The erbium's amphoteric behavior effects on sodium bismuth titanate properties

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Abstract

The effects of erbium doping on lead-free ferroelectric $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics are investigated. The scanning electron microscopy shows a highly dense grain structure for all specimens. A pure perovskite structure was observed by X-ray diffraction for all compositions. However, Raman spectroscopy investigations suggest that Er$^{3+}$ doping is associated with local structural disorder. Doping with Er$^{3+}$ ions also leads to photoluminescence effect. The depolarization temperature in the dielectric measurement vanishes gradually as the Er$^{3+}$ amount increases. The ferroelectric properties display a slight decrease in coercive field for the $x=0.01$ composition.

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1. Introduction

In the past, luminescence of rare-earth ions doped in perovskite-type oxides was actively investigated in the 1960s and 1970s with an interest in ferroelectricity, phase transitions and semiconducting properties of these materials [1,2]. On the other hand, in the last years, ferroelectric materials have been considered for applications in different kinds of devices, such as storage information, piezoelectric actuators, infrared sensors and ultrasonic transducers in medical and sonar applications [3–5]. Rare-earth-doped ferroelectric oxides are of particular interest and offer the possibility of fabricating simple devices that take advantage of their electric-optical and nonlinear optical properties such as self-frequency-doubled, self-Q-switched and self-modulated lasers, as well as amplified integrated optical circuits with no insertion losses are possible [6–8]. Among all lead-free materials, sodium bismuth titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT/BNT), has attracted considerable attention mainly for its interesting ferroelectric properties [9,10]. Because of its high Curie temperature ($T_c \approx 325 ^\circ C$), high remanent polarization $P_r \approx 38 \mu \text{C cm}^{-2}$ and piezoelectric coefficient ($d_{33} \approx 73 \text{pC/N}$), comparable to that one of BaTiO$_3$ [11], NBT is considered a good candidate as lead-free piezoelectric ceramic. It is well known that at room temperature, this ferroelectric perovskite compound has a rhombohedral symmetry with the polar $R3c$ space group [12–14]. However, recent work has been undertaken on single NBT crystal by Thomas et al. [15] using high resolution XRD, who postulated a monoclinic model with $Cc$ space group to describe the symmetry of NBT. The authors [15] suggested that the presence of superstructure reflections constitute a fingerprint of this monoclinic symmetry. Their results were confirmed by Aksel et al. [16] on NBT powder. All the properties above make NBT of both fundamental and practical interest. However, one of the main drawbacks of pure NBT is its high conductivity resulting from the volatility of bismuth during the sintering process that prevents proper poling. In order to improve the electrical properties, a number of NBT-based solid solutions such as $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3–\text{BaTiO}_3$ (NBT–BT), $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3–\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT–KBT)
have been developed [17–23]. For example, co-doping NBT with K⁺ and Li⁺ was reported [22,24] to improve the piezoelectric and coupling coefficients of NBT to $d_{33}$ ≈ 164 pCN and 36% respectively, while reducing the coercive field to 3.7 kV mm⁻¹ and maintaining a high depolarization temperature. On the other hand, Nd, Ce, Eu, La and Sm ions modified the NBT or NBT-based compositions. The mentioned modification has improved piezoelectric properties and has lead to easier polarization in comparison with pure NBT ceramics [25–31]. For instance, in our previous work [25] we have demonstrated that the introduction of Nd³⁺ in the NBT matrix leads to improve the pyroelectric coefficient along with a high photoluminescence in the near infrared wavelength range. Optically active lanthanide ions such as Eu³⁺, Pr³⁺, Sm³⁺ and Nd³⁺ may therefore be used to develop multifunctional materials adapted for the modern technology [25,32–33]. On the other hand, due to their rich energy level structure, trivalent erbium ions hosted in crystal matrices are very attractive optical activators as they can emit in the ultraviolet, visible and infrared (IR) wavelength range. This emission depends on excitation energy, concentration of the dopant as well as on the properties of the host crystal. Er³⁺ ions have showed laser action in a variety of hosts at room temperature (RT) [34–37]. For instance, Er³⁺ ions have been used in the development of broadband erbium-doped fiber amplifiers (EDFA) in the optical communication technology field [38,39]. The introduction of erbium into the PbTiO₃ matrix has been reported to provide a great potential for photonic applications [40]. Only few authors have investigated the effects of erbium on NBT’s properties [41–43].

