlO_3$ or $CaTiO_3$) ratio.[3,4] In the ternary La_2O_3–TiO_2–CaO system, a number of compounds were identified. Nanot et al. reported a perovskite-related series of compounds with a general formula $A_nB_nO_{3n+2}$, where n = 4.5, 5 and 6 along the compositional line $CaTiO_3$–$La_2Ti_2O_7$. Thus, the stable compounds with n = 4.5, 5 and 6 are $CaLa_8Ti_9O_{31}$, $CaLa_4Ti_5O_{17}$ and $Ca_2La_4Ti_6O_{20}$, respectively.[5]

Furthermore, along the composition line $CaTiO_3$–$La_4Ti_3O_{12}$ two compounds $CaLa_4Ti_4O_{15}$ and $Ca_2La_4Ti_5O_{18}$ were reported.[6] $CaTiO_3$ dissolves up to 40 mol % of La_2O_3. The end member of this solid solution is the componds $Ca_3La_4Ti_3O_{15}$.[7] Some of these componds e.g. $CaLa_4Ti_4O_{15}$, $Ca_2La_4Ti_5O_{18}$, $CaLa_8Ti_9O_{31}$ and $CaLa_4Ti_5O_{17}$ have been reported to have promising microvawe dielectric properties with permitivity over 44, quality factor (Qxf) higher than 17350 and low temperature coefficient (τ_f) in the range of –25 to +6 ppm/K.[8]

To date no detailed structure report has been published on Ca–La–Ti–O or Sr–La–Ti–O ceramic materials. Extensive crystallographic database search yielded no match for any compound of the $CaLa_4Ti_5O_{17}$ or $SrLa_4Ti_5O_{17}$ stoichiometry. However, it was found that the two structures are

most probably isostructural with $La_5Ti_4FeO_{17}$. This resulted in a motivation to explore structures of these materials by X-ray powder diffraction techniques.

The scope of this paper is to analyze the structures of the title materials by X-ray powder diffraction, based on the Rietveld refinement. Additionally, the ceramics based on these compounds were characterized according to their microwave dielectric properties.

2. Experimental Details

Synthesis. The ceramic samples were prepared by the solid-state reaction technique using La_2O_3 (99.99% Alfa Aesar), TiO_2 (99.8% Alfa Aesar), $CaCO_3$ (99.5% Alfa Aesar) and $SrCO_3$ (99.9% Alfa Aesar). Since La_2O_3 shows a strong tendency to form a hydroxide and a carbonate with the moisture and the CO_2 in the air, the oxide was routinely checked prior to weighing with an ignition–loss measurement at 1300 °C. Samples were weighed out according to the stoichiometry and homogenized in ethanol media using YTZ ball mill for 0.5 h. The dried powders were uni-axially pressed into pellets and fired in a tube furnace in air on a Pt foil. Heating rate up to 600 °C was 5 °C/min, followed by 0.9 °C/min up to the different final temperatures between 1420 °C and 1580 °C and soaked there for 10 to 20 h. The final sintering temperatures were optimized for maximum density of the pellets. After the heat treatment, the samples were furnace-cooled to room temperature. The bulk densities were measured using the Archimedes method.

Dielectric measurements. The microwave dielectric properties were measured using a network analyzer (HP, Model HP 8719 C). We used the closed resonant cavity method using $TE_{01\delta}$ mode.

X-ray diffraction measurements. The X-ray powder patterns were collected on a PANalytical X'Pert PRO MPD diffractometer in Bragg-Brentano geometry using $CuK_{\alpha 1}$ radiation. The data was collected in the 2θ range of 3–150° in steps of 0.017° with the total collection time of 64 hours for the Sr-compound and 16 hours for the Ca-compound. Preliminary search-match analyses were carried out with Crystallographica Search-Match software using the PDF data base release 2007[9]. The structural data was obtained from the ICSD[10] data base and the structure refinement was performed using the Rietveld method incorporated in the program package TOPASR2-1[11].

