Scientific paper

Crystal Structures of CaLa$_8$Ti$_9$O$_{31}$ and Ca$_2$La$_4$Ti$_6$O$_{20}$ Determined from Powder Diffraction Data

Katarina Stare,[1,2] Radovan Černý,[3] Srečo D. Škapin,[4] Danilo Suvorov[4] and Anton Meden[1,2]

[1] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia*

[2] *EN-FIST Centre of Excelence, Dunajska 156, Ljubljana, Slovenia*

[3] *University of Geneva, Geneva, Switzerland*

[4] *Jožef Stefan Institute, Ljubljana, Slovenia*

* *Corresponding author: E-mail: katarina.stare @fkkt.uni-lj.si*

Dedicated to Professor Dušan Hadži on the occasion of his 90th birthday

Abstract

The ceramic materials of CaLa$_8$Ti$_9$O$_{31}$ and Ca$_2$La$_4$Ti$_6$O$_{20}$ were synthesized using the solid-state reaction method. The crystal structures were determined from powder diffraction data using direct space methods. Like in similar compounds of the general formula A$_n$B$_n$O$_{3n+2}$, the title compounds are composed of perovskite-like slabs, separated by oxygen-rich layers, where Ca or La occupy the A site.

Keywords: ceramic materials, Ca-La-Ti-O system, crystal structures, powder diffraction.

1. Introduction

Perovskite structures have been extensively investigated due to the important properties exhibited by many members of this series of materials. With the rapid increase of demands in communication and broadcasting, the development of good dielectric resonator materials for application in microwave frequency range are needed. Compounds, based on La$_2$O$_3$-TiO$_2$ system, were also examined as microwave frequency dielectric ceramics.[1] The addition of CaO[2] causes formation of perovskite structural type. In the ternary system La$_2$O$_3$-TiO$_2$-CaO, a number of compounds were identified. Nanot et al.[3] reported series of compounds of perovskite structural type with general formula A$_n$B$_n$O$_{3n+2}$. Among those there were CaLa$_4$Ti$_5$O$_{17}$,[4] CaLa$_8$Ti$_9$O$_{31}$ and Ca$_2$La$_4$Ti$_6$O$_{20}$. The scope of this paper was to determine and analyze the last two structures by synchrotron and laboratory X-ray powder diffraction.

2. Experimental Procedure

The ceramic samples were prepared by the solid-state reaction technique using La$_2$O$_3$ (99.99% Alfa Aesar), TiO$_2$ (99.8% Alfa Aesar), and CaCO$_3$ (99.5% Alfa Aesar). Since La$_2$O$_3$ 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. Dried powders were uni-axially pressed into pellets and calcined in a tube furnace in air at 1300 °C for 12 h. The heat treated samples were ground, well homogenized in a ball mill and sintered at 1400 °C for 20 h.

The X-ray powder diffraction patterns, used for solving the structures and preliminary refinements, were collected on a PANalytical X'Pert PRO MPD diffractometer in reflection geometry using CuK$_{\alpha 1}$ radiation. The data

were collected in the 2θ range of 3–150° in steps of 0.017° with the total collection time of 16 hours. Preliminary search-match analyses were carried out with Crystallographica Search-Match software using the PDF-4 database release 2010.[5] Indexing was performed using Treor and Ito programmes incorporated in X'Pert High Score Plus.[6] The Fox programme[7] was used for structure solution and the structure refinement was performed using the Rietveld method incorporated in the programme package TOPASA-4.[8]

The measurements, used for the final Rietveld refinements, were carried out on the Swiss-Norwegian beam line at the European Synchrotron Radiation Facility, Grenoble, France. The sample was mounted in a glass capillary (o. d. 0.5 mm). The data were collected using the Debye-Scherrer geometry and MAR345 image plate detector at a sample to detector distance 150 mm, and radiation with selected wavelength of λ = 0.701378 Å. The capillary was oscillated by 60° during exposure to the X-ray beam for 60 s, followed by a readout for ~83 s. Obtained raw images were transformed to 2D-powder diffraction patterns in 2θ range of 1–48° in steps of 0.03580° using the FIT2D programme.[9]

