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X-ray and dielectric studies of ferroelectric phase in the $Ba_{1-x}(Yb_{0.5}Na_{0.5})_x TiO_3$ system for low doping level

L. Khemakhem[1,2*], I. Kriaa[2], M. Derbel[2], N. Abdelmoula[2]

[1]*Laboratoire des Sciences des Matériaux et Environnement, Faculté des Sciences de Sfax, B.P. 802, 3018 Sfax, Tunisie.*
[2]*Laboratoire des Matériaux Ferroélectriques, Faculté des Sciences de Sfax B.P. 802, 3018 Sfax, Tunisie.*

Abstract

Ceramics of solid solution $Ba_{1-x}(Yb_{0.5}Na_{0.5})_xTiO_3$ were sintered in the temperature range 1220-1400°C. Dielectric properties of ceramics belonging to the whole composition domain were investigated in a broad range of temperatures (75-450 K) and frequencies (0.1-100 kHz). These ceramics were prepared using the conventional mixed-oxide technique. The temperature dependence of the dielectric constant of these ceramics were investigated. The rombohedral–orthorhombic and orthorhombic-quadratic perovskite transitions are characterized by two weak peaks but the tetragonal-cubic or ferroelectric-paraelectric one is characterized by a pronounced peak with weak frequency dispersion. Excellent dielectric properties have been obtained. The single phase of these prepared ceramics was characterizedby X-ray diffraction.

Keywords: Perovskite; Lead-free ceramics; Dielectric; Ferroelectric; Relaxor.
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1. Introduction

According to their behavior, the ferroelectric materials with perovskite-like structure may be divided into different classes depending on whether they are classical or relaxor ferroelectris [1]. Relaxor materials are characterized mainly by frequency dispersion and broad peaks in the dielectric susceptibility versus temperature [2]. Many investigations have been devoted to the study of the relaxation parameters in order to achieve their use in satisfactory capacitors and actuators [3]. The relaxor behavior was mainly obtained in lead-based ceramics for examples $PbMg_{1/3}Nb_{2/3}O_3$ and derived compounds [4, 5]. However, these materials have a drawback due to the volatility and the toxicity of PbO. Up to now, current research is oriented to environment friendly applications using lead-free materials [6–8]. Ceramics based on barium titanate ($BaTiO_3$) are frequently used to manufacture multilayer ceramic capacitor and thermistors owing to their high dielectric constant [9]. Barium titanate ($BaTiO_3$) is the most common ferroelectric oxide in the perovskite ABO_3 structure [10]. In $BaTiO_3$ a phase transition occurs from rhombohedra (C3v) to cubic (Oh) through orthorhombic (C2v) and tetragonal (C4v) as temperature increases to about 400 K.

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[*]) For Correspondence, E-mail: khemakhemimmea2009@yahoo.fr

Each transition is a first-order transition [11]. Homovalent or heterovalent substitutions of barium or titanium ions were shown to give rise to various behaviours and properties [12–17]. In addition, the aim for application was to prepare lead-free ceramics with such properties close to room temperature. In fact, up to now, lead-free relaxor presented value of Tm often widely lower than room temperature [18]. The present report is aimed as designing and characterizing new lead-free ferroelectric derived from $BaTiO_3$. We investigate the system $Ba_{1-x}(Yb_{0.5}Na_{0.5})_xTiO_3$.The temperature and frequency dielectric response of the lead free ceramics sample were correlated with the unit cell symmetry and parameters obtained by X-ray powder diffraction In order to investigate the morphology and the grain size a MEB study was also carried out using JEOL JED2300.