3. Results and Discussion

3. 1. Rietveld Refinement and Structure Consideration

The diffraction pattern of the $CaLa_4Ti_5O_{17}$ compound did not correspond to any known structure of Ca–La–Ti–O compound. However, we found that the position of the diffraction peaks in the XRD-pattern coincided with the ones of $La_5Ti_5O_{17}$[12,9] (281282-ICSD[10]), which is monoclinic with the space group $P2_1/c$. For that reason the structure of $La_5Ti_5O_{17}$ was used as an initial model for $CaLa_4Ti_5O_{17}$ crystal structure refinement. On the basis of the reduced cell search, another suitable model was found in the ICSD database – $La_5FeTi_4O_{17}$,[13] which is orthorhombic with the space group *Pmnn*. The following transformation matrix between the unit cells was determined: 1/2 0 0, 0 1 0, 1/2 0 1.

The volume of the orthorhombic unit cell was two times smaller than the monoclinic one and explained all observed peaks. A very careful investigation of, whether there is anything in the pattern that would justify the use of a larger monoclinic unit cell (peak splitting or broadening, weak reflections, indexed only by the larger cell) gave no support to the large monoclinic unit cell. To verify the model, we also performed the Le–Bail fit with both unit cells and the results were insignificantly different (the R_{wp} value was 3.115 for the larger monoclinic $P2_1/c$ cell and 3.483 for the smaller *Pmnn* orthorhombic cell). Therefore we decided to use the more symmetric $La_5FeTi_4O_{17}$ structural model in further studies.

The $CaLa_4Ti_5O_{17}$ diffraction pattern was then fitted using Rietveld refinement to adjust the unit cell and structural parameters. The atomic positions and occupancies were refined, taking into account the fact that the lanthanum sites can be occupied by calcium, while the sum of the occupancies at all sites was constrained to be unity and the net stoichometric ratio between calcium and lanthanum was preserved. Isotropic displacement parameters were set to be equal for all the atoms of the same type. No

Table 1. Crystal data and refinement parameters of $CaLa_4Ti_5O_{17}$ and $SrLa_4Ti_5O_{17}$.

Compound	$CaLa_4Ti_5O_{17}$	$SrLa_4Ti_5O_{17}$
Space group	Pmnn	Pmnn
a	3.89534(3) Å	3.91122(4) Å
b	31.2774(3) Å	31.3193(4) Å
c	5.51568(48) Å	5.53561(6) Å
V	672.008 (8) Å^3	678.094(1) Å^3
Profile function	Fundamental Parameters	Fundamental Parameters
No. of profile points	8058	8058
No. of reflections	747	747
No. of structural parameters	33	33
No. of profile parameters*	14	14
R_p	4.43	4.67
$R_{p\text{-dash}}$	16.73	15.95
R_{wp}	6.14	7.13
$R_{wp\text{-dash}}$	16.75	18.29
R_{exp}	3.60	1.70
$R_{exp\text{-dash}}$	9.82	4.37

*Profile parameters: 10 background – Chebyshev 10th order, 1 zero correction, 1crystal size L (nm), 1 strain L, 1 scale factor.

