

Structural Investigation of $Ba_{6-x}Ln_{8+2/3x}Ti_{18}O_{54}$ Isostructural Ce Compound

Strukturne raziskave izostrukturalne Ce spojine s trdnimi raztopinami tipa $Ba_{6-x}Ln_{8+2/3x}Ti_{18}O_{54}$

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Single crystals were synthesized and single crystal x-ray diffraction data revealed an orthorhombic unit cell with lattice parameters $a = 22.377(6)$, $b = 7.629(2)$ and $c = 12.233(3)$ Å. The majority of the systematic extinctions were indicative of a primitive cell, with the intensity data best fitting the centrosymmetric statistics, indicating the correct space group was $Pnma$ (number 62). The structure is isostructural with crystals obtained from the $Ba_{6-x}Ln_{8+2/3x}Ti_{18}O_{54}$ ($Ln = La, Pr, Nd, Sm, Eu, \text{ and } Gd$) solid solution series. Refinements in space group $Pnma$, resulted in $R = 11.03\%$. The formula, calculated from refined site occupancies, results in 8.0 ± 0.1 Ba atoms and 19.3 ± 0.3 Ce atoms requiring 109.0 ± 0.6 O atoms for charge neutrality. Taking into account that the single crystal synthesis was in flowing Ar at high temperatures, some of the Ti^{4+} could be reduced to Ti^{3+} . A minimum Ti^{3+}/Ti^{4+} ratio of 1.9/34.1 would result in 108 O atoms for a formula of $Ba_{8.0}Ce_{19.3}Ti^{3+}_{34.1}Ti^{4+}_{34.1}O_{108}$ corresponding to 4.7 ± 0.1 at.% Ba, 11.3 ± 0.2 at.% Ce, 21.01 at.% Ti, and 63.03 at.% O. Electron probe wavelength dispersive spectroscopic (WDS) microanalysis results in 4.9 ± 0.1 at.% Ba, 10.9 ± 0.2 at.% Ce, 20.4 ± 0.4 at.% Ti, and 63.8 ± 0.6 at.% O.

Key Words: barium cerium titanate, single crystal x-ray diffraction, wavelength dispersive spectroscopic microanalysis, structure

Monokristale smo pripravili z žganjem zmesi $BaTiO_3 : CeO_2 : TiO_2$ v pretoku Ar pri 1350°C. Monokristalna rentgenska difrakcija je pokazala primitivno ortorombsko osnovno celico s celičnimi parametri $a = 22,377(6)$ Å, $b = 7,629(2)$ Å in $c = 12,233(3)$ Å in $c = 7,629(2)$ Å in prostorsko grupo $Pnma$ (številka 62). Strukturo, ki je izostrukturalna s strukturo trdnih raztopin tipa $Ba_{6-x}Ln_{8+2/3x}Ti_{18}O_{54}$ ($Ln = La, Pr, Nd, Sm, Eu \text{ in } Gd$), lahko opišemo kot mrežo TiO_6^{2-} oktaedrov, ki tvorijo pentagonalne in rombine (perovskitne) kanale, v katerih se nahajajo Ba in Ce atomi. V formuli spojine, izračunani na osnovi predhodno določene zasedenosti posameznih mest v strukturi, je $8,0 \pm 0,1$ atomov Ba in $19,3 \pm 0,3$ atomov Ce, kar zahteva $109,0 \pm 0,6$ atomov O za izenačitev naboja. Ker so bili monokristali sintetizirani pri visoki temperaturi v atmosferi Ar, lahko pričakujemo, da je del Ti v reducirani obliki Ti^{3+} . Razmerje $Ti^{3+}/Ti^{4+} = 1,9/34,1$ odgovarja formuli $Ba_{8,0}Ce_{19,3}Ti^{3+}_{34,1}Ti^{4+}_{34,1}O_{108}$ s sestavo 4,7 ± 0,1 at.% Ba, 11,3 ± 0,2 at.% Ce, 21,01 at.% Ti in 63,03 at.% O. Mikroanaliza WDS v 19 točkah na štirih različnih monokristalih je pokazala sestavo: 4,9 ± 0,1 at.% Ba, 10,9 ± 0,2 at.% Ce, 20,4 ± 0,4 at.% Ti in 63,8 ± 0,6 at.% O.

