

Investigations of the “tungsten–bronze”-type $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions

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Abstract

A study of the Ba/La/Sr ordering in the $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions was carried out by X-ray diffractometry and dielectric measurements. The maximum of substitution is obtained for $x=0$ and $\alpha=0.33$, i.e. for $\text{Ba}_4\text{Sr}_2\text{La}_8\text{Ti}_{18}\text{O}_{54}$ composition. The crystal structure is closely related to the tungsten–bronze-type structure with 3×3 octahedral units of perovskite columns (orthorhombic symmetry, s.g. Pnma, $a \approx 22.4$ Å, $b \approx 7.7$ Å, $c \approx 12.2$ Å). The A2 sites (pentagonal channels) and the A1 sites (rhombic channels within the perovskite-like columns) are occupied by Ba and La respectively. Sr always occupies the particular rhombic A1' sites located at the junction of two perovskite-like columns which can also accept excess Ba and La. The A2 and A1' sites may be cation deficient. The structure of $\text{Ba}_4(\text{Sr}_2\text{La}_8)\text{Ti}_{18}\text{O}_{54}$ with structural composition $\text{A}2_4(\text{A}1'_2\text{A}1_8)\text{Ti}_{18}\text{O}_{54}$, is fully ordered. The thermal behaviour of the permittivity and, for some compositions, the occurrence of a strong dispersion in a wide temperature range, would likely be connected both to a cationic disorder (Sr, Ba and/or La) and vacancies in the rhombic A1' sites.

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1. Introduction

The $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ (Ln = La, Nd, Pr, Sm, Eu) solid solutions were reported to be interesting materials for the fabrication of microwave resonators (high permittivities, low dielectric loss and a temperature coefficient of the resonant frequency close to zero in the hyperfrequency range.^{1–3} Studies mainly concern with optimisation of the dielectric properties and few papers are devoted to accurate determinations of their crystal structure.^{4–6} Closely related to the tungsten–bronze-type structure, their crystal structure are constituted in columns of 3×3 octahedral units of perovskite structure arranged in such a way to form triangular, rhombic and pentagonal channels. Recently we have carried out a thorough study of the Ba/La order in $\text{Ba}_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions by means of both single crystal X-ray and powder neutron diffractometry.⁷ In order to enhance our knowledge about the origin of the Ba/La order (charge or size difference between La^{3+} and Ba^{2+}) we have started on a structural and electrical

investigation of the $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions.

2. Experimental

Powders with compositions corresponding to various x and α values were prepared by solid state reaction of TiO_2 , La_2O_3 , SrCO_3 and BaCO_3 at high temperature. The compounds were thoroughly mixed in an agate mortar and heated at 1350 °C for 12 h. Completions of the reaction as well as the occurrence of impurities were controlled by X-ray diffractometry.

Dense ceramic samples (94–95% of theoretical) used for dielectric measurements were obtained by conventional sintering uniaxially cold pressed pellets at 1450–1600 °C for 8 h in air. Dielectric properties were measured using a HP4194A impedance analyser (100 Hz–1 MHz) between room temperature and 900 °C.

3. Results and discussion

The investigations concerning the substitution of Sr for Ba showed that the substitution rate never reached α

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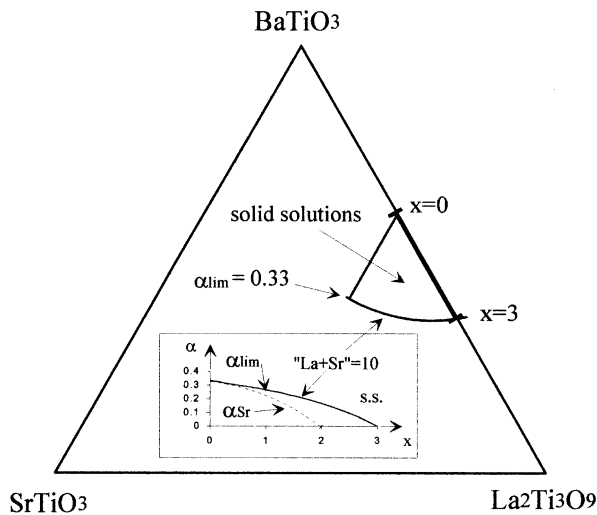


Fig. 1. Domain of $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions. Insert: α vs x .

