

Crystal structure and dielectric properties of layered perovskite-like solid solutions $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) with high Curie temperature

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The Aurivillius phases $[\text{Bi}_2\text{O}_2][\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]$ are well-known ferroelectrics with high Curie temperatures T_C . High-temperature piezoceramics $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ (BGdTTa, $x = 0.0, 0.1, 0.2, 0.3$) were prepared by a solid-state reaction method. The structural and electrophysical characteristics of BGdTTa ceramics have been studied. According to the data of powder X-ray diffraction, all the compounds are single-phase with the structures of two-layer Aurivillius phases ($m = 2$) with the orthorhombic crystal lattice (space group $A2_1am$). The temperature dependence of the relative permittivity $\epsilon/\epsilon_0(T)$ of the compounds was measured and showed that the Curie temperature T_C of perovskite-like oxides $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ increases linearly with an increase in the substitution parameter x to $T_C = 925^\circ\text{C}$. The activation energies of charge carriers have been found in different temperature ranges.

Keywords: Aurivillius phases; $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$; Curie temperature T_C ; tolerance factor.

1. Introduction

The Aurivillius phases (APs)¹⁻³ are a large family of bismuth-containing layered perovskite-like compounds, the chemical compositions of which are described by the general formula $\text{A}_{m-1}\text{Bi}_2\text{B}_m\text{O}_{3m+3}$. The crystal structure of APs is alternating $[\text{Bi}_2\text{O}_2]^{2+}$ layers, between which there are m perovskite-like $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$ layers, where positions A are occupied by ions with large radii (Bi^{3+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Y^{3+} , Pb^{2+} , Na^+ , K^+ , Th^{4+} , and Ln^{3+} , Lu^{3+} (lanthanides)) and the positions B inside oxygen octahedra are occupied with ions with small radii (Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} , Mo^{6+} , Fe^{3+} , Mn^{4+} , Cr^{3+} , and Ga^{3+}). Layered perovskite-like compounds of bismuth oxides of the APs family are promising lead-free materials for applying in piezoelectric devices, in particular, at high temperatures and high frequencies. They demonstrate low temperature coefficients of dielectric and piezoelectric losses, low aging temperatures, in addition to high Curie temperatures ($T_C \leq 965^\circ\text{C}$).⁴⁻⁶ In recent years, more attention has been placed on the design and studies of new APs. The APs such as $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN), $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (SBTi), $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBTa), $\text{La}_{0.75}\text{Bi}_{3.25}\text{Ti}_3\text{O}_{12}$ (BLT), and so on were accepted as excellent materials for the energy independent ferroelectric memory with small access time (FeRAM).⁷⁻¹⁴ $\text{Bi}_3\text{TiTaO}_9$ (BTNO) with $m = 2$ which consists of $(\text{Bi}_2\text{O}_2)^{2+}$ layers between where there are $(\text{BiTiTaO}_7)^{2-}$ layers is a

promising material for fabricating high temperature piezoelectric sensors because of their very high Curie temperature T_C (870°C), despite the fact that the piezoelectric modulus of BTNO ceramic is fairly low ($d_{33} < 7$ pC/N). Atomic substitutions in positions A and B of the crystal lattice of APs lead to changes in the structure, dielectric properties, and significantly affect the polarization processes in these compounds. In this work, we have synthesized a number of new solid solutions of layered perovskite-like oxides $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) in which proportions between amounts of Bi^{3+} and Gd^{3+} ions entering in position A was varied and have studied their crystal lattices, the dielectric and electrophysical characteristics. The ionic radius of Gd^{3+} is significantly smaller than the ionic radius of Bi^{3+} ion, which must lead to significant distortions of the crystal structure of the obtained substitutional solid solutions and influence their dielectric characteristic and the value of the Curie temperature T_C .

2. Experimental Procedure

The polycrystalline solid solutions of layered perovskite-like oxides $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) were synthesized by solid-phase reaction of corresponding oxides Bi_2O_3 , TiO_2 , Ta_2O_5 , and oxide Gd_2O_3 . After the initial compounds were weighted and preliminarily ground, the synthesis

was carried out at a temperature of 860 °C for 6 h; then, the repeated grinding was performed, and the powder was pressed into 1–1.5-mm thick pellets 10 mm in diameter, and the final burning was carried out at a temperature of 1100 °C for 4 h.