This paper is concerned with doping effects of erbium on the pyroelectric and light source (DH-2000-BAL). Ferroelectric polarization was investigated at room temperature using a ferroelectric test system (TF Analyzer 2000, aixACCT, equipped with a voltage amplifier). The dielectric properties were studied on ceramic discs after deposition of gold electrodes on the circular faces by cathodic sputtering using an impedance analyzer (Agilent 4284A) in the frequency range from 20 Hz to 1 MHz.

3. Results and discussion

3.1. Phase formation and microstructure

The powder XRD patterns of Na₀.₅[Bi₁₋ₓErₓ]₀.₅TiO₃, ($x$=0–0.01) in 2θ=20–90° range is shown in Fig. 1. The XRD results indicate pure perovskite for all samples within the accuracy limit of the solid-state method suggesting that Er³⁺ has diffused into the NBT lattices. The XRD data could be completely indexed according to rhombohedral symmetry with $R3c$ space group. No phase transition could be detected in the used range of Er³⁺ concentration. The measured data fits well to $R3c$ phase. In our measurements no additional peaks supporting a monoclinic structure as seen by Thomas et al. [15] are visible. That might be due to limited device resolution, as we used standard XRD diffraction with Bragg–Brentano geometry. In Fig. 1 inset, we have presented the evolution of the phase. In our measurements no additional peaks supporting a monoclinic structure as seen by Thomas et al. [15] are visible. That might be due to limited device resolution, as we used standard XRD diffraction with Bragg–Brentano geometry. In Fig. 1 inset, we have presented the evolution of the (024) peak position. We can clearly see that for all samples, except the composition $x$=0.005, the (024) peak shifts toward higher angles suggesting the decrease in the solid solution lattice parameters. However, the composition $x$=0.005 exhibits a shift toward lower angles. This result suggests that Er³⁺ was randomly distributed over the NBT’s sites: Bi/Na-site (A-site) and Ti-site (B-site). The substitution can occur in one of these sites depending on the dopant’s electrovalence and ionic radius which itself depends on the coordination number (CN). In fact, the ionic radius of Er³⁺ (1.22 Å, 12 coordinate) [44] is close to Bi³⁺ (1.32 Å, 12 coordinate) [45]. Hence, Er-ions occupy A-site in the NBT ceramics. As a result, the

![Fig. 1. X-ray diffraction patterns of Na₀.₅[Bi₁₋ₓErₓ]₀.₅TiO₃ sintered ceramics.](image)
(024) peak shifts to the larger-angle sides. However, the downshift of this peak toward lower angles for the composition $x=0.005$ maybe attributed to the substitution of Ti$^{4+}$ ions by the Er$^{3+}$ ions, because the ionic radius of Ti$^{4+}$ (0.605 Å, 6 coordinate) is smaller than that of Er$^{3+}$ (0.89 Å, 6 coordinate) [46]. It should be noticed that rare earth ions with medium size as Er$^{3+}$, Dy$^{3+}$, Y$^{3+}$ and Ho$^{3+}$, have been reported to show an amphoteric behavior in BaTiO$_3$ [47], e.g. they behave as an acceptor when Ti-site is substituted or as donor when the substitution occurs at Ba-sites. That influenced considerably the electrical properties of BaTiO$_3$ (semiconducting properties, change of resistivity etc.). Yongping et al. [47] reported also that the thermodynamic conditions, such as the partial pressure of oxygen in the sintering atmosphere and temperature, play an important part in the distribution of rare earth elements with amphoteric behavior in A-site or B-site of BaTiO$_3$ [48,49]. On the other hand, Garg et al. [50] reported that only 38% of Er$^{3+}$ ions tend to substitute in the B site [41,46,51]. We can conclude from all the mentioned and observed XRD results that we cannot have a total control over the distribution of erbium in the NBT sites.

Fig. 2 shows typical SEM ceramic specimens micrographs. For all compositions, the grain boundaries are well delineated and with the exception of triple boundaries no porosity is observed which confirms the result of the density measurement. Fig. 2 also shows large equiaxed grains obtained for pure NBT with the main grain size of approximately 4 μm. For the doped ceramics, a slight increase in the grain size for all the specimens has been found, although the grain size remains within the limit of 5 μm and might be also ascribed to slight variations in the solid state reaction method used for the processing of the ceramics. We have to note that the same effect was observed by Du et al. [42] in the same solid solution through different solid state method conditions.