Ključne besede: barijev cerijev tianat, monokristalna rentgenska difrakcija, mikroanaliza, struktura

1 Introduction

$Ba_{6-x}Ln_{8+2/3x}Ti_{18}O_{54}$ based microwave dielectrics are of commercial interest since they display: 1) High dielectric constants (κ') that enable the miniaturization of devices. 2) Modest Q factors that transport, filter, and/or store electromagnetic energy with minimal losses ($Q = 1/\tan\delta$). 3) Low temperature coefficients of resonant frequency (τ_f) that minimizes frequency drift due to temperature fluctuations attributed to the environment and/or circuit heating. Past investigations have focused on the properties, phase equilibria, and crystal structures for analogues where $Ln = La, Pr, Nd, Sm, \text{ or } Gd$. This present investigation focuses on the isostructural single crystals that result when Ce substitutes for the Ln atom.

In the single crystal x-ray diffraction investigation of the Pr-analogue, Matveeva et al.¹ obtained a formula of $Ba_4Pr_{9.3}Ti_{18}O_{54}$ (4.69 at.% Ba, 10.90 at.% Pr, 21.10 at.% Ti, and 63.31 at.% O) by refining on the site occupancies and a formula of $Ba_{3.75}Pr_{9.5}Ti_{18}O_{54}$ (4.40 at.% Ba, 11.14 at.% Pr, 21.11 at.% Ti, and 63.34 at.% O) from x-ray spectral microanalysis. In the single crystal x-ray diffraction refinements of the Nd-² and Sm-analogues³ the re-

sulting compositions of the crystals were determined only by the site occupancies. An analytical method of determining the composition is preferred over the statistical composition that results from refining on the site occupancies, especially with $Ba_{6-x}Ln_{8+2/3x}Ti_{18}O_{54}$ type crystals where the two heavy cations have a similar number of electrons (in the case of La^{3+} and Ba^{2+} the number of electrons is equal) creating difficulty in resolving between the two atoms using x-ray diffraction. Due to the strong overlapping of the most intense Ba and Ti spectral lines, compositional analysis using Energy Dispersive X-ray (EDX) microanalysis is also difficult. In this present study, WDS microanalysis was employed as the technique to determine the composition of the crystals. WDS microanalysis, of samples containing both Ce and Ba, is also difficult due to the strong overlapping of the $CeL\alpha_{1,2}$ and $BaL\beta_{1,4}$ lines. To overcome this difficulty the calibration curve method was employed⁴.

2 Experimental

Single crystals were prepared by firing an oxide mixture of 8.5 mol% BaO, 16.5 mol% CeO₂, and 75 mol% TiO₂ ($BaTiO_3$ - Transelco 219-8, CeO₂ - Koch - Light Lab., 99.9%, and TiO₂ - anatase modification, Fluka AG, > 99%). The mixed powders were pressed into a pellet,

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with a 8 mm diameter and approximately 8 mm high, in flowing Ar at 1350°C for 12 h. The pellet was partially melted and on the surface needle-like crystals, approximately 0.20 x 0.04 x 0.04 mm, were present.

2.1 Single crystal x-ray diffraction data collection, processing, and refinement

Single crystal x-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). By examining the systematic extinctions it was found that the majority of the systematic absences were indicative of a primitive cell, space group Pna2₁ (number 33) or Pnma (number 62). Data were processed using MULTAN 11/82⁵ and the structure was refined using SHELXL-93⁶ against the structure factor, F. The reflections were corrected for Lorentz and polarization effects. The crystal faces were well defined making an analytical absorption correction a suitable choice. Once the composition was determined the data were reprocessed using the corrected composition to be applied to the absorption correction.