X-ray diffraction spectra of the powder were measured using a DRON-3M diffractometer with a BSV21-Cu X-ray tube. The Cu $K\alpha_{1,2}$ radiation was selected from the total spectrum using a Ni filter. The X-ray diffraction patterns were measured in the range of 2θ angles from 10° to 65° with an angular pitch of 0.04° and exposition in a point of 4 s. The spectrum profile of the X-ray diffraction was analyzed, the line position was determined, their indexing (hkl) according to the chosen unit cell model was performed using the PCW-2.4 program.¹⁵

To perform the electric measurements, Ag–Pd electrodes were deposited on the plane surface of the ceramic samples (1–1.5 mm thick discs 10 mm diameter); the past was annealed at 820 °C (20 min). The temperature and frequency dependences of the characteristics were measured using an E7-20 immittance meter in the frequency range 100 kHz–1 MHz and at temperature from room temperature to 950 °C.

3. Results and Discussion

The crystal structure of APs $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) was determined by X-ray powder diffraction. The data of diffractions obtained (Fig. 1) demonstrate that all prepared solid solutions represent a single phases compounds isostructural to the known perovskite like oxide $\text{Bi}_3\text{TaTiO}_9$ (ICDD PDF2,00-0390233). The diffraction patterns of all the compounds correspond to the AP with $m = 2$ (Fig. 1).

The unit cell parameters and unit cell volumes determined from the X-ray diffraction data are presented in Table 1.

The dependence of the unit cell parameters on the parameter x is shown in Fig. 2. As can be seen from Fig. 2, the change dependence of the unit cell parameters a , b , c of the synthesized $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) on the parameter x is linear.

This is related to the difference in the values of ionic radii in positions A of the perovskite like layers, where Bi^{3+} ions are replaced with Gd^{3+} ions with smaller radius ($R_{\text{Bi}^{3+}} = 1.38 \text{ \AA}$, $R_{\text{Gd}^{3+}} = 1.26 \text{ \AA}$, see Ref. 16).

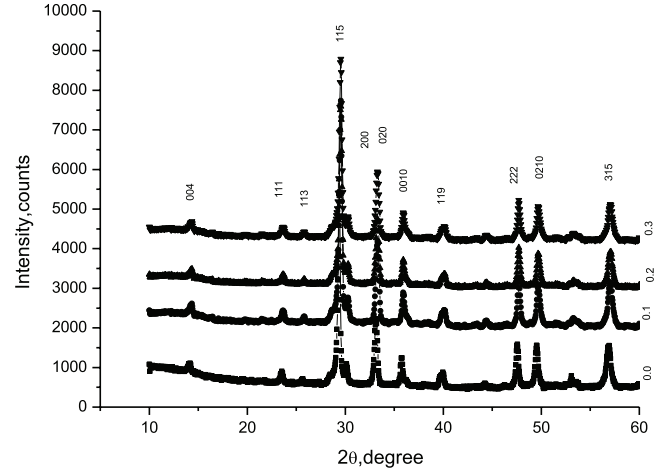


Fig. 1. Experimental curve of the X-ray powder diffraction patterns of the $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) compound.

It can be noted that a decrease in the unit cell volume (Fig. 3) with an increase in x is due to significant decrease in parameter c along the crystallographic direction [001], whereas, in this case, the parameters a and b are almost unchanged. The changes of the unit cell parameters of the $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) solid solutions with the AP structure are according to the Vegard law (Fig. 2).

The obtained values of the rhombic $\delta b = (b-a)/a$ and tetragonal $\delta c = (c'-a_i)/a_i$ deformations (where $a_i = (a+b)/(2\sqrt{2})$ is the average tetragonal period and $c' = 3c/(8+6m)$ is the average thickness of the single perovskite layer (Table 2)).¹⁷

All the APs series demonstrates decrease in the tolerance factor due to a decrease in the amount of Bi^{3+} ions with the largest ionic radius, while the average tetragonal period at and the average thickness of a single perovskite-layer decrease systematically.

The tetragonal distortion of APs insignificantly changes in the range $x = 0.0-0.3$; the octahedral are in a compressed state along axis c in pseudo-perovskite layers.