3. Results and Discussion

The two studied compounds were previously identified by Nanot et al.[3] Here presented diffraction patterns correspond well with those published. The unit cells obtained by the indexing procedure seems to be similar to the proposed ones, but the unit cell for the compound $CaLa_8Ti_9O_{31}$ was found to be doubled in *b*-direction regarding the prediction. On the basis of extinction conditions the most probable space groups were determined, being $P2_12_12_1$ and $Pbn2_1$ for $CaLa_8Ti_9O_{31}$ and $Ca_2La_4Ti_6O_{20}$, respectively.

According to the cell volume, most probable symmetry and expected material density for the $Ca_2La_4Ti_6O_{20}$ three independent atoms for La/Ca positions and three independent TiO_6 octahedra were put into the Fox program. Since we expected calcium and lanthanum to share the same positions in atomic ratio 1:2 we substituted them by rhodium whose number of electrons roughly corresponds to the occupancy – weighted average number of electrons of lanthanum and calcium. For $CaLa_8Ti_9O_{31}$ we applied the same strategy, where nine free atom positions were occupied by tellurium and nine octahedra were used. The resulting structural models were treated manually in order to exclude all the redundant oxygen atoms in the model due to the shared corners of the octahedra. For $CaLa_8Ti_9O_{31}$ higher symmetry was observed in the solved structure so we increased the symmetry to Pnma and removed the obsolete atoms.

Table 1. Crystal data and refinement parameters.

Compound	$CaLa_8Ti_9O_{31}$	$Ca_2La_4Ti_6O_{20}$
Crystal system, Space group	Orthorombic, *Pnma*	Orthorombic, *Pbn2_1*
a (Å)	5.528(3)	3.88104(19)
b (Å)	7.798(4)	36.771(3)
c (Å)	57.01(3)	5.5031(3)
V (Å^3)	2457.4(2)	785.35(8)
Temperature (K)	293	293
No of reflections	2246	740
No of independent parameters	138	88
R_p	4.657	4.645
$R_{p\text{-}dash}$	6.748	8.063
R_{wp}	6.049	6.047
$R_{wp\text{-}dash}$	8.292	9.341
R_{exp}	1.519	2.103
$R_{exp\text{-}dash}$	2.082	3.248
Excluded regions	None	None
No of Anti-Bump restraints	4	4