$= 1$. The domain of $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions is shown in Fig. 1. The maximum substitution rate $\alpha_{\max} = 0.33$ is obtained for $x = 0$ whereas no substitution was observed for $x = 3$.

The domain of solid solutions is therefore limited by the composition $\text{Ba}_{4-(x/3)}\text{Sr}_{2-(2x/3)}\text{La}_{8+(2x/3)}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$), in which one can find a constant number of 10 “La + Sr” atoms per formula unit and a number of Ba atoms ≤ 4 . When trying higher substitution rates, the samples appeared biphasic with always SrTiO_3 as a second phase.

The variations of the lattice parameters and of the unit cell volume of the solid solution are given in Fig. 2. Fig. 2a and b represents their evolutions as a function of x ($0 \leq x \leq 1.5$) for $\alpha = 0.1$ and as a function of α for $x = 0$, respectively. The progressive and steady decrease of the lattice parameters and volume with increasing x logically corresponds to the decrease of the total number of cations, mainly Ba, which is larger than the others

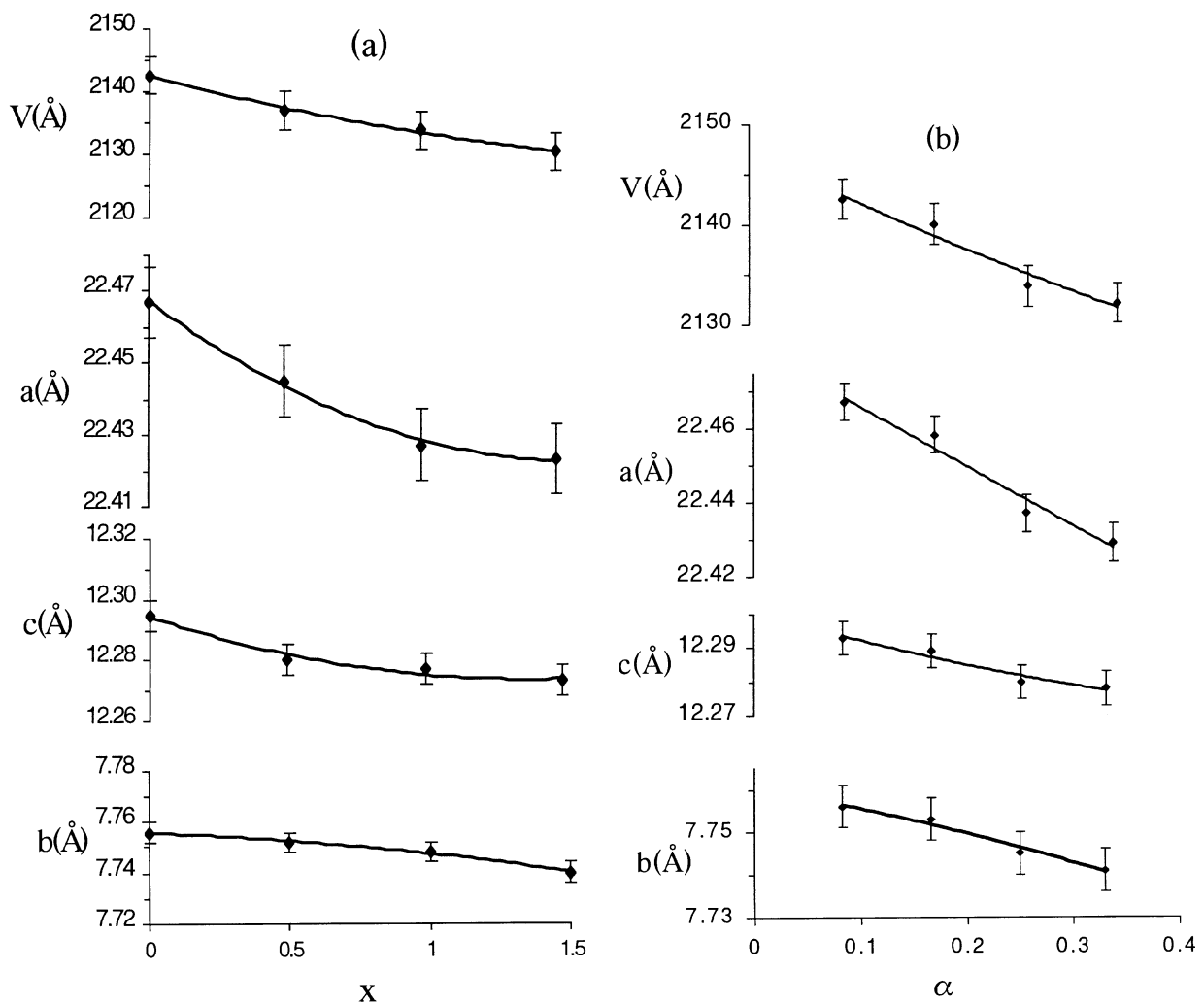


Fig. 2. Variations of the lattice parameters and of the unit cell volume of $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$): (a) as a function of x for $\alpha = 0.1$; (b) as a function of α for $x = 0$.

