Effect of doping by Bi and Ca on ferroelectric properties and relaxor character in the (Ba$_{1-x}$Ca$_x$)$_{1-3y/2}$Bi$_y$TiO$_3$ solid solution

H. Zaghouene$^a$, F. Bahri$^a$, M. Boujelbene$^b$, H. Khemakhem$^a$, A. Simon$^c$

$^a$ Laboratoire des Matériaux Ferroélectriques (LMF), Unité de Physique-Mathématiques 05UR15-04, Université de Sfax, Faculté des Sciences de Sfax (FSS), Route de Soukra km 3.5, B.P. 1171, 3000 Sfax, Tunisie

$^b$ Laboratoire de l'Etat Solide, Faculté des Sciences de Sfax, P.B. 1171, 3000 Sfax, Tunisie

$^c$ Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), CNRS, Université de Bordeaux, 87 Avenue du Dr. A. Schweitzer, Pessac F-33608, France

Abstract

The temperature dependence of the real and imaginary parts of dielectric permittivity for (Ba$_{1-x}$Ca$_x$)$_{1-3y/2}$Bi$_y$TiO$_3$ solid solution prepared using the solid-state reaction technique, suggests that the relaxor character in this solid solution depends strongly on the Bi than on the Ca doping percent.

Keywords:
- A. Ceramics
- B. Oxides
- C. X-ray diffraction
- D. Dielectric properties

1. Introduction

The materials with a perovskite structure have been found to be very useful and interesting for different solid-state solutions [1,2]. Much attention has been given to investigate on materials of perovskite structures with disordered anion. This type of structures can present an important disorder which favors the relaxor character. This type of materials was characterized by its broad dielectric transition and a diffuse phase transition accompanied by a strong frequency dispersion at low temperature. Such behavior was observed, especially in lead-containing complex-compounds as Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_5$. This type of behavior was observed in systems in which a perovskite lattice is substituted by other ions, lead to a diffuse transition (DPT). This type of behavior was observed in systems with B substitution than that with A substitution [9–11]. The origin of relaxor character was widely discussed in many works [7,12,13]. In the present work, we study the origin of relaxor character and its relation with the presence of bismuth and/or calcium anions in the solid solution (Ba$_{1-x}$Ca$_x$)TiO$_3$.

2. Experimental procedure

(Ba$_{1-x}$Ca$_x$)$_{1-3y/2}$Bi$_y$TiO$_3$ ceramics were prepared by a conventional solid state reaction. Powders of BaCO$_3$, CaCO$_3$, Bi$_2$O$_3$ and TiO$_2$ of high purity 99.99% were taken in stoichiometric ratio and have been mixed in an agate mortar for 1 h. The mixture was pressed into pellets and calcined at 850°C in air for 12 h. After calcination, powder has been mixed for 1 h and pressed under 100 MPa into 8 mm diameter and about 1 mm in thickness. Finally, the pressed pellet was sintered in air atmosphere at 1250°C for 2 h followed by furnace cooling. Room temperature powder X-ray diffraction (XRD) was performed on a Philips diffractometer using Cu-K$_\alpha$ radiation ($\lambda=1.5418$ Å) in the angle range 5° ≤ 2θ ≤ 120° with 700 s counting time for each step of 0.02° in order to determine the structure for all prepared ceramic compositions. Dielectric measurements were performed on ceramic disks after deposition of gold electrodes on the circular faces by dc sputtering. The real and imaginary parts of permittivity $\varepsilon'$ and $\varepsilon''$, were measured under helium as a function of both temperature (85–500 K) and frequency (5 × 10$^2$–2 × 10$^5$ Hz) using a Wayne-Kerr 6425 component analyzer.
3. X-ray study

Figs. 1 and 2, show the X-ray diffraction pattern of the (Ba$_{1-x}$Ca$_x$)$_{1-y}$Bi$_y$TiO$_3$ samples taken at room temperature for the classic ($x=0.05; y=0.1$) compositions and the relaxor ($x=0.1; y=0.1$) compositions. In addition to the peaks which characterize the (Ba$_{1-x}$Ca$_x$)$_{1-y}$Bi$_y$TiO$_3$ phase; we note the presence of additional new peaks in XRD pattern which characterize the parasitic phases with minor percents. Good agreement between the observed and calculated interplaner spacing suggests that these compositions having tetragonal structure at room temperature, with a space group P4/mmm and $\alpha=\beta=\gamma=90^\circ$. The lattice parameters for the two compositions classic and relaxor one respectively are: $a=b=4.000(5)\,\text{Å}, c=3.988(4)\,\text{Å}$ and $a=b=3.992(3)\,\text{Å}, c=3.984(2)\,\text{Å}$.