Electron probe WDS microanalysis

Polished surfaces were prepared by conventional metallographic techniques. The WDS microanalysis was performed on a JEOL JXA 840A electron probe microanalyser using TRACOR software for quantitative analysis. Measurements for Ba, Ce, and Ti were carried out on a LiF crystal at 20 kV and 15 nA. Counting time

was set to assure a less than 1% of the standard counting deviation. Oxygen content was calculated by difference.

3 Results and discussion

MULTAN showed the intensity data best fit the centrosymmetric statistics, indicating the correct space group was Pnma. Refinement of the data in space group Pnma, using 131 parameters, resulted in R1 = 11.03%, wR2 = 36.19%, and a goodness of fit = 0.991, with the thermal parameters of the Ce and Ba atoms refined isotropically and the thermal parameters of the Ti and O atoms refined anisotropically. The basic framework of the crystal structure, shown in **Figure 1** (the ORTEP⁷, of the xz projection, generated from the fractional coordinates), is made up of corner sharing TiO₆²⁻ octahedra linking to produce pentagonal and rhombic channels, identical to the framework for Ba_{6-x}Ln_{8+2/3x}Ti₁₈O₅₄ type analogues.

Refinement on the Ba and Ce site occupancies revealed the Ce1 site to be 95.8% occupied (4.2% vacancies), the Ce2 site to be 95.6% occupied (4.4% vacancies), the Ce4 site to be 86.2% occupied (13.8% vacancies), the Ce5 site to be 98.8% occupied (1.2% vacancies), the Ce3 site is shared with Ba (Ce/Ba 97.2%/4.88%, resulting in a site occupancy greater than 100%), the Ba1 site is shared with Ce (Ba/Ce 96.6%/4.92%, resulting in a site occupancy greater than 100%), and the Ba2 site is shared with Ce (Ba/Ce 99.0%/4.80%, resulting in a site occupancy greater than