(r_{Ba}^{2+} [12] = 1.61 Å; r_{Sr}^{2+} [12] = 1.41 Å and r_{La}^{3+} [12] = 1.36 Å). In addition, the decrease observed with increasing α (for $x=0$) is a consequence of the substitution of Ba^{2+} by the smaller Sr^{2+} cations.

Owing to the difference between the scattering factors of Ba and Sr, the Ba/Sr/La ordering in $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) was carried out by Rietveld refinement of X-ray powder diffraction patterns (space group Pnma; $a \approx 22.43$ Å, $b \approx 7.72$ Å and $c \approx 12.26$ Å; $Z=2$). This study was based on the knowledge of the Ba/La order in the $\text{Ba}_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions we had already obtained from a thorough structural investigation by single crystal X-ray and powder neutron diffractometry.

For the two investigated compositions, the distributions of Ba, La, and Sr cations among the A sites are given in Table 1. The projection of the structure on the $x-z$ plane is given in Fig. 3. It is similar to the tetragonal

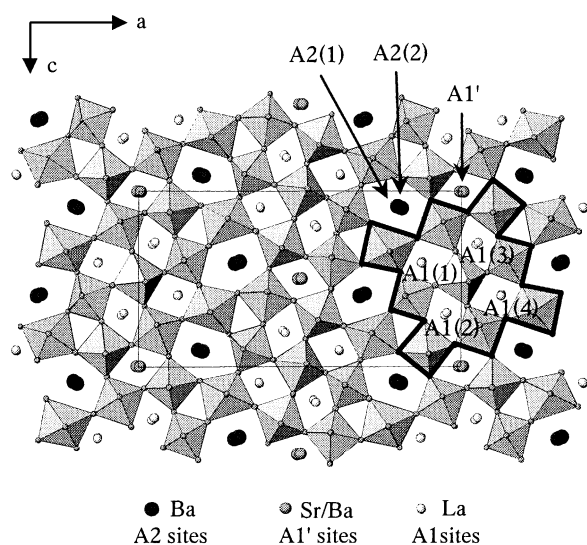


Fig. 3. Projection of the structure of $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) on the $x-z$ plane.