The interatomic distances Ti-O, O-O, Ca-O, La-O, anti-bump values used were 1.96 Å, 2.77 Å, 2.40 Å, 2.40 Å respectively.[10]
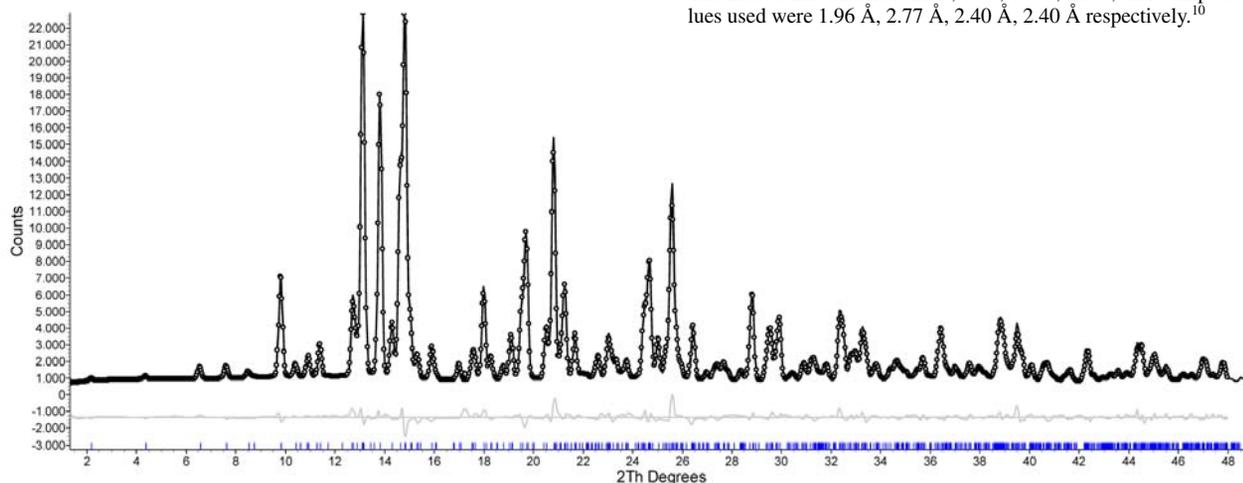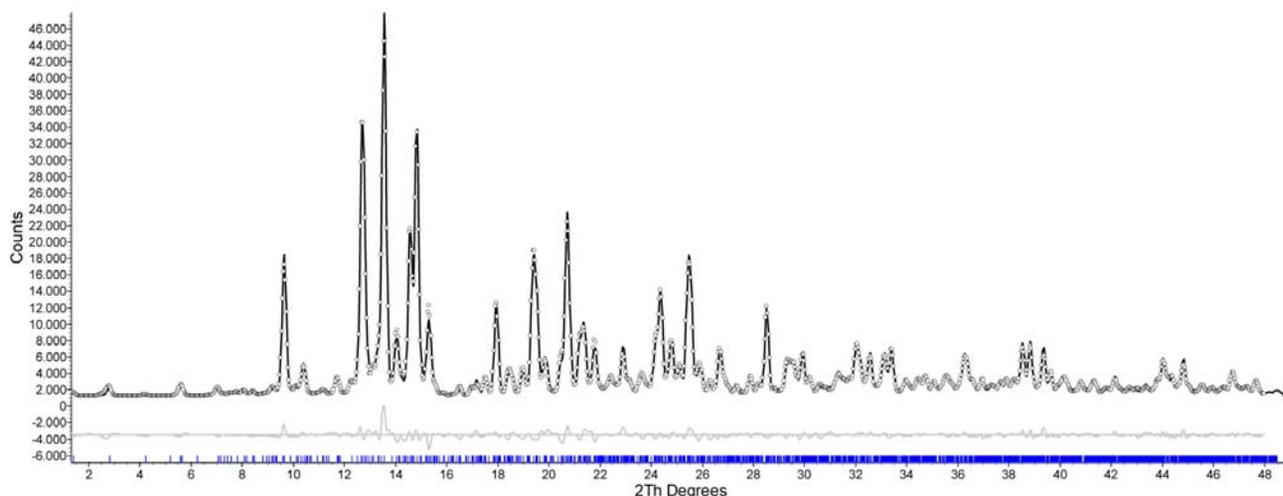

Figure 1. Final Rietveld plot of $Ca_2La_4Ti_6O_{20}$– solid black line – measured, circles – calculated, gray line below – difference. Vertical bars at the bottom mark reflection positions.

Figure 2. Final Rietveld plot of $CaLa_8Ti_9O_{31}$ – solid black line – measured, circles – calculated, gray line below – difference. Vertical bars at the bottom mark reflection positions.

Both structure models were refined by Rietveld method to adjust the unit cell and structural parameters. All the atomic positions were refined, while inter-atomic bond distances were restrained against becoming unreasonably short by using anti-bump restraints, as implemented in TOPASA-4. The site occupancies were fitted only for calcium and lanthanum, which are expected to share the positions in the structure; the sum of the occupancies at all sites was constrained to unity and the net stoichiometric ratio between calcium and lanthanum was preserved; the exact atomic positions for both were

fitted independently. Isotropic displacement parameters were set to be equal for all the atoms of the same type, including calcium and lanthanum. Applying all those conditions in the refinement, we obtained good agreement between calculated and observed powder diffraction patterns (Figs. 1 and 2). All the details are given in Table 1, final atomic parameters are given in Tables 2 and 3.