Fig. 2. SEM Micrographs of Na$_{0.5}$Bi$_{1-x}$Er$_x$TiO$_3$ ceramics: (a) NBT; (b) 0.0025ErNBT; (c) 0.005NBT; (d) 0.0075ErNBT and (e) 0.01ErNBT.
3.2. Raman spectroscopy study

The room temperature Raman spectra of all sintered ceramics are shown in Fig. 3. For pure NBT, the Raman bands are relatively broad which can be caused by the disorder in the A-site. Using the Lorentzian functions, the Raman spectrum of pure NBT can be deconvoluted into six peaks. The mode at ~138 cm⁻¹ is assigned to Na–O vibration and the broad band centered at ~277 cm⁻¹ is dominated by Ti–O vibration. The modes in the region between 500 and 600 cm⁻¹ (centered at 520 and 582 cm⁻¹) are associated with the vibration of TiO₆-octahedra. The broad bands in the high-frequency region (centered at 767 and 845 cm⁻¹) are attributed to the oxygen octahedra vibrations/rotations. The deconvolution results are in good agreement with the published literature [25,52–56]. We have to note that, due to the high mass of the bismuth atom, a Bi–O band would be located at very low frequencies that are not available in our experimental device.

With the introduction of Er³⁺ into the NBT matrix, several interesting changes in the local symmetry can be observed as follows:

(1) The doped ceramics intensity peaks are higher compared to the pure NBT intensity peaks. That is why we have normalized their intensities in order to follow the evolution of the spectra. The drastic increase in intensity can be ascribed to the fluorescence effect of Er³⁺. This effect will be discussed later.

(2) As far as the doped ceramics are concerned, the mode assigned to Na–O vibration at 138 cm⁻¹ in pure NBT shifts toward a lower frequency and stabilizes at approximately 110 cm⁻¹. Its normalized intensity decreases compared to pure NBT. Further, this mode becomes broader probably due to the increase of the disorder in the A-site of this perovskite structure.

(3) The peak centered at 277 cm⁻¹ in pure NBT shifts toward a higher frequency and splits into two peaks of lower intensity. This splitting was previously observed in the solid solution of (Na₁₋ₓKₓ)₀.₅Bi₀.₅TiO₃ for x = 0.5 [54]. Kreisel et al. [54] surmised the appearance of this new shoulder as the rise of an underlying structural component. However, the same authors attributed the peak shifts to structural changes. In our case, in the light of the above, both the anharmonic low-wavenumber shift (mode at ~138 cm⁻¹) and the dramatic intensity breakdown and shift in the mid-wavenumber region (mode at ~277 cm⁻¹) have provided a spectral signature for a structural rearrangement which is related to changes of the TiO₆ octahedral without any phase transition as provided by the XRD measurement. We believe that fluorescence effects induced by the introduction of erbium into the NBT matrix could also contribute to the changes in the Raman spectra. Similar effects were also observed in our previous work in Nd-doped NBT [25] using the same excitation wavelength (532 nm) because both erbium and neodymium are known as photoluminescence active ions.

(4) The bands situated at higher frequency (from 400 to 700 cm⁻¹) in pure NBT become sharper with the introduction of Er³⁺. It is well known for perovskite structure that the high frequency modes are commonly dominated by vibrations of oxygen atoms when the cations are almost at rest [57]. There are no mass effects in this region. However, the chemical nature of the cation can influence the frequency of these bands via other determining factors, e.g. bonding, repulsion effects etc.

(5) Further, the doublet observed at high frequency (767, 845 cm⁻¹) in pure NBT is a bit smeared by the higher doped ceramic background. An additional mode appears in this region at around 700 cm⁻¹. It is well known that in the perovskite structure the modes existing in this region are generally attributed to oxygen vibration or displacement [54,57].

The Raman investigation reveals that the introduction of a small amount of Er³⁺ into the NBT matrix leads to short-range disorder (structural change) due to octahedral-distortion, while the samples still possess long-range order as confirmed by XRD. The Raman measurement (especially at the wavelength used) seems, therefore, to be very sensitive to the introduction of the lanthanide elements with optical activity such as Er³⁺ or Nd³⁺. The same effect was observed in our previous work [25] where also structural changes could be revealed via Raman investigations. In order to eliminate the luminescence effect, most authors in the literatures [60–63] have used the 488 nm or 514 nm wavelength. They found that the introduction of erbium in different hosted materials increases the charge fluctuations and the octahedra distortion which lead to the increase of disorder. We have found similar results but through 532 nm wavelength.