Table 1

A site occupancies (number of atoms) for $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$

Sites	Atoms	Starting compositions	
		$\text{Ba}_{5.5}\text{Sr}_{0.5}\text{La}_8\text{Ti}_{18}\text{O}_{54}$ $x=0; \alpha=0.083$	$\text{Ba}_5\text{SrLa}_8\text{Ti}_{18}\text{O}_{54}$ $x=0; \alpha=0.167$
Number of atoms/site (refined; $Z=2$)			
A2(1)	Ba	4	4
A2(2)	Ba	4	4
A1'	Ba	2.94(1)	2.27(1)
	Sr	1.06(1)	1.73(1)
A1(1)	La	4	4
A1(2)	La	4	4
A1(3)	La	4	4
A1(4)	La	4	4
Formula obtained		$\text{Ba}_{5.47}\text{Sr}_{0.53}$	$\text{Ba}_{5.14}\text{Sr}_{0.86}$
from refined occupancy		$\text{La}_8\text{Ti}_{18}\text{O}_{54}$	$\text{La}_8\text{Ti}_{18}\text{O}_{54}$

tungsten–bronze structure but with 3×3 rather than 2×2 octahedral units (TiO_6 octahedra) of perovskite-like columns parallel to [010]. The arrangement of such columns of octahedra joined by the corner leads to trigonal, rhombic and pentagonal channels parallel to [010] which would be filled by cations. Within each 3×3 perovskite-like columns, rhombic channels are also present. The triangular channels are always empty. The pentagonal channels are exclusively occupied by Ba [A2(1) and A2(2) sites] and the rhombic channels [A1(1), A1(2), A1(3) and A1(4) rhombic sites] located within the perovskite-like columns are occupied by La. The Sr atoms lie only in the A1' site located between two perovskite columns.

The refinement allowed to confirm the peculiar role played by the A1' site, which is the only rhombic 12-coordinated site of the structure to be filled by Ba in $\text{Ba}_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$). For $x=0$, the A1' site is fully occupied by Ba and thus the structure is perfectly ordered. As a consequence, the chemical formula can be written as $\text{Ba}_4(\text{Ba}_2\text{La}_8)\text{Ti}_{18}\text{O}_{54}$ corresponding to the structural formula $\text{A2}_4(\text{A1}'_2\text{A1}_8)\text{Ti}_{18}\text{O}_{54}$: 4 Ba in the A2(1) and A2(2) pentagonal channels (A site), 2 Ba in the A1' rhombic sites and 8 La in the A1(1), A1(2), A1(3) and A1(4) rhombic sites (A1 sites) of the 3×3 perovskite columns. Rawn et al. have already shown that, in the $\text{Ba}_{6-x}\text{Sm}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ solid solutions with $x=0.27$, the A1' sites were the only 12-fold coordinated sites to be simultaneously occupied by Ba and Sm.⁶

In the $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions, for each composition x , α_{max} corresponds to the saturation of the rhombic sites by “Sr + La”. This means that Sr^{2+} —which has the same charge as Ba^{2+} but a smaller size (r_{Sr}^{2+} [12] = 1.41 Å; r_{Ba}^{2+} [12] = 1.61 Å)—never lies the pentagonal channels which therefore can be cation deficient according to previous results. The corresponding structural formula is $[\text{Ba}_{6-x-\alpha(6-x)}\square_q]_{\text{A2}}[\text{Sr}_{\alpha(6-x)}\text{La}_{2x/3}]_{\text{A1}'}[\text{La}_8]_{\text{A1}}\text{Ti}_{18}\text{O}_{54}$ [$q=x-2+\alpha(6-x)$]. The substitution maximum is reached when the A1' sites are saturated, i.e. for $\alpha_{\text{lim}} = \frac{6-2x}{3(6-x)}$ (Fig. 1).