The crystal structures of both compounds belong to the group of compounds with general formula $A_nB_nO_{3n+2}$ (where site A can be occupied eider with Ca or La, and site B is Ti). These are oxygen rich perovskite type structures that consist of slabs of the perovskite structure separated by layers of additional oxygen atoms, where the thickness of the slabs depends on the *n*-value. The consecutive blocks are shifted with respect to each other by one half of the unit cell edge. In the $CaLa_8Ti_9O_{31}$ (n = 4.5) compound the four and five octahedra thick perovskite blocks are alternating, while in the $Ca_2La_4Ti_6O_{20}$ (n = 6) structure the building blocks have the thickness of six octahedra (Figs 3 and 4).

The TiO_6 octahedra in both structures are rather regular, also due to anti-bump restraints that had to be used to prevent unrealistically short interatomic distances. The ranges and average values of distances and angles are given Table 4.

In the $Ca_2La_4Ti_6O_{20}$ compound, the positions of calcium and lanthanum, occupying the same crystallographic sites, do not coincide exactly. The differences between their positions are moderate [0.41–0.85 Å], and it can be seen that they are larger in-between the slabs than within them. Within the perovskite structure region the calcium and lanthanum atoms are surrounded by twelve oxygen atoms; the cation – anion distances ranges are presented in Table 5. The interatomic distances between these two atoms and ti-

Table 2. Fractional atomic coordinates, displacement parameters and site occupancies of $Ca_2La_4Ti_6O_{20}$ ceramics.

	x	*y*	*z*	B_{iso}	Occ. (<1)
La1	0.002(4)	0.54086(15)	0.38037	0.58(7)	0.513(5)
Ca1	1.016(9)	0.5297(5)	0.376(5)	0.58(7)	0.487(5)
La2	0.996(3)	0.38447(11)	0.3755(14)	0.58(7)	0.630 (6)
Ca2	0.005(15)	0.3964(7)	0.399(5)	0.58(7)	0.370(6)
La3	0.514(2)	0.78304(9)	0.9527(12)	0.58(7)	0.857(8)
Ca3	0.51(4)	0.8050(14)	0.906(7)	0.58(7)	0.143(8)
Ti1	0.492 (5)	0.46252(18)	0.3772(16)	0.31(8)	
O21	0.485(17)	0.5654(4)	0.175(3)	1.13(16)	
O31	0.989(15)	0.4635(4)	0.374(4)	1.13(16)	
O41	0.484(17)	0.4924(4)	0.083(3)	1.13(16)	
Ti2	0.502(6)	0.68740(15)	0.9095(17)	0.31(8)	
O22	0.469(12)	0.3452(4)	0.094(2)	1.13(16)	
O42	0.517(17)	0.7174(4)	0.192(3)	1.13(16)	
O52	0.51(3)	0.7285(4)	0.702(3)	1.13(16)	
O62	0.988(16)	0.3161(3)	0.415(3)	1.13(16)	
Ti3	0.488(4)	0.38412(17)	0.8863(16)	0.31(8)	
O13	0.982(12)	0.3902(3)	0.891(3)	1.13(16)	
O23	0.516(19)	0.6381(4)	0.082(2)	1.13(16)	
O43	0.00(3)	0.0809(4)	0.684(3)	1.13(16)	

Table 3. Fractional atomic coordinates, displacement parameters and site occupancies of $CaLa_8Ti_9O_{31}$ ceramics.