Along with the structural studies, we measured the temperature dependences of relative permittivity $\varepsilon(T)$ at various frequencies of 100–1000 kHz and activation energies E_a of the charge carriers over wide temperature range. Figure 4

Table 1. Unit cell parameters a , b , c ; unit cell volume V ; relative permittivity $\varepsilon/\varepsilon_0$, at frequency of 100 kHz, tolerance factor t ; Curie temperature T_C .

Compounds	a (Å)	b (Å)	c (Å)	V (Å ³)	$\varepsilon/\varepsilon_0$	t	T_C (°C)
1 $\text{Bi}_3\text{TiTaO}_9$	5.4053	5.429	25.291	738.615	1500	0.98	895
2 $\text{Bi}_{2.9}\text{Gd}_{0.1}\text{TiTaO}_9$	5.4059	5.4237	25.128	736.752	2430	0.9792	905
3 $\text{Bi}_{2.8}\text{Gd}_{0.2}\text{TiTaO}_9$	5.4013	5.4214	25.12	735.58	1180	0.9778	915
4 $\text{Bi}_{2.7}\text{Gd}_{0.3}\text{TiTaO}_9$	5.399	5.4152	25.08	733.255	920	0.9764	925

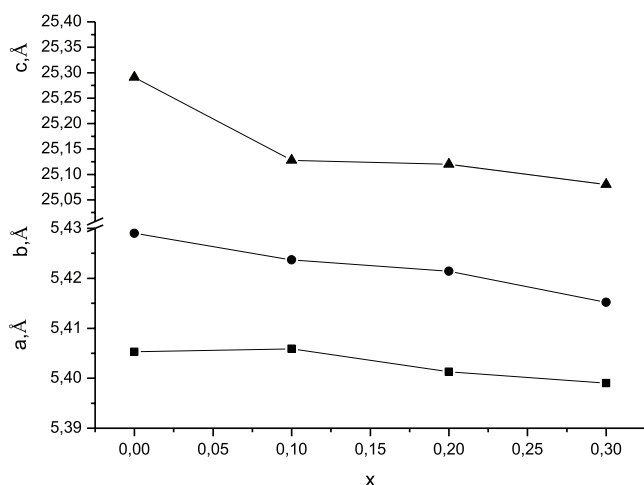


Fig. 2. Dependence of the unit cell parameters a , b , c of the synthesized $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) on the parameter x .

shows temperature dependences of relative permittivity $\varepsilon(T)$ and dielectric losses $\tan\delta(T)$ for $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.2$) at 0.1–1.0 MHz.

All the temperature dependences of the permittivity have sharp maxima, the positions of which are associated with the

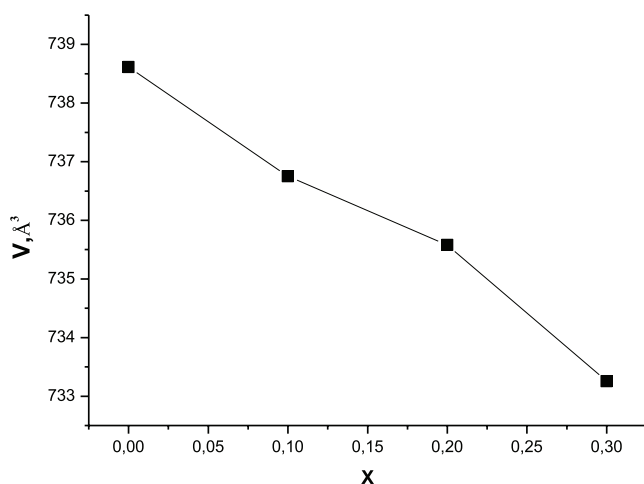


Fig. 3. Dependence of the unit cell volume of the synthesized $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) on the parameter x .

Curie temperatures of these compounds. Correspondingly, the dielectric loss curves have clear minima at the Curie temperatures T_C . The positions of the dielectric loss maxima are independent of frequency for all APs, which indicate the absence of relaxor properties in these compounds.