These results may support the short range disorder already discussed for pure NBT by Schutz et al. [58] and Levin and Reaney [59]. Erbium doping might increase the disorder, but
not to such an extent that it can be deduced from XRD measurements, despite its sensitivity.

3.3. Optical properties

The absorption spectrum at room temperature of 0.01ErNBT ceramic in the 300–1100 nm range is shown in Fig. 4a. Within this range, each characteristic absorption band can be attributed to the transition from the \( ^4I_{15/2} \) ground state to the corresponding excited states of the Er\(^{3+} \) ion. The peaks centered at 970, 795, 654, 543, 487, 450 and 390 nm are assigned to the excited states \( ^4F_{9/2}, ^4S_{3/2}, ^4H_{11/2}, ^4F_{7/2}, ^4H_{9/2} \) and \( ^4G_{11/2} \) respectively \[64\]. It should be noticed that Er\(^{3+} \) exhibits other peaks at around 406 nm and 1530 nm that correspond to the excited states \( ^4F_{5/2}, ^4F_{3/2} \) and \( ^4I_{13/2} \) respectively \[64\]. However, the first peak cannot be observed because the measurement was recorded at room temperature which clearly influences the peaks’ resolution and broadness. The second one cannot be observed because of device limitation. On the other hand, the obtained absorption spectrum exhibits absorption bands situated at 390, 450 and 543 nm which are not observed in the recent work of Luo et al. \[43\] for the same composition. This result is maybe due to device resolution.

Fig. 4b shows the emission spectra of the Na\(_{0.5}\)(Bi\(_{1-x}\)Er\(_{x}\))\(_{0.5}\)TiO\(_3\) \((x = 0.0025–0.01)\) solid solution measured at room temperature under 532 nm laser excitation. All peaks are indexed corresponding to energy level transitions. The spectrum shows a strong green and near infrared emission situated at around 545 nm, 850 nm and 975 nm respectively, with a weak emission at 660 nm and 800 nm. We have to notice that only few studies have undertaken the emission at 850 and 975 nm which are used as the current standard for short haul optical links in the application of data transmission [65–67]. The highest intensity of all peaks was observed for the 0.01ErNBT sample, the lowest for 0.005ErNBT composition. This result is related to the distribution of erbia into the NBT matrix. In fact, for the composition \(x = 0.01\) the erbium was located in A-site as shown in XRD measurement. Therefore, the distance between two adjacent erbium ions (Er–Er) is large and the interactions between Er\(^{3+} \) ions would be so weak as well as the concentration quenching effect is minimal. On the other hand, it is well known that B-site of the ABO\(_3\) perovskite structure is smaller than the A-site. So, when the erbium was located in B-site as the case of the composition \(x = 0.005\), the distance between erbium ions (Er–Er) is small and the interactions between Er\(^{3+} \) ions becomes pronounce leading to an increase of the concentration quenching effect which by itself leads to a decrease in the emission intensity as observed for this composition.

However, the emission intensity does not scale clearly with Er concentration. Haro-González et al. \[68\] have found the same emissions for the Strontium barium niobate (SBN) glass ceramic samples doped with Er\(^{3+} \) under the same excitation with the only exception of the green emission at 545 nm that was not observed, probably, because of the different chemical environment of in the Er\(^{3+} \) ions (it is well known that the luminescence associated with Er\(^{3+} \) is very sensitive to the site occupied \[68\]). This result is also a sign of the randomly distribution of Er\(^{3+} \) inside NBT matrix.