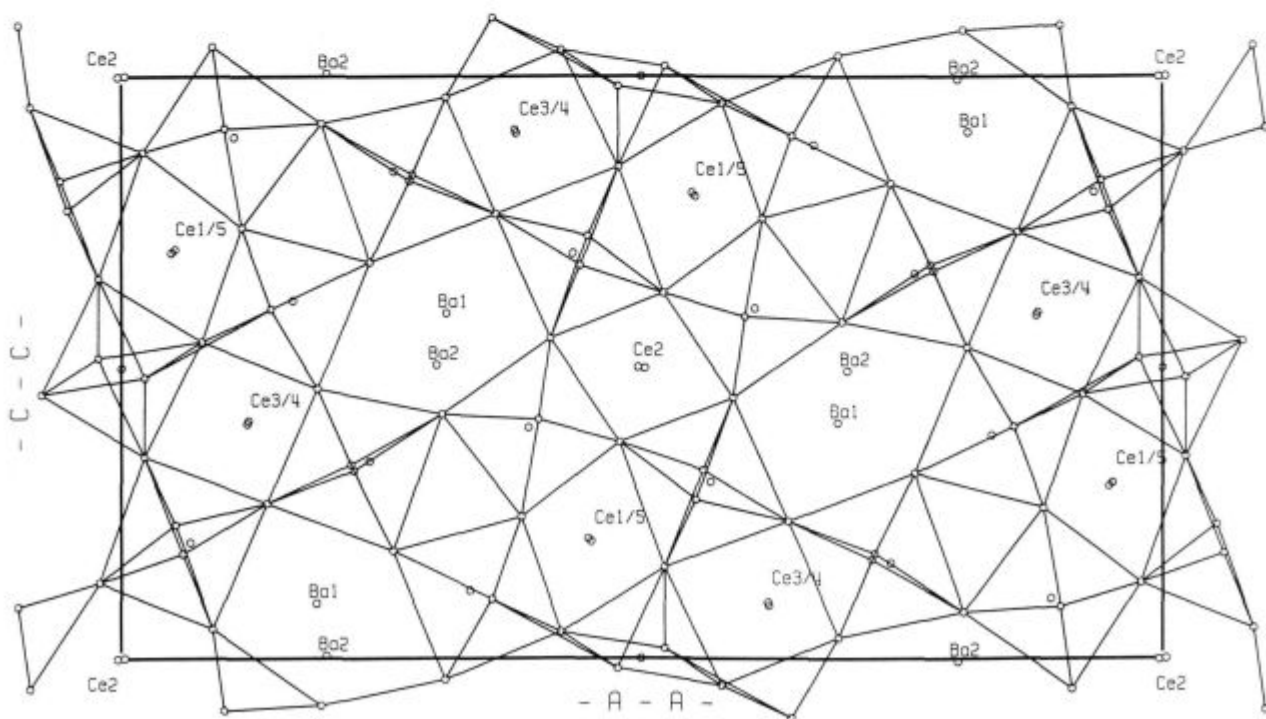


Figure 1: The ORTEP⁷ of the xz projection, generated from the atomic coordinates, showing the basic framework of the crystal structure, made up of corner sharing TiO₆²⁻ octahedra linking to produce pentagonal and rhombic channels

Slika 1: Slika strukture spojine v xz projekciji. Slika je bila narejena s pomočjo računalniškega programa ORTEP⁷. Strukuro sestavljajo oktaedri TiO₆²⁻, med seboj povezani preko oglišč, tako da tvorijo pentagonalne in romboederske kanale

Table 1: Summary of the refinements on site occupancies of the Ce and Ba atoms

Site	% Ce	Ce atoms	% Ba	Ba atoms	% vacancy	atom total
Ce1	95.8	3.832±0.054	0	0	4.2	3.832±0.054
Ce2	95.6	3.824±0.054	0	0	4.4	3.824±0.054
Ce3	97.2	3.888±0.062	4.88	0.195±0.003	0	4.083±0.065
Ce4	86.2	3.448±0.059	0	0	13.8	3.448±0.059
Ce5	98.8	3.952±0.055	0	0	1.2	3.952±0.055
Ba1	4.92	0.197±0.003	96.6	3.864±0.066	0	4.061±0.069
Ba2	4.80	0.192±0.003	99.0	3.960±0.063	0	4.152±0.066
total		19.3±0.3		8.0±0.1		

100%). The sites with occupancies totaling greater than 100% could result from the difficulty in distinguishing between atoms, differing by only one e^- ($Ba^{2+} = 54e^-$ and $Ce^{3+} = 55e^-$), using x-ray diffraction. The above site occupancies are summarized in **Table 1**. For $8.0 \pm 0.1 Ba^{2+}$ atoms, $19.3 \pm 0.3 Ce^{3+}$ (all of the Ce^{4+} reduced to Ce^{3+}) atoms, and 36 Ti^{4+} atoms, $109.0 \pm 0.6 O^{2-}$ atoms would be required to charge balance the cations, however, only 108 O atoms were found to be present in the refinement. Taking into account the single crystal synthesis in flowing Ar at high temperatures, some of the Ti^{4+} could be reduced to Ti^{3+} , requiring a minimum Ti^{3+}/Ti^{4+} ratio of 1.9/34.1 to account for 108 O atoms and result in the formula $Ba_{8.0}Ce_{19.3}Ti^{3+}_{1.9}Ti^{4+}_{34.1}O_{108}$.

The formula $Ba_{8.0}Ce_{19.3}Ti^{3+}_{1.9}Ti^{4+}_{34.1}O_{108}$ represented in at.% is 4.7 ± 0.1 at.% Ba, 11.3 ± 0.2 at.% Ce, 21.01 at.% Ti, and 63.03 at.% O. This agrees well with the WDS microanalysis, averaged from nineteen measurements on four crystals, resulting in 4.9 ± 0.1 at.% Ba, 10.9 ± 0.2 at.% Ce, 20.4 ± 0.4 at.% Ti, and 63.8 ± 0.6 at.% O. WDS measurements, taken from nine points on one crystal, supports the claim that the crystals are compositionally homogeneous.