The maximum Curie temperature $T_C \approx 925^\circ\text{C}$ was obtained for the $\text{Bi}_{2.7}\text{Gd}_{0.3}\text{TiTaO}_9$ composition. The Curie temperatures of the studied APs increases with a decrease in the unit cell parameters a and b and its volume V and a decrease in parameter c . This dependence is directly related to the correlation between the tolerance factor and the value of T_C characteristic of APs. Tolerance factor t was introduced by Goldschmidt¹⁸ as a parameter that determines the ionic packing in cubic cells

$$t = (R_A + R_O) / (\sqrt{2}(R_B + R_O)), \quad (1)$$

where R_A and R_B are cation radii in positions A and B, respectively, and R_O is the oxygen ion radius. Later this rule was also used for determination of the stability of the perovskite-like $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$ layers. In this work, we calculated tolerance factor t using the values of the ionic radii by Shannon (O^{2+} (coordination number (CN) = 6) $R_{\text{O}} = 1.40 \text{ \AA}$; $R_{\text{Bi}^{3+}} = 1.33 \text{ \AA}$; $R_{\text{Gd}^{3+}} = 1.26 \text{ \AA}$, $R_{\text{Ta}^{4+}} = 0.64 \text{ \AA}$; $R_{\text{Ti}^{4+}} = 0.605 \text{ \AA}$). The ionic radii for the coordination with $R_{\text{Bi}^{3+}}$ (CN = 12) and $R_{\text{Gd}^{3+}}$ (CN = 12) are not given in Ref. 17, and these values were determined from the dependences of their ionic radii on the coordination numbers extrapolated to the region of high values. As seen from Table 1, the members of the series $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) demonstrated dependence of T_C on the calculated values t of the tolerance factors, which enables us to predict its value for other values of x .

The temperature dependences of the loss $\tan\delta$ (Fig. 4) show the sharp increase in the dielectric loss at high temperatures ($>600^\circ\text{C}$) for $\text{Bi}_3\text{TiTaO}_9$ and at lower temperatures ($>350^\circ\text{C}$) for the $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x = 0.0, 0.1, 0.2, 0.3$) series. This was due to a high amount of charge carriers, whose concentration sharply increases at high temperatures due to the formation of oxygen vacancies. However, the consideration of the values of $\tan\delta$ for various APs at a certain temperature, T_C , showed that they differ by several times, indicating substantially different degrees of imperfection of the APs crystal structure.

The typical dependence of $\ln\sigma$ on $1000/T$, where σ is the specific conductivity that was used for determination of E_a is

Table 2. a_t is the parameter of the tetragonal period, c' is the octahedron height along axis c , δc is the deviation of the unit from the cubic shape, δb is the rhombic distortion, $V - V_x/V$ is the relative change in the unit cell volume, and c_0 is the bismuth-oxygen layer.

	Compounds	a_t (Å)	c' (Å)	δc (%)	δb (%)	$V - V_x/V$ (%)	c_0 (Å)
1	$\text{Bi}_3\text{TiTaO}_9$	3.829	3.762	-1.4	0.43	0	5.058
2	$\text{Bi}_{2.9}\text{Gd}_{0.1}\text{TiTaO}_9$	3.828	3.758	-1.5	0.032	0.25	5.0256
3	$\text{Bi}_{2.8}\text{Gd}_{0.2}\text{TiTaO}_9$	3.83	3.756	-1.5	0.037	0.41	5.024
4	$\text{Bi}_{2.7}\text{Gd}_{0.3}\text{TiTaO}_9$	3.82	3.755	-1.3	0.3	0.68	5.016