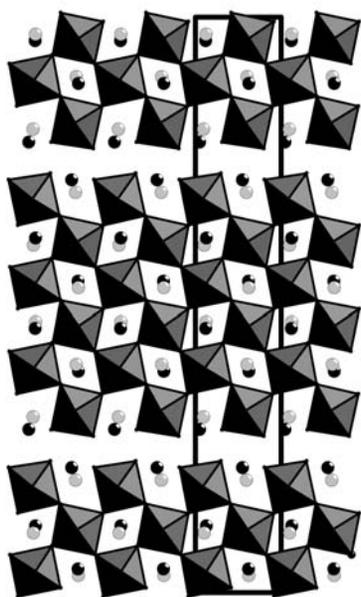|	x	y	z	B_{iso}	Occ. (<1)
La1	0.4260(13)	0.0008(16)	0.61590(10)	0.63(7)	0.923(9)
Ca1	0.39(2)	0.02(3)	0.6209(16)	0.63(7)	0.077(9)
La3	0.5	0	0.5	0.63(7)	0.883(14)
Ca3	0.5	0	0.5	0.63(7)	0.117(14)
La4	0.496(2)	0.25	0.2740(2)	0.63(7)	0.94(3)
Ca4	0.51(6)	0.25	0.269(4)	0.63(7)	0.06(3)
La5	0.956(2)	0.25	0.66283(17)	0.63(7)	0.95(3)
Ca5	1.00(6)	0.25	0.675(3)	0.63(7)	0.05(3)
La8	1.0019(15)	0.5008(18)	0.45056(11)	0.63(7)	0.845(9)
Ca8	–0.038(10)	0.50(2)	0.4469(11)	0.63(7)	0.155(9)
La7	0.092(2)	0.25	0.34304(19)	0.63(7)	0.91(2)
Ca7	0.01(3)	0.25	0.321(2)	0.63(7)	0.09(2)
La6	0.990(3)	0.25	0.7736(3)	0.63(7)	0.79(6)
Ca6	0.030(14)	0.25	0.7850(11)	0.63(7)	0.21(6)
Ti1	0.458(4)	0.75	0.9044(3)	0.26(9)	
Ti2	–0.001(2)	0.997(3)	0.72401(18)	0.26(9)	
Ti3	0.471(3)	1.006(3)	0.6761(2)	0.26(9)	
Ti4	0.978(4)	0.25	0.9489(4)	0.26(9)	
Ti6	0.519(4)	0.75	0.5493(3)	0.26(9)	
Ti8	0.492(5)	0.25	–0.0006(4)	0.26(9)	
Ti10	0.459(4)	0.25	0.8987(4)	0.26(9)	
O1	0.549(7)	0.25	0.7737(6)	0.46(19)	
O2	0.782(4)	0.965(5)	0.7921(4)	0.46(19)	
O3	0.303(4)	0.025(5)	0.8029(4)	0.46(19)	
O4	0.560(8)	0.25	0.2276(6)	0.46(19)	
O5	0.286(5)	0.527(5)	0.2565(4)	0.46(19)	
O9	0.911(8)	0.25	0.8230(7)	0.46(19)	
O10	0.045(8)	0.75	0.8191(6)	0.46(19)	
O11	0.5	0.5	0	0.46(19)	
O12	0.257(8)	0.25	0.0242(7)	0.46(19)	
O13	0.772(8)	0.25	0.0183(7)	0.46(19)	
O14	0.306(8)	0.75	0.0286(7)	0.46(19)	
O15	0.230(9)	0.25	0.9795(7)	0.46(19)	
O16	0.990(5)	0.488(6)	0.9534(3)	0.46(19)	
O18	0.771(7)	0.25	0.9234(7)	0.46(19)	
O20	0.966(5)	0.484(6)	0.5947(3)	0.46(19)	
O21	0.287(7)	0.25	0.9344(7)	0.46(19)	
O22	0.300(7)	0.75	0.9347(7)	0.46(19)	
O23	0.293 (8)	0.75	0.5719(7)	0.46(19)	
O24	0.649(8)	1.25	0.6123(8)	0.46(19)	
O25	0.133(8)	0.25	0.6273(7)	0.46(19)	
O26	0.207(8)	0.75	0.8842(8)	0.46(19)	
O27	0.690(7)	0.75	0.8805(7)	0.46(19)	
O28	0.314(4)	0.987(6)	0.3498(4)	0.46(19)	
O30	0.800(4)	0.034(4)	0.3414(4)	0.46(19)	