2. Experimental

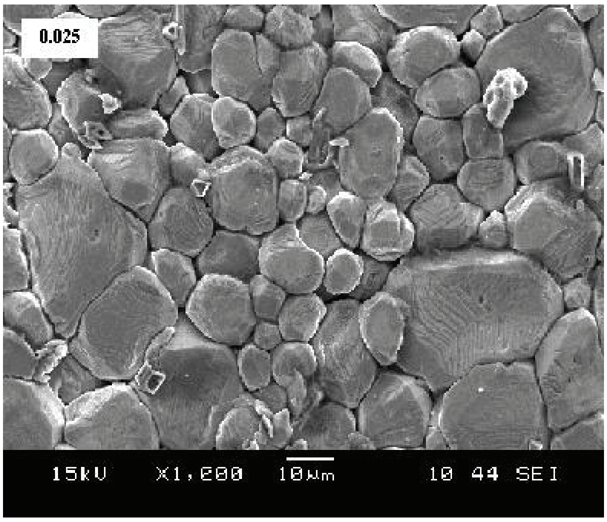
The polycrystalline ceramic sample was prepared by a conventional solid state synthesis technique. The starting materials were $BaCO_3$, TiO_2, Na_2CO_3, Yb_2O_3 (99.9% of purity). The mixture was ball milled in ethanol for 1h dried and then calcined in oxygen atmosphere at 1100°C for 15h. The obtained material was then ball milled and calcined again under same conditions. The calcined material was ball milled in water, oven dried and then pelletized as cylindrical samples which were finally sintered in oxygen atmosphere at 1350°C for 2 h. The experimental density was determined from the weight and geometrical dimensions of the cylindrical pellets and then compared to the theoretical density determined from X-ray measurements. The compactness value, C (defined as ratio between experimental density, d_{exp}, and theoretical density, d_{theor}) obtained for sintered ceramics was 0.92. A scanning microscope (SEM), JEOL JED2300, was used to characterize the microstructure.

XRD measurements were performed on the milled ceramic powder using CuKα radiation at room temperature. The scanning record was run at preset 2θ range from 10-110° with 0.02° step and 10 second counting time.

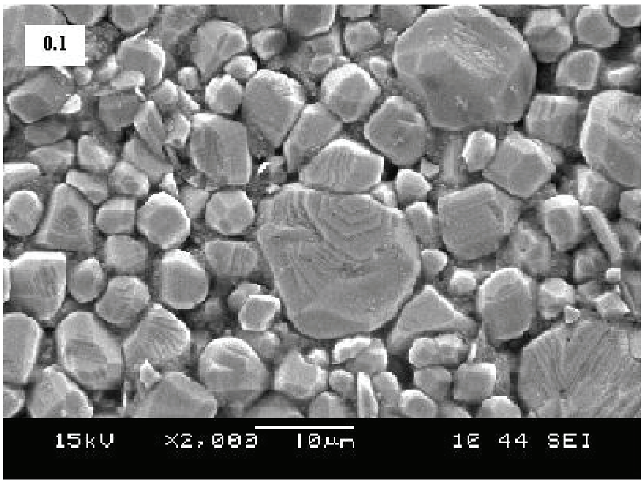
The dielectric measurements were made on polished ceramic discs with evaporated gold electrodes. The relative dielectric permittivities ε'_r and ε''_r were measured as parametric functions of frequency vs temperature in the range 75-450K at a rate of $2Kmin^{-1}$ and frequency from 0.1 to 200 kHz using a Wayne- Kerr 6425 component analyser.

3. Results and Discussion

3 (a) MEB observation



(a)



(b)

Fig. 1: SEM micrograph of the surface of ceramics $Ba_{1-x}(Yb_{0.5}Na_{0.5})_xTiO_3$

Figure 1(a and b), show the MEB observation for both ceramics compositions x = 0.025 and x = 0.075 respectively. The average grain size of the ceramic samples were about 10 µm for x = 0.025 and about 5 µm for x = 0.075 (Figure 1). These sizes which are relatively higher can be considered as optimal for important values of permittivity. We can deduce from these observations that defects are more important in the composition x = 0.075 that's way we consider only low doping percents.