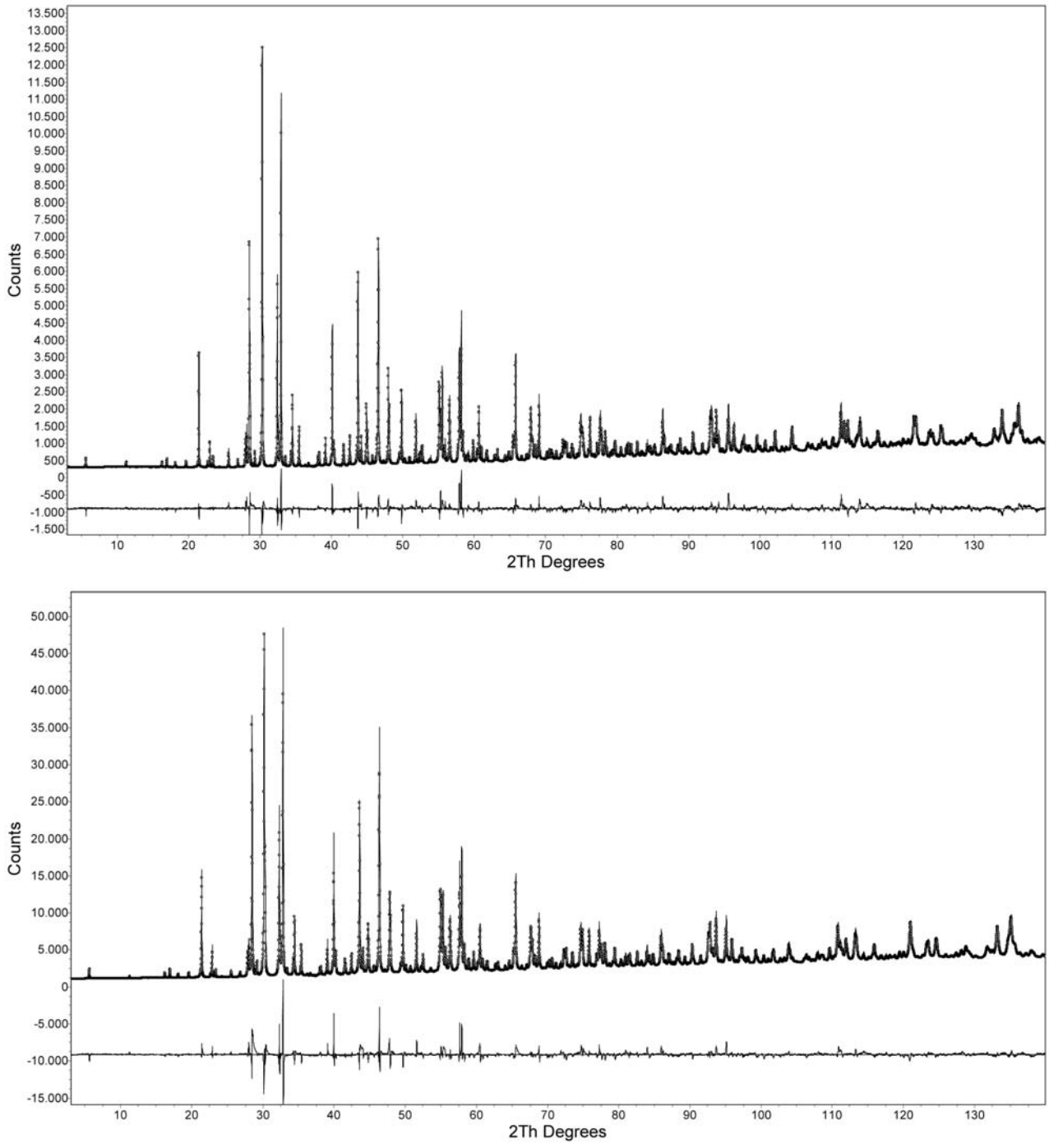

Figure 1. Final Rietveld plot of $CaLa_4Ti_5O_{17}$ (top) and $SrLa_4Ti_5O_{17}$ ceramics (bottom): solid black line – measured, circles – calculated, black line below – difference.

further constraints or restraints were used. After such refinement of all atomic parameters the calculated pattern corresponded well to the experimental one (R_{wp}= 6.14, further details are presented in Tables 1 and 2 and in Fig. 1).