As for the non-stoichiometry of this phase, two ranges for x would be considered:

(i) $0 \leq x < 2$: for $\alpha=0$ the structural formula can be written as $[\text{Ba}_4]_{\text{A2}}[\text{Ba}_{2-x}\text{La}_{2x/3}\square_{x/3}]_{\text{A1}'}[\text{La}_8]_{\text{A1}}\text{Ti}_{18}\text{O}_{54}$. When α increases, Ba and vacancies in the A1' sites are progressively replaced by Sr:

- in a first step, Sr replace Ba in the A1' sites up to a limit α_{Sr} obtained from $(2-x)\text{Ba} = \alpha(6-x)\text{Sr}$ i.e. $\alpha_{\text{lim}} = \frac{2-x}{6-x}$ (Fig. 1).
- in a second step, the vacancies in the A1' sites are filled by Sr which are substituted for Ba up to $\alpha_{\text{lim}} = \frac{6-2x}{3(6-x)}$; the A2 sites become Ba deficient.

(ii) $2 \leq x \leq 3$: for $\alpha=0$ the structural formula is $[\text{Ba}_{6-x}\square_{x-2}]_{\text{A2}}[\text{La}_{2x/3}\square_{2-2x/3}]_{\text{A1}'}[\text{La}_8]_{\text{A1}}\text{Ti}_{18}\text{O}_{54}$. The A1' sites

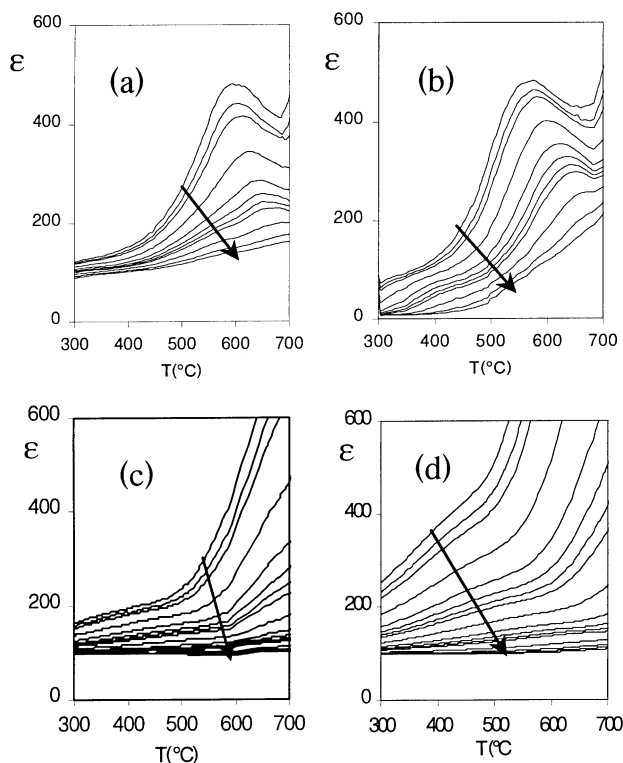


Fig. 4. Thermal variations of the permittivities of $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$. (a) $\text{Ba}_4(\text{Sr}_{0.5}\text{La}_9)\text{Ti}_{18}\text{O}_{54}$, $x=1.5$, $\alpha=0.11$; (b) $\text{Ba}_4(\text{Ba}_{0.5}\text{La}_9)\text{Ti}_{18}\text{O}_{54}$, $x=1.5$, $\alpha=0$; (c) $\text{Ba}_{3.5}(\text{SrLa}_9)\text{Ti}_{18}\text{O}_{54}$, $x=1.5$, $\alpha=0.22$; (d) $\text{Ba}_{3.16}(\text{Sr}_{0.34}\text{La}_{9.66})\text{Ti}_{18}\text{O}_{54}$, $x=2.5$, $\alpha=0.097$ (the arrows indicate increasing frequencies from 100 Hz to 1 MHz).

are occupied by La and vacancies. When α increases, the vacancies are progressively replaced by Sr. For $x=3$, the Al' sites are saturated by La so that the Sr substitution is no longer possible ($\alpha_{\text{lim}}=0$).