3 (b) X-ray diffraction analysis

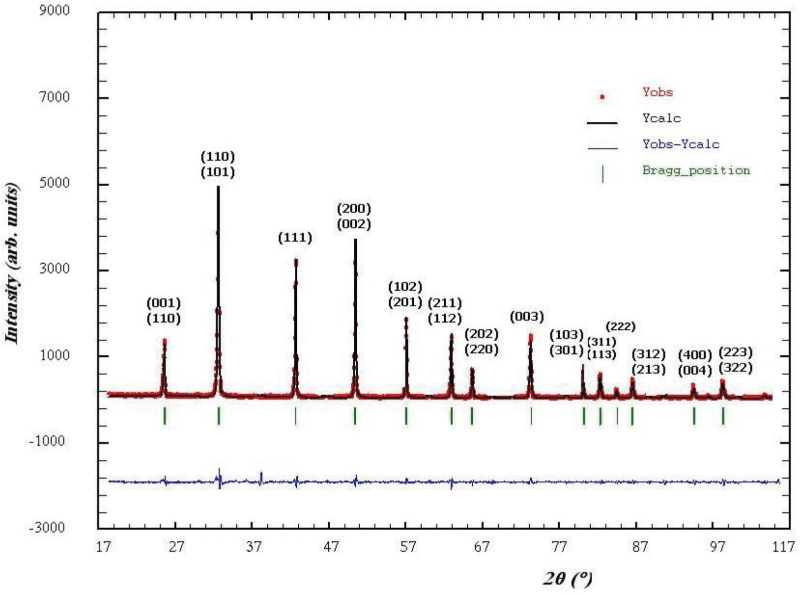


Fig. 2: X-ray diffraction pattern for $Ba_{0.9}(Yb_{0.5}Na_{0.5})_{0.1}TiO_3$ ceramic.

Figure 2 shows the X-ray diffraction pattern of some compositions of the $Ba_{1-x}(Yb_{0.5}Na_{0.5})_xTiO_3$ solid solution with x = 0.1 as example taken at room temperature which reveal that this ceramic is single phased. All the reflection peaks of the X-ray profile were indexed, and lattice parameters were determined using a global profile-maching method with the fullprof software [19].

Good agreement between the observed and calculated interplaner spacing suggests that the compound has a tetragonal structure at room temperature with a space group P4/mmm and a = 3.968(4) and c = 3.972(4) Å.

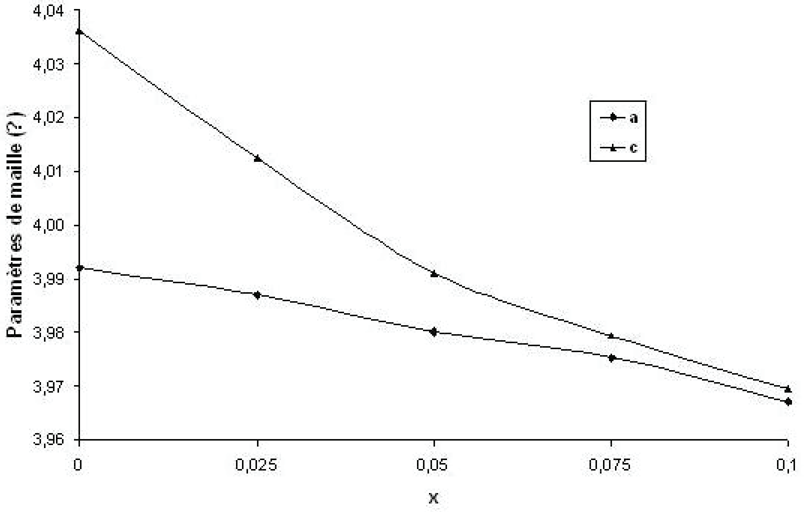


Fig. 3: The variations of the lattice parameters a function of x

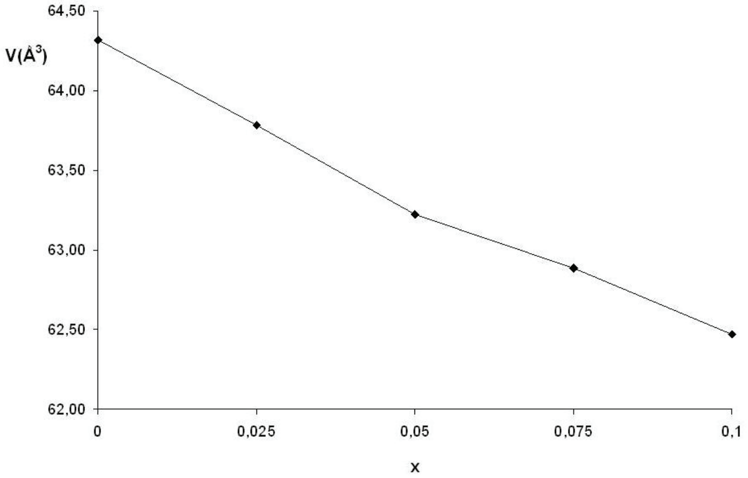


Fig. 4: The variations of cell volume a function of x

Figures 3-4, show the variations of the lattice parameters and cell volume respectively for x = 0.025 - 0.05 - 0.075 - 0.1 of the solid solution $Ba_{1-x}(Yb_{0.5}Na_{0.5})_xTiO_3$.