As the structure is rather constrained by symmetry in the space group *Pmnn* (all the atoms lie on the mirror plane *m* perpendicular to *x* at *x* = 0 or *x* = 1/2), an attempt to relax these symmetry restraints and improve the structural model has been made by decreasing the symmetry. By removing certain symmetry elements, structural models based on two orthorhombic (*P*2*nn* and *Pm*2_1*n*) and two monoclinic subgroups (*P*2_1/*c* and *Pc*) of the *Pmnn* space group were constructed. Structural parameters of these four models were subjected to Rietveld refinement. However, since the resulting R_{wp} factors obtained with these space subgroups were not significantly better (e.g., 6.033, 6.100, 5.950 and 6.063

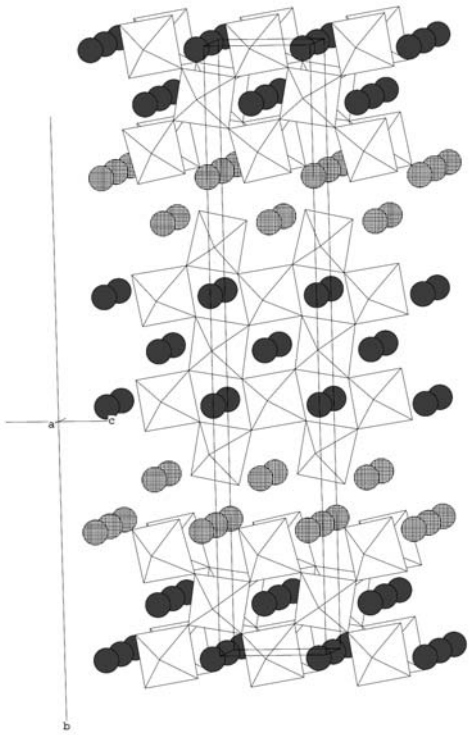

Figure 2. Crystal structure of $CaLa_4Ti_5O_{17}$ viewed along the a axis. Gray spheres are lanthanum or calcium atoms, of which shaded positions are more preferably occupied by lanthanum and thus less preferably by calcium. The white octahedra have oxygen atoms in the corners and titanium atoms in the centre.

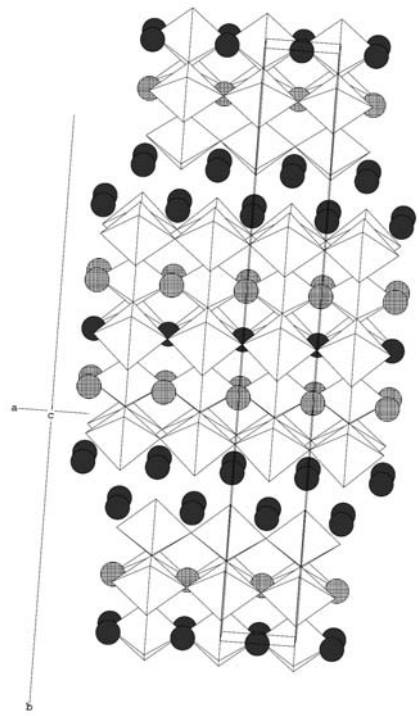

Figure 3. Crystal structure of $SrLa_4Ti_5O_{17}$ viewed along the c axis. Gray spheres are lanthanum or strontium atoms, of which shaded positions are more preferably occupied by lanthanum but less so by strontium. The white octahedra have oxygen atoms in the corners and titanium atoms in the centre.

for the *P*2*nn*, *Pmn*2_1, *P*2_1/*c* and *Pc* space group, respectively) and atomic positions did not change notably with respect to the original model (maximum difference in the respective atom positions were 0.25 Å for oxygen, 0.18 Å for lanthanum and calcium, and 0.07 Å for titanium), none of the lower symmetry models was recognized as a better solution and the model that explains all the available data with the lowest number of parameters was accepted.

The structural model of $SrLa_4Ti_5O_{17}$ was treated in the same manner as for the calcium analog; the same space groups were considered and the *Pmnn* group was again determined to provide the most suitable model. The final

Table 2. Fractional atomic coordinates and site occupancies of $CaLa_4Ti_5O_{17}$ ceramics.