As a check on the reliability of the structure the bond-valence sums, as outlined by Brese and O'Keeffe⁸, were determined. **Table 2** summarizes the average cation-oxygen bond lengths, bond-valence sums, the number of oxygens bonded to each cation, and the average cation-oxygen bond length, for positionally similar cations, of the isostructural Sm-analogue³. The bond-valence sum should be approximately equal to the valence of the cation and for chemically similar sites the bond-valence sum should be nearly equal. Refinement on the site occupancies suggest that the Ce1, Ce2, and Ce5 sites are chemically similar, however, this is not reflected in the bond-valence sums for these cations. The bond-valence sum for Ce1 is exceptionally high, the bond-valence sums for Ce2 and Ce4 are similar although refinement on the Ce4 site occupancy suggests a much higher vacancy content than the Ce2 site, and the bond-valence sums for Ce3 and Ce5 are similar although refinement on the Ce3 site occupancy suggests that the site is shared by both Ce and Ba while refinement on the Ce5 site occupancy suggest a small number of sites vacant. The results from the refinements on site occupancies suggest that the

two pentagonal Ba sites are similar, however, this is not indicated by the bond-valence sums. The bond-valence sum for Ba2 is exceptionally low due to the scarcity of short Ba-O bond lengths, this is also reflected in the high average bond length. Only five oxygens are found to be bonded to Ti3 while Ti2 and Ti5 both have one bond length that is unusually long (Ti2-O18 = 2.25 Å and Ti5-O4 = 2.37 Å). The bond-valence sums for these three Ti atoms are lower than for Ti1 and Ti4, suggesting a greater deviation from the ideal octahedral symmetry. A wider range of average bond lengths is observed for the structure reported here compared to the isostructural Sm-analogue.

Table 2: Summary of average cation-anion bond lengths, bond-valence sums, and the number of anions bonded to each cation

cation	anion bonds	average bond length (Å)	bond-valence sum	average bond length (Å) for the isostructural Sm-analogue ³
Ce1	11	2.63	3.44	Sm1 2.69
Ce2	11	2.68	2.97	Sm2 2.70
Ce3	12	2.74	3.10	Sm3 2.71
Ce4	10	2.65	2.99	Sm4 2.70
Ce5	12	2.73	3.11	Sm5 2.69
Ba1	12	2.98	2.15	Ba1 3.07
Ba2	13	3.14	1.76	Ba2 3.09
Ti1	6	1.94	4.35	Ti1 1.95
Ti2	6	2.02	3.72	Ti2 1.95
Ti3	5	1.93	3.64	Ti3 1.95
Ti4	6	1.97	4.05	Ti4 1.96
Ti5	6	2.01	3.90	Ti5 2.00

The high R factor (11.03%), for a structure dominated by heavy atoms, and the low correlation between bond-valence sums, for chemically similar Ce and Ba sites, indicates that not all the structural details are fully understood. The high R factor, shared Ce/Ba sites with occupancies greater than 100%, and bond-valence sums that show no correlation for chemically similar sites most likely occur due to the inability of x-ray diffraction techniques to distinguish between atoms that differ by only one electron ($Ba^{2+} = 54e^-$ and $Ce^{3+} = 55e^-$).

4 Conclusions

Single crystals, isostructural with $\text{Ba}_{6-x}\text{Ln}_{8+2/3x}\text{Ti}_{18}\text{O}_{54}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{and Gd}$) type crystals, were grown with Ce in the Ln position. The single crystal x-ray diffraction refinement was conducted in space group Pnma and resulted in $R = 11.03\%$. The uncertainties of the at% Ba and Ce, determined from WDS microanalysis and by refining on the site occupancies of the Ce and Ba positions, overlap. The resulting composition supports the idea that some of the Ti^{4+} has been reduced to Ti^{3+} ($\text{Ba}_{8.0}\text{Ce}_{19.3}\text{Ti}^{4+}_{34.1}\text{Ti}^{3+}_{1.9}\text{O}_{108}$). WDS microanalysis also indicates that the crystals are compositionally homogeneous.

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5 References

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