tanium are slightly shorter for calcium atoms (3.09 Å and 3.08 Å as opposed to 3.34 Å and 3.28 Å for La). In between the slabs ten neighboring oxygen atoms are found around calcium or lanthanum. The distances to titanium are approximately the same for both atoms –3.34 Å.
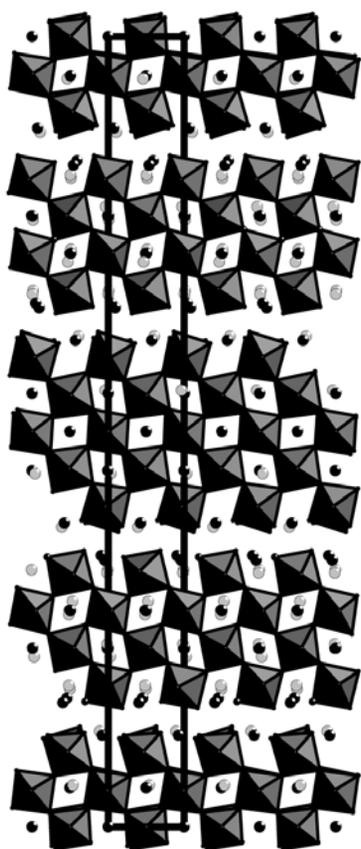
For the $CaLa_8Ti_9O_{31}$ the Ca-La position differences are more notable [0.30–1.33 Å], but the same trend can be found. Within the slabs the Ca,La coordination by oxygen is 12 and the distances ranges are in Table 5; distances to

titanium are shorter for calcium atoms. In-between the slabs the coordination is ten and also the Ca-Ti distance is shorter than La-Ti.

The average distances Ca-O and La-O are expectedly very similar and close to the values for similar structures. As the two cations occupy the same voids, the differences to the surrounding oxygen atoms average out and the differences in positions are best viewed and understood on Figs 3 and 4.

Table 4. Interatomic distances between Ti and oxygen atoms.

	Distance range [Å]	Angle range [°]	Average distance [Å]
	$CaLa_8Ti_9O_{31}$		
Ti1	1.80–2.29	80.7–102.9	2.00
Ti2	1.83–2.21	76.5–96.0	1.97
Ti3	1.82–2.20	80.0–95.6	2.01
Ti4	1.85–2.23	82.5–102.3	1.96
Ti6	1.80–2.11	83.8–103.5	1.99
Ti8	1.84–1.95	85.6–91.7	1.92
Ti10	1.76–2.24	75.9–103.1	1.97
	$Ca_2La_4Ti_6O_{20}$		
Ti1	1.92–2.01	86.7–93.6	1.95
Ti2	1.89–2.11	82.9–97.6	1.97
Ti3	1.83–2.19	82.0–102.7	1.98

Figure 3. Projection of the structure of $Ca_2La_4Ti_6O_{20}$ along the a-axis. Gray spheres are calcium atoms, black spheres are lanthanum. The octahedra have oxygen atoms in the corners and titanium atom in the centre. The unit cell is outlined.

Table 5. Interatomic distances between Ca/La and oxygen atoms.

	Distance range [Å]	N*	Average distance [Å]
	$CaLa_8Ti_9O_{31}$		
La1	2.31–3.27	10	2.74
Ca1	2.34–2.79	7	2.76
	3.19	1	
	3.51–3.52	2	
La3	2.54–3.05	12	2.74
Ca3			
La4	2.32–3.21	12	2.79
Ca4	2.35–3.06	10	2.80
	3.38	2	
La5	2.25–3.35	10	2.71
Ca5	2.31–3.23	10	2.72
La8	2.41–3.05	12	2.74
Ca8	2.41–3.05	10	2.76
	3.20–3.25	2	
La7	2.34–3.19	9	2.74
	3.78	1	
Ca7	2.35–3.11	11	2.74
La6	2.34–3.09	12	2.75
Ca6	2.26–2.94	9	2.80
	3.35–3.25	3	
	$Ca_2La_4Ti_6O_{20}$		
La1	2.37–3.15	12	2.75
Ca1	2.39–2.96	10	2.75
	3.14–3.25	2	
La2	2.37–3.19	12	2.74
Ca2	2.41–2.95	10	2.74
	3.10–3.26	2	
La3	2.40–3.20	10	2.70
Ca3	2.38–3.14	10	2.75