3.4. Dielectric and ferroelectric properties

Fig. 5 shows the temperature dependence of the relative dielectric permittivity \(\varepsilon_r\) and dielectric losses, measured at 100 kHz for unpoled ceramics. It is well known that pure NBT exhibits two dielectric anomalies centered approximately at 473 K and 595 K that are ascribed to the ferroelectric–antiferroelectric–paraelectric (or ferroelastic \[69\]) phase transitions, respectively. This result is in agreement with earlier reports \[25,69,70–72\]. The maximum of permittivity \((T_m, \text{Fig. 5a})\) observed at ~595 K may originate from relaxation processes connected with both electrical and mechanical interaction between polar regions and the nonpolar matrix \[73\]. The diffuse
hump observed at around 470 K was attributed to the depolarization temperature ($T_d$ in Fig. 5b) that was explained in the literature by the presence of an intermediate anti-ferroelectric phase [12]. But, we have found recently [74] that pure NBT exhibits a third dielectric anomaly near $T_m$ centered approximately at 550 K denoted as $T_1$ in Fig. 5b. This result was correlated with Dorcet et al. work [72] who confirmed by transmission electron microscopy (TEM) the existence of modulated orthorhombic phase in this temperature range.

The substitution of Bi$^{3+}$ by Er$^{3+}$ in NBT leads to marked specific effects despite the low amount. First of all, the dielectric loss significantly decreased (see Fig. 5b) for all doped samples. However, for the composition $x=0.005$ the dielectric loss increases in comparison to the other doped samples. This result confirms the diffusion of erbium ion in B-site of the perovskite structure leading to some oxygen vacancies due to a difference in the valence between Ti$^{4+}$ and Er$^{3+}$. On the other hand, the observed dielectric loss for this ceramic is still lower than the observed one in the pure NBT.

Secondly, both $T_d$ and $T_m$ exhibit an obvious dependency on the amount of Er$^{3+}$. Compared to pure NBT, both $T_d$ and $T_m$ shift toward higher temperatures, with maximum values of 510 and 635 K respectively, for $x=0.01$. This result was explained in the case of NBT doped-La [75] by the increase in translational symmetry and the size of the polar region with the increase of La content. The same effect was also observed for Er$_2$O$_3$ doped 0.82Bi$_{0.5}$Na$_{0.5}$TiO$_3$–0.18Bi$_{0.5}$K$_{0.5}$TiO$_3$ (BNKT18) lead-free ceramics [76]. On the other hand, the maximum in dielectric permittivity observed at $T_m$ becomes broader as $x$ increases and accentuates the diffuse behavior of the phase transition [77]. This result can be attributed to the local structural disorder and compositional fluctuation associated with the arrangement of A-site cations caused by the introduction of erbium. However, the hump of depolarization temperature ($T_d$) and the new dielectric anomalies ($T_1$) become fuzzy and indistinguishable which means that those dielectric anomalies are sensitive to the chemical modification resulting from the erbium introduction. The same behavior was observed in the work of Wu et al. [41] in the composition NBT–0.6Er without providing any explanation.

We have to note that we zoom in the domain range of $T_d$ and $T_1$ scale to observe their evolution. The room temperature $P$–$E$ hysteresis loops of Na$_{0.5}$[Bi$_{1-x}$Er$_x$]$_{0.5}$TiO$_3$ (xErNBT, with $x=0$, 0.0025, 0.005 and 0.01) solid solution are shown in Fig. 6. Due to the high coercive field of this material (pure NBT) and the conventional ceramic way used, it was difficult to obtain $P$–$E$ loops for all samples. The ceramic with composition $x=0.0075$ (0.0075ErNBT) breakdowns below the coercive field and our entire attempt to obtain the $P$–$E$ hysteresis loop for this composition are failed. All studied samples exhibit well shaped $P$–$E$ hysteresis loops. Pure NBT shows a well saturated $P$–$E$ hysteresis loop with similar polarization values to those reported in literature [9,12,77]. The incorporation of erbium on the NBT matrix leads to the following ferroelectric modifications: in the case of the composition $x=0.005$, we observe a consistent decrease in the polarization values which reach 28 μC cm$^{-2}$. This result confirms the introduction of Er$^{3+}$ ion into the B-site (Ti-site) in perovskite structure has already been observed in the XRD measurement. The introduction of Er$^{3+}$ into Ti$^{3+}$ site leads to the creation of some oxygen vacancies which are the main

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**Fig. 5.** Evolution of the dielectric constant versus temperature for Na$_{0.5}$[Bi$_{1-x}$Er$_x$]$_{0.5}$TiO$_3$ ceramics at 100 kHz.

**Fig. 6.** Room temperature ferroelectric hysteresis loops of Na$_{0.5}$[Bi$_{1-x}$Er$_x$]$_{0.5}$TiO$_3$ ceramics.
cause of domain walls clamping responsible of the observed decrease in the polarization value [41]. On the other hand, Luo et al. [43] attributed this result to the decrease of TiO$_6$ octahedral number per unit volume.