4. Dielectric study

4.1. Effect of Bi doping

Figs. 3 and 4, show the variation of the real and imaginary parts of dielectric permittivity as a function of temperature for the ceramic compositions $x=0.05$ (5% Ca) as example with $y=0.1$ (classical ferroelectric) and $y=0.15$ (relaxor).
From the evolution of dielectric permittivity, we remark that $\varepsilon_0 r_{max}$ decreases remarkably with increasing $y$ (Bi percent) (Fig. 5).

The variation of ($T_{max}$) and ($\Delta T_{max}$) versus Bi-composition is given in Fig. 6. We note a decreasing of $T_{max}$ and an increasing of $\Delta T_{max}$ when the Bi percent increases. From this behavior, we can deduce that the introduction of Bi in this solid solution favors the relaxor character near room temperature: $\Delta T_{max}$ is maximum for $y = 0.2$ for which $T_{max} = 312$ K.

4.2. Effect of Ca doping

Figs. 7 and 8, show the variation of dielectric permittivity with temperature for (Ba$_{0.95}$Ca$_{0.05}$)$_{1-y/2}$Bi$_y$TiO$_3$ with $y = 0.1$ in the classic ($x=0.3$) and the relaxor ($x=0.1$) compositions.

$\varepsilon_0 r_{max}$ decreases generally with increasing $x$ (Fig. 9). The variation of ($T_{max}$) and ($\Delta T_{max}$) versus Ca-composition ($x$) is given in Fig. 10. We note that $T_{max}$ decreases, presents a minimum at $x=0.1$, then increases, presents a maximum at $x=0.2$ and decreases again to presents a minimum at $x=0.3$ then increases again. However, for $\Delta T_{max}$ it increases from $x=0.05$ to $x=0.1$, on which it presents a maximum, then decreases and presents a stable value for $x$ in the range of $0.2 \leq x \leq 0.4$.

From this behavior, we can deduce that

- The introduction of Ca in this solid solution does not favor the relaxor character as the case of Bi.

5. Discussion

If we consider the first variation of dielectric properties as a function of Bi percent, we can deduce a strong frequency
If we consider the second direction of variation as a function of the Ca percent, we can deduce that in spite of, we introduce this element in the same site as the Bi but it does not have the same effect. In fact, for the compositions with y=0.1 and x=0.1 or 0.3, we remark that the introduction of Ca weakened the relaxor degree and the solid solution becomes classic. From this analysis we can attribute the presence of relaxor character in this solid solution essentially to the nature of substituent element, such as Bi which is an element having a special character that favors the shift from micro-polar region representation to a nano-polar region one, and not to the heterogeneity introduced by any substitution.

Materials of relaxor ferroelectric type are generally subject to the Vogel–Fulcher relation [18,19] which has the form $f = f_0 \exp\left[\frac{-E_\alpha}{k_B T_m}\right]$, where $f$, $E_\alpha$, $k_B$, $T_m$ and $f_0$ are the applied frequency, the activation energy, the Boltzmann constant, the freezing temperature of the dipoles and the Debye frequency, respectively. In our case, the compositions ($x=0.05$; $y=0.15$) and ($x=0.1$; $y=0.1$) are also subject to this relation. In Fig. 11, we present the variation of ln($f$) as a function of $1/T_m$ for the two compositions. The fitting parameters of Vogel–Fulcher relation were ($E_\alpha=0.164$ eV, $T_f=180.207$ K and $f_0=24.53 \times 10^{10}$ Hz) and ($E_\alpha=0.008$ eV, $T_f=288.535$ K and $f_0=29.284 \times 10^3$ Hz), respectively.