* number of neighboring oxygen atoms

Figure 4. Projection of the structure of $CaLa_8Ti_9O_{31}$ along the b-axis. Gray spheres are calcium atoms, black spheres are lanthanum. The octahedra have oxygen atoms in the corners and titanium atom in the centre. The unit cell is outlined.

4. Conclusions

In this work we have characterized two microwave dielectric crystalline ceramic materials, namely Ca-La$_8$Ti$_9$O$_{31}$ and Ca$_2$La$_4$Ti$_6$O$_{20}$, found as single phases in the ternary phase diagram of the corresponding metal oxides. They crystallize in a perovskite-like structure type with a general formula A$_n$B$_n$O$_{3n+2}$, n being 4.5 and 6, respectively. The structures of the two compounds were determined by X-ray powder diffraction using laboratory data and direct space methods. Sinchrotron radiation measurements were used for final Rietveld refinement. The structural analysis reveals rather well ordered perovskite slabs of 6 and alternating 4 and 5 octahedral layers for Ca$_2$La$_4$Ti$_6$O$_{20}$ and CaLa$_8$Ti$_9$O$_{31}$ respectively, separated by oxygen-rich layers. It was found that the positions of Ca and La, which occupy the same crystallographic sites (A), do not coincide exactly. The voids among the oxygen atoms in the structure allows for a moderate differences in the positions of Ca and La, thus allowing somewhat different distribution of individual coordination distances of the two atoms according to their different charge and slightly different ionic radii.

5. Acknowledgements

6. References

1. S. D. Škapin, D. Kolar, D. Suvorov, D, *J. Am. Ceram. Soc.* **1993**, *76*, 2359–2362.
2. I-S. Kim, W-H. Jung, Y. Inaguma, T. Nakamura, M. Itoh, *Mat. Res. Bull.* **1995**, *30*, 307–316.
3. M. Nanot, F. Queyroux, J-C. Gilles, A. Carpy, J. Galy, *J. Solid State Chem.* **1974**, *11*, 272–284.
4. K. Demsar, S. D. Skapin, A. Meden, D.Suvorov, *Acta Chim. Slov.* **2008**, 55, 966–972.
5. PDF-2_ Release 2006; McClune, W. F., Ed.; International Centre for Diffraction Data: Newtown Square, PA, 2006.
6. X'Pert High Score Plus 2007; P. A. Nalytical B.V., Almelo, The Netherlands.
7. V. Favre-Nicolin, R. Černý, *J. Appl. Cryst.* **2002**, *35*, 734–743. http://vincefn.net/Fox/FoxWiki
8. Coelho, A. A. TOPAS-Academic, Version 4.1. 2007; Coelho Software, Brisbane, Australia.
9. Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Häusermann, D. *High Pressure Res.* **1996**, *14*, 235–248.
10. ICSD (2010). Inorganic Crystal Structure Database. FIZ-Karlsruhe, Germany, and the National Institute of Standards and Technology (NIST), USA.

Povzetek

Enofazna keramična materiala na osnovi spojin CaLa$_8$Ti$_9$O$_{31}$in Ca$_2$La$_4$Ti$_6$O$_{20}$ sta bila pripravljena z reakcijo v trdnem. Kristalno strukturo smo jima določili na osnovi rentgenske praškovne difrakcije z uporabo metod v direktnem prostoru. Kot v podobnih strukturah s splošno formulo A$_n$B$_n$O$_{3n+2}$ smo opazili plasti perovskitnega strukturnega tipa, ki so med seboj ločeni s plastmi bogatimi s kisikom, atomi La in Ca pa si delijo ista kristalografska mesta.