In the case of $x=0.0025$ and 0.01, we can observe a decrease in the coercive field which leads to a better saturated $P-E$ loop shape as observed in Fig. 6. However, no significant decrease in the remnant polarization can be detected as the case of 0.005ErNBT sample. This result confirms the introduction of Er$^{3+}$ ions in the Bi-site for the two last mentioned compositions. Table 1 summarizes the evolution of the electrical properties versus compositions.

Our observations in the electrical investigations lead us to say that the introduction site of erbium into the NBT matrix has directly affected the properties of this material despite the low amount used.

### Table 1

<table>
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<th>Composition (x)</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>$T_d$ (K)</th>
<th>$T_c$ (K)</th>
<th>$T_m$ (K)</th>
<th>$P_r$ (µC cm$^{-2}$)</th>
<th>$E_c$ (kV cm$^{-1}$)</th>
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<td>615</td>
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<td>65</td>
</tr>
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<td>500</td>
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<td>633</td>
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<tr>
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<td>510</td>
<td>580</td>
<td>635</td>
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</table>

### 4. Conclusion

In summary the present paper shows that Na$_{0.5}$[Bi$_{1-x}$Er$_x$]$_{0.5}$TiO$_3$ (x=0, 0.0025, 0.005, 0.0075 and 0.01) solid solutions prepared by the conventional solid-state reaction method may present an interesting multifunctional ceramic material that combines ferroelectricity and optical activity. We have shown that due to the erbium amphoteric behavior we cannot control the emplacement of this ion (Er$^{3+}$ ion) with exactitude. We have also shown that all properties of the mentioned solid solution are related to the site substitutions. When Er$^{3+}$ ion is in Bi-site, the optical and ferroelectric properties are enhanced. However, when Er$^{3+}$ ion takes Ti-site, we noticed a decrease in the mentioned properties. Finally, the $x=0.01$ composition exhibits highest ferroelectric polarization with an almost square hysteresis loop along with highest photoluminescence emission in the green and near IR regions.

### References


[12] K. Sakata, Y. Masuda, Ferroelectric and antiferroelectric properties of (Na$_{0.5}$Bi$_{0.5}$)$_{0.5}$TiO$_3$–SrTiO$_3$ solid solution ceramics, Ferroelectrics 7 (1974) 347–349.


[20] A. Sasaki, T. Chiba, Y. Mamiya, E. Otsuki, Dielectric and piezoelectric properties of (Bi$_{0.5}$Na$_{0.5}$)$_3$TiO$_5$(Bi$_{0.5}$K$_{0.5}$)$_3$TiO$_5$ systems, Jpn. J. Appl. Phys. 38 (1999) 5564–5567.


[23] W.-C. Lee, H.H.U. Huang, L. Kuo-Tsao, Y.-C. Wu, Chemical composition and tolerance factor at the morphotropic phase boundary in
(Bi0.5Na0.5)TiO3-based piezoelectric ceramics, J. Eur. Ceram. Soc. 29 (2009) 1443–1448.

[24] S. Said, J.P. Mercurio, Relaxor behaviour of low lead and lead free ferroelectric ceramics of Na0.6Bi0.4TiO3–PoTiO3 and Na0.6Bi0.4TiO3–K0.5Bi0.5TiO3 systems, J. Eur. Ceram. Soc. 21 (2001) 1333–1336.


[71] M. Otoničar, S.D. Škapin, M. Spreitzer, D. Suvorov, Compositional range and electrical properties of the morphotropic phase boundary in the Na_{0.5}Bi_{0.5}TiO_3–K_{0.5}Bi_{0.5}TiO_3 system, J. Eur. Ceram. Soc. 30 (2010) 971–979.


[73] J. Suchanicz, Behavior of Na_{0.5}Bi_{0.5}TiO_3 ceramics in the A.C. electric field, Ferroelectrics 209 (1998) 561–568.


[76] Peng Fu, Zhijun Xu, Huimin Zhang, Ruqing Chu, Wei Li, Meiju Zhao, Structure and electrical properties of Er_2O_3 doped 0.82Bi_{0.5}Na_{0.5}TiO_3−0.18Bi_{0.5}K_{0.5}TiO_3 lead-free piezoelectric ceramics, Mater. Des. 40 (2012) 373–377.