	x	***y***	***z***	B_{iso}	**Occ. (<1)**
La1	0.5	0.08991(5)	0.5010(3)	0.393(18)	0.7747(31)
Ca1	0.5	0.08991(5)	0.5010(3)	0.393(18)	0.2253(31)
La2	0.5	0	0	0.393(18)	0.7712(82)
Ca2	0.5	0	0	0.393(18)	0.228(82)
La3	0.5	0.20982(5)	0.0721(3)	0.393(18)	0.8397(27)
Ca3	0.5	0.20982(5)	0.0721(3)	0.393(18)	0.1603(27)
Ti1	0	0.09337(12)	-0.0001(8)	0.30(4)	
Ti2	0	0.17790(12)	0.5398(8)	0.30(4)	
Ti3	0	0	0.5	0.30(4)	
O1	0.5	0.0823(4)	-0.010(3)	0.67(9)	
O2	0	0.9637(5)	0.212(3)	0.67(9)	
O3	0.5	0	0.5	0.67(9)	
O4	0	0.1356(5)	0.215(3)	0.67(9)	
O5	0	0.2253(5)	0.347(3)	0.67(9)	
O6	0.5	0.1699(4)	0.550(3)	0.67(9)	
O7	0	0.1211(5)	0.697(3)	0.67(9)	
O8	0	0.2086(5)	0.793(3)	0.67(9)	
O9	0	0.0515(5)	0.288(3)	0.67(9)	

Table 3. Fractional atomic coordinates and site occupancies of $SrLa_4Ti_5O_{17}$ ceramics.

	x	*y*	*z*	B_{iso}	Occ. (<1)
La1	0.5	0.09003(5)	0.5037(4)	0.66(2)	0.8427(84)
Sr1	0.5	0.09003(5)	0.5037(4)	0.66(2)	0.1573(84)
La2	0.5	0	0	0.66(2)	0.768(22)
Sr2	0.5	0	0	0.66(2)	0.232(22)
La3	0.5	0.20986(7)	0.0733(4)	0.66(2)	0.7731(70)
Sr3	0.5	0.20986(7)	0.0733(4)	0.66(2)	0.2269(70)
Ti1	0	0.09415(16)	0.0033(11)	0.30(4)	
Ti2	0	0.17822(16)	0.5433(11)	0.30(4)	
Ti3	0	0	0.5	0.30(4)	
O1	0.5	0.0859(6)	-0.016(4)	0.78(11)	
O2	0	0.9627(7)	0.226(4)	0.78(11)	
O3	0.5	0	0.5	0.78(11)	
O4	0	0.1317(6)	0.212(4)	0.78(11)	
O5	0	0.2245(6)	0.349(4)	0.78(11)	
O6	0.5	0.1690(6)	0.531(4)	0.78(11)	
O7	0	0.1219(7)	0.718(4)	0.78(11)	
O8	0	0.2083(7)	0.800(4)	0.78(11)	
O9	0	0.0541(7)	0.281(4)	0.78(11)	

crystallographic data for both compounds are presented in Table 1. The fitted diffraction patterns are shown in Fig. 1, the crystal structures are presented in Figs. 2 and 3 and atomic fractional coordinates with site occupancies and isotropic atomic displacement parameters are collected in Tables 2 and 3.

The crystal structures of both compounds are related to the group of compounds with the chemical formula $A_nB_nO_{3n+2}$ (where A is Sr, La or Ca and B is Nb or Ti)[12] in which part of the A or B site is occupied by two different atom types. Structures of this type consist of slabs of the perovskite-like structure, separated by layers of additional oxygen atoms and do not differ much from the structure of $La_5Ti_5O_{17}$.[12] Compared to the $La_5Ti_5O_{17}$ analogue, the unit cell of $CaLa_4Ti_5O_{17}$ is two times smaller, and the structure can be described as orthorhombic while the organization of the polyhedra remains the same. Worthy to note is that our choice of the smaller orthorhombic unit cell was based on the fact that we observed no particular peak in the diffraction pattern that could have been explained only by a larger unit cell.