The regular decrease of the cell volume for rising x is in good agreement with the existence of a perovskite solid solution on the whole composition domain 0≤ x ≤0.1. This decrease should be related to the values of ionic radii : r(Yb^{3+} = 1.08 Å) and r(Na^+= 1.02 Å) quite lower than r(Ba^{2+}=1.42Å) .

3 (c) Dielectric studies

The evolution of the real (ε_r') part of the complex permittivity for the $Ba_{1-x}(Yb_{0.5}Na_{0.5})_xTiO_3$ the solid solution as a function of both temperature and frequency was determined. Two different dielectric behaviours were observed.

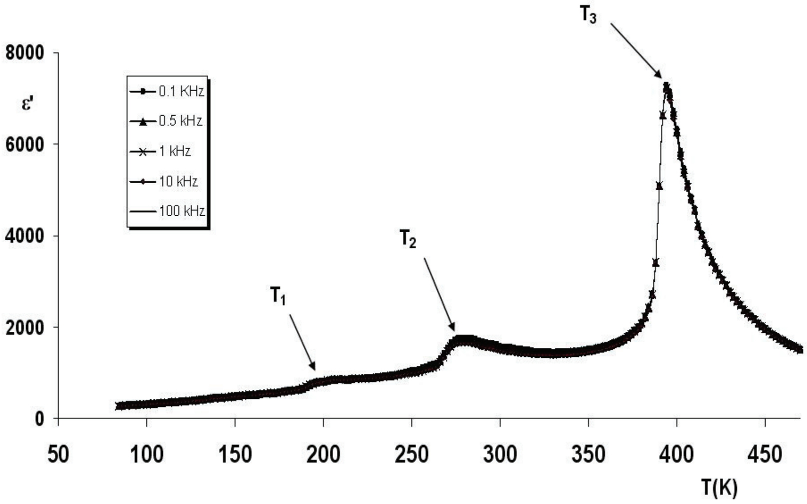


Fig . 5: Temperature dependence of the permittivity ε'_r for x = 0.025

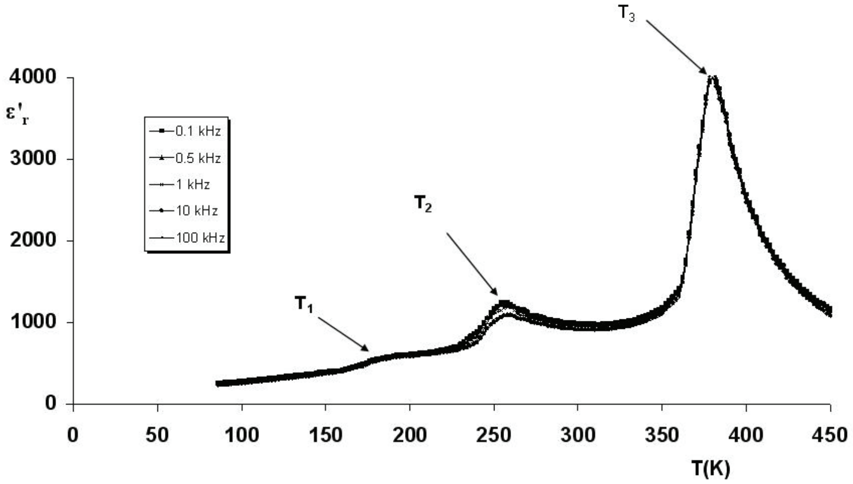


Fig. 6: Temperature dependence of the permittivity ε'r for x = 0.075

For composition in the region $0 \leq x \leq 0.075$, the samples are of normal ferroelectric behaviour. For example Figures 5 and 6, show the temperature dependence of the real ε'r part of the permittivity at several selected measured frequencies