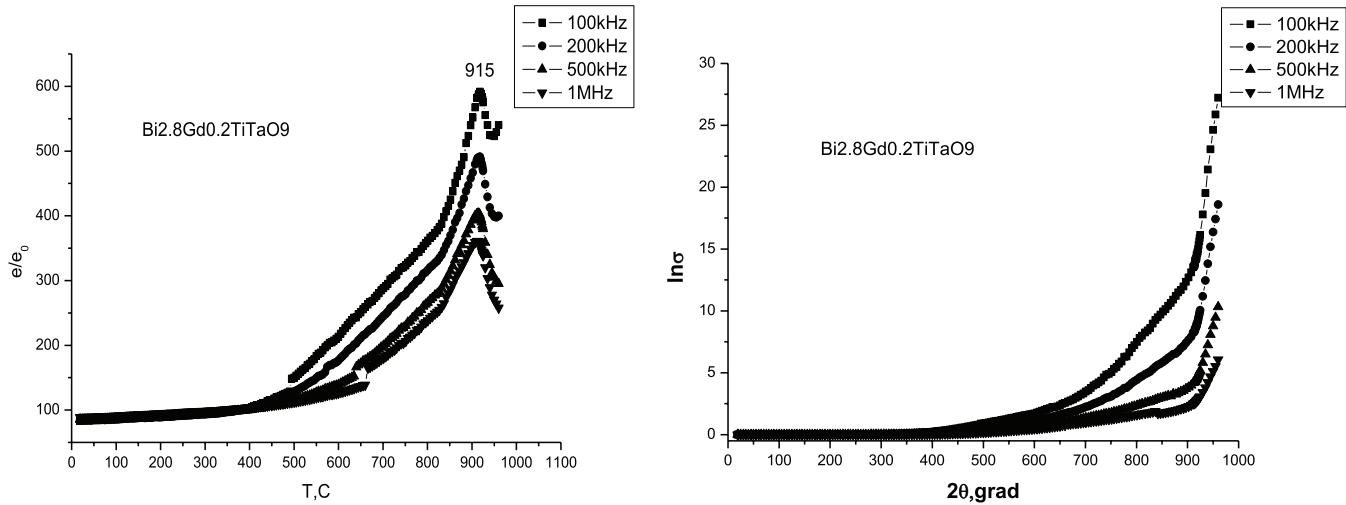


Fig. 4. Temperature dependence of the relative permittivity $\varepsilon/\varepsilon_0$ and the loss $\tan \delta$ of $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x=0.2$) measured at 100 kHz–1.0 MHz.

shown in Fig. 5 for APs $\text{Bi}_{2.9}\text{Gd}_{0.1}\text{TiTaO}_9$. From Fig. 5, it is well seen that there are two temperature regions in which E_a has substantially different values. The activation energy E_a is calculated using the Arrhenius relationship:

$$\rho = \rho_0 \exp(E_a/kT) \ln(\sigma) = -(W/kT) + \ln(\sigma_0), \quad (2)$$

where E_a is the activation energy of the charge carriers, k_B is the Boltzmann constant, and T is the absolute temperature. From this above equation, it can be seen that the relationship between $\ln \sigma$ and $1000/T$ is a linear relationship. This is due to the fact that, at high temperatures, intrinsic defects formation of which requires high activation energies are main charge carriers. At low temperatures, the activation energy E_a is mainly determined by impurity defects and has significantly lower values.

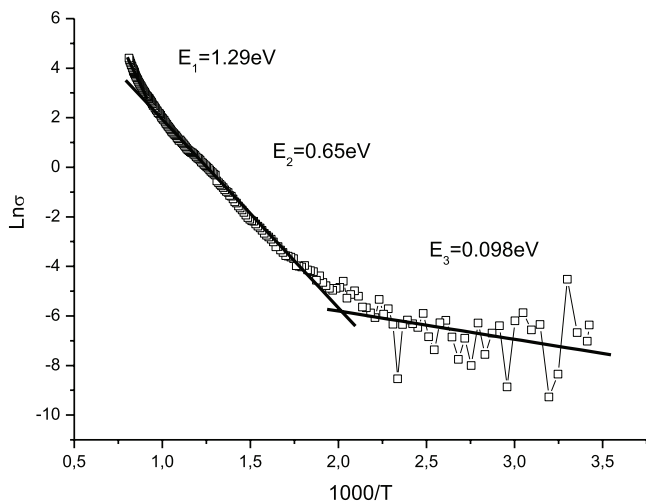


Fig. 5. Dependence of $\ln \sigma_0$ on $1000/T$ for the $\text{Bi}_{2.9}\text{Gd}_{0.1}\text{TiTaO}_9$ sample.

4. Conclusion

A new series of layered perovskite-like oxides $\text{Bi}_{3-x}\text{Gd}_x\text{TiTaO}_9$ ($x=0, 0.1, 0.2, 0.3$) has been synthesized. The X-ray diffraction studies that all the compounds are single phase and have the APs structure with orthorhombic unit cells (space group $A2_1am$). Dependence of T_C on the calculated values of t tolerance factors allows us to predict its value for other values of x . The permittivity was measured to a temperature of 950°C . The Curie temperatures increase from 895°C ($x=0$) to 925°C (for $x=0.3$).

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“Features of crystalline systems with local structural disturbances at meso- and nanoscale scale levels, experiencing successive structural and magnetic phase transitions”, hands. I.P. Raevsky., 2020–2022.

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