The coordination polyhedra of Ti are tilted octahedra. The Ti–O distances are in the range of 1.7–2.2 Å and the O–Ti–O angles from 79 to 104 degrees. Similar distortions of Ti–O octahedra have been observed in some related systems.[10] The La atoms are coordinated by 12 oxygen atoms, the distances are in the range from 2.4 to 3.1 Å (see Table 4). Exception is the La3 site, located between two individual slabs of the perovskite structure, where two oxygen atoms are on a notably larger distance of 3.9 Å. The second neighbors of the lanthanum sites within the perovskite slabs are eight Ti atoms which form a distorted cube, while the La3 site has seven Ti atoms as second neighbors.

Additional insight into the structure of La/Ca and La/Sr polyhedra was obtained by performing a Bond Valence calculation on both systems.[14] The bond valence sums together with the corresponding ranges of atomic distances are listed in Table 4. For the Ca compound the bond valence sums of La1 and La2 are close to the nominal valence of 3, but the bond valence sum of La3 is notably smaller. This is consistent with the fact that the La3 site lies between the perovskite slabs so that it is less tightly coordinated than the La1 and La2 sites which are located within the slabs. As expected, the corresponding bond valences of calcium at all sites is considerably smaller than 2.0, mainly due to the notably smaller size of the Ca^{2+} ion. Similar features can be found in the Sr compound; however the calculated bond valence sum of La2 is much lower than in the Ca compound, apparently due to longer La–O distances. This possibly originates form the fact that the Sr occupancy at this site is relatively high, inducing strain to the polyhedron and resulting in its expansion. Although Sr^{2+} is still slightly smaller than La^{3+}, it

Tabele 4. Bond valence calculations for La/Ca and La/Sr structures

$CaLa_4Ti_5O_{17}$	BVS*	Distance range [Å]	N**
La1	3.139	2.432–3.018	12
Ca1	1.804		12
La2	3.009	2.540–2.985	12
Ca2	1.730		12
La3	2.753	2.379–3.139	10
Ca3	1.582		10

$SrLa_4Ti_5O_{17}$	DVS*	Distance range [Å]	N**
La1	3.089	2.478–2.880	12
Sr1	2.670		12
La2	2.559	2.599–3.017	12
Sr2	2.212		12
La3	2.523	2.402–2.854	7
Sr3	2.180		7

* Bond valence sums
** No of neighboring atoms included

probably cannot accommodate the same amount of oxygen counterions because of the lower valence. Note that this effect is not observed in the Ca compound, because the much smaller size of Ca^{2+} ion compensates for the lack in its valence capability. In contrast to the Ca compound in which the valences of Ca^{2+} are notably lower than 2.0, the bond valence sums of strontium are considerably higher than 2.0 (about 2.6 at sites 1 and 2), because strontium ion is much larger than calcium ion and the resulting computed valences of Sr^{2+} are higher. On the whole, part of the bond valence calculations fairly reproduce the assumed valences of the atoms considered (mainly for lanthanum ion), while the agreement is poorer for calcium ion and strontium ion. The discrepancies can readily be assigned to the fact that calcium and strontium ion share their sites with lanthanum, hence the resulting structure represents an average weighted by relative occupancies of the respective atoms.

While the net occupancies of calcium and strontium are clearly the same, a very slight difference has been observed in their preferential location in the crystal structure. In the calcium compound the calcium atoms are less preferably located at the sites between the perovskite slabs, while in the strontium analogue the strontium atoms are altogether less likely to be located within the slabs (see Tables 2 and 3, Figs. 1 and 2). This observation is consistent with the fact that the ionic radius of calcium is slightly smaller than that of lanthanum; hence the former can be more easily incorporated into the perovskite slab than the strontium ion, whose radius is slightly larger than that of lanthanum.[15]

3. 2. Microwave Dielectric Properties

The ceramics based on $MLa_4Ti_5O_{17}$ (M=Ca, Sr) compounds exhibit interesting microwave dielectric characteristics. The $TE_{01\delta}$ modes of the samples were obtained in the range of 5.5–6GHz. Dielectric properties of the ceramics are given in Table 5. The $CaLa_4Ti_5O_{17}$ shows relative permittivity at 20 °C ε = 51.1 and negative temperature coefficient of resonant frequencies τ_f = –29 ppm/K, however the $SrLa_4Ti_5O_{17}$ has ε = 39.1 and positive value of τ_f = 58 ppm/K. Both compounds show high quality factor (Qxf) = 13 140 for $CaLa_4Ti_5O_{17}$ and 14 200 for $SrLa_4Ti_5O_{17}$.