From these data, we remark that in spite of the activation energy in the case of the more relaxor composition ($x=0.05$; $y=0.15$) is higher than that of the low relaxor one ($x=0.1$; $y=0.1$) which indicate that potential barrier between two potential wells is higher in the first case, the freezing temperature is lower for the more relaxor composition. This state shows that dipoles become free at lower temperatures for the more relaxor composition.

Previous studies on the dielectric properties of Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics have shown that the compositions with $x < 0.8$ exhibit classic ferroelectric behavior [20,21]. However, the relaxor character was observed in Bi doped Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics for $x < 0.8$ [17]. It was suggested that Bi ions were located at the off center positions of A-site. In Bi doped SrTiO$_3$ [16] and Bi doped Ba$_{1-x}$Sr$_x$TiO$_3$ [17], A-site vacancies appear to compensate the charge due to the introduction of Bi$^{3+}$ in A-sites which caused the displacement of charge center. This displacement of charge centers form dipoles and thus set up local electric fields, which suppress the ferroelectricity in material and result the presence of relaxor behavior. This character increases with Bi doping percent [16,17].

dispersion which increases with Bi percent. The relaxor degree characterized by $\Delta T_m = T_{\text{max}(200 \text{ kHz})} - T_{\text{max}(5 \text{ kHz})}$ increases with increasing y. These results indicate that the presence of Bi in the lattice has an important effect on the relaxor character, so it favors this character. This deduction is in agreement with early reports which introduce Bi in other solid solutions [14–17].
According to the above suggestions, the Bi$^{3+}$ ions substitutions for Ca$^{2+}$ in Ba$_{1-x}$Ca$_x$TiO$_3$ can also be located at off-center positions and A-site vacancies may also appear to compensate the charge imbalance by Bi substitution. An electric field appears to be responsible of suppressing the ferroelectricity in Bi doped Ba$_{1-x}$Ca$_x$TiO$_3$ solid solution. This behavior is due to the fact that, the ionic radius of Bi$^{3+}$ is smaller than the ionic radius of Ba$^{2+}$ and Ca$^{2+}$. So the values of polarizabilities of Ca$^{2+}$ ($3.16 \times 10^{-24}$ cm$^3$), Ba$^{2+}$ ($6.40 \times 10^{-24}$ cm$^3$) and Bi$^{3+}$ ($6.12 \times 10^{-24}$ cm$^3$) [22] indicate that Bi$^{3+}$ is between those of Ca$^{2+}$ and Ba$^{2+}$. This is in agreement with that, suggested before: the substituting ions with smaller ionic radius and greater polarization forces will favor off-center location. This interpretation can give an explanation of the effect described above, that the Bi ion is the responsible of relaxor character in the system (Ba$_{1-x}$Ca$_x$)$_{1-y/2}$Bi$_{y/2}$TiO$_3$ and not Ca.

6. Conclusion

The dielectric properties of (Ba$_{1-x}$Ca$_x$)$_{1-y/2}$Bi$_{y/2}$TiO$_3$ ceramics were investigated. The maximal dielectric permittivity $\varepsilon_{r_{\text{max}}}$ remarkably decreases with increasing of $x$ and $y$. A typical relaxor behavior, similar to lead-based relaxor ferroelectrics, is observed for some selected compositions.

If we consider the two directions of variation as a function of Ca and Bi percents, we can deduce that in spite of, we introduce the Ca element in the same site as the Bi one, it does not have the same effect. In fact, for some compositions, we remark that the introduction of Ca can weaken the relaxor degree not as in the case of Bi which always increases the relaxor character. From this analysis we can attribute the presence of relaxor character in this solid solution essentially to the nature of substituent element, such as Bi which is an element having a special character that favors the shift from micro-polar region representation to a nano-polar region one, and not to the heterogeneity introduced by any substitution.

We can conclude that the substituting ions with smaller ionic radius and greater polarization forces than the lattice ions will favor the off-center location, and Bi$^{3+}$ ions are in such case. This can give an explanation of the effect described above, that relaxor behavior is more important in compositions with increasing of Bi substitution percent than that with Ca substitution percent.

References