The thermal variations of the permittivity as a function of temperature up to 1 MHz are consistent with those already observed for $\text{Ba}_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$: a strong dispersion of the permittivity whose maximum is shifted towards the high temperature side as the frequency increases occurred only for compositions in which there is a cationic disorder among the Al' sites. This dispersion is shown in Fig. 4a and b for two structurally equivalent solid solutions. Both are cation deficient with respect to the Al' sites which contain “1 La + 0.5 Sr + 0.5 □” (a) and “1 La + 0.5 Ba + 0.5 □”

(b). On the contrary, for the compositions in which there are no vacancies in the Al' sites, i.e. “1 La + 1 Sr” (c) and “1.66 La + 0.34 Sr” (d), the permittivities do not show any maximum as the temperature increases.

Even though the high temperature/low frequency permittivities are not fully confident due to increasing conductivity of the samples, the dispersion of the permittivity cannot be assigned only to space charge phenomena. Among the assumptions likely to explain such a behaviour, the most probable would consist in a cation relaxation within the rhombic Al' sites when not fully occupied by both Ba (and/or Sr) and La. In these conditions, the relaxation would not occur when there are no vacancies (Fig. 4c and d).

4. Conclusion

The structural investigations of the $(\text{Ba}_{1-\alpha}\text{Sr}_\alpha)_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($0 \leq x \leq 3$) solid solutions have clearly shown the peculiar role of the Al' sites, which are the only 12-fold coordinated sites of the structure able to be occupied by Ba, Sr and La. The statistical disorder of both cations and vacancies has been connected to the thermal behaviour of the permittivity.

References

1. Wakino, K., Minai, K. and Tamura, H., Microwave characteristics of $(\text{Zr},\text{Sn})\text{TiO}_4$ and $\text{BaO-PbO-Nd}_2\text{O}_3\text{-TiO}_2$ dielectric resonators. *J. Am. Ceram. Soc.*, 1984, **67**, 278–281.
2. Nishigaki, S., Kato, H., Yano, S. and Kamimura, R., Microwave dielectric properties of $(\text{Ba},\text{Sr})\text{O-Sm}_2\text{O}_3\text{-TiO}_2$ ceramics. *Am. Ceram. Soc. Bull.*, 1987, **66**, 1405–1410.
3. Mercurio, J.-P., Manier, M. and Frit, B., Microwave dielectric properties of $\text{BaNd}_{2(1-x)}\text{Sm}_{2x}\text{Ti}_5\text{O}_{14}$. *Mater. Lett.*, 1989, **8**(3), 112.
4. Valant, M., Suvorov, D. and Kolar, D., X-ray investigations and determination of the dielectric properties of the compound $\text{Ba}_{4.5}\text{Gd}_9\text{Ti}_{18}\text{O}_{54}$. *Jpn. J. Appl. Phys.*, 1996, **35**, 144.
5. Matveeva, R. G., Varfolomeev, M. B. and Il'yushenko, L. S., Refinement of the composition and crystal structure of $\text{Ba}_{3.75}\text{Pr}_{9.5}\text{Ti}_{18}\text{O}_{54}$. *Russ. J. Inorg. Chem.*, 1984, **29**, 17.
6. Rawn, C. J., Birnie, D. P., III, Bruck, M. A., Enemark, J. H. and Roth, R. S., Structural investigation of $\text{Ba}_{6-3x}\text{Ln}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ ($x=0.27$, Ln = Sm) by single crystal X-ray diffraction in space group $\text{Pnma}(N^\circ 62)$. *J. Mater. Res.*, 1998, **13**(1), 187–196.
7. Harre, N., *Etude structurale par DRX et METHR et Caractérisation diélectrique de Quelques Phases du Système $\text{BaO-La}_2\text{O}_3\text{-TiO}_2$* . PhD thesis, University of Limoges, France, 1996.