The compounds show very promising microwave dielectric properties. Their opposite value of temperature coefficient of resonant frequencies is not understood satisfyingly but applying this phenomenon a to solid solution of both compounds which would show τ_f near zero value, required for the use in electronic devices, may be prepared.

4. Conclusions

In this work we have characterized two microwave dielectric crystalline ceramic materials, namely $CaLa_4Ti_5O_{17}$ and $SrLa_4Ti_5O_{17}$, found as single phases in the ternary phase diagrams systems of the corresponding metal oxides. They are isostructural and crystallize in a perovskite-like structure type with a general formula $A_nB_nO_{3n+2}$. The structures of the two compounds were determined by powder diffraction X-ray crystallography using the pattern matching, followed by Rietveld refinement method. The final structures are of the orthorhombic symmetry (*Pmnn* space group).

We have presented the dielectric properties in microwave frequency range of two isostructural compounds. Their high dielectric constants ε in the range 39 to 51, high quality factor (13 140 for $CaLa_4Ti_5O_{17}$ and 14 200 for $SrLa_4Ti_5O_{17}$) and temperature coefficient of resonant frequencies τ_f = –29 – +58 ppm/K make them interesting for use in electronic devices, especially where a narrow bandwidth is necessary.

The final structural data (including coordinates, displacement and geometrical parameters) have also been deposited with FIZ Karlsruhe Crystal Structure Deposition (CSD) Center as supplementary material with the deposition numbers 419425 and 419426 for compounds $CaLa_5Ti_5O_{17}$ and $SrLa_5Ti_5O_{17}$, respectively. Copies of the data can be obtained, free of charge, contacting crysdata @fiz-karlsruhe.de

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Table 5. Microwave dielectric properties of the $MLa_4Ti_5O_{17}$ ceramics (M=Ca, Sr)

Compound	Theor. density [g/cm^3]	Rel. density [%]	Tsint. [°C]	$\varepsilon_{20°C}$	Qxf [GHz]	τ_f [ppm/K]	f [GHz]
$CaLa_4Ti_5O_{17}$	5.471	94	1550	51.1	13 140	29	5.56
$SrLa_4Ti_5O_{17}$	5.655	92	1580	39.1	14 200	58	5.96

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Povzetek

Keramična materiala $CaLa_4Ti_5O_{17}$ in $SrLa_4Ti_5O_{17}$ smo pripravili z reakcijo v trdnem. Strukture smo določili na osnovi že poznanih struktur iz baze podatkov, ki smo jih uporabili kot začetne modele za Rietveldovo prilagajanje na izmerjenih difraktogramih. Za obe spojini se je izkazalo, da je najbolj ustrezen ortorombski strukturni model s prostorsko skupino *Pmnn*. Tako kot v podobnih strukturah s splošno formulo $A_nB_nO_{3n+2}$ smo opazili perovskitne plasti, ločene z dodatnimi plastmi kisikov, v katerih Ca/La oziroma Sr/La naključno zasedata mesto A. Prilagajanje zasedenosti na mestu A je pokazalo, da Ca preferenčno zaseda mesta znotraj perovskitne plasti, Sr pa mesta znotraj plasti, bogatih s kisikom. Meritve mikrovalovnih dielektričnih lastnosti keramik na osnovi teh spojin pokašejo, da le-te izkazujejo vrednost dielektrične konstante od 39 do 51, visok faktor kvalitete (Qxf) od 13100 do 14200 in negativno vrednost temperaturnega koeficienta resonančne frekvence $\tau_f = -29$ ppm/K v primeru spojine $CaLa_5Ti_5O_{17}$, oziroma pozitivno vrednost $\tau_f = 58$ ppm/K v primeru spojine $SrLa_4Ti_5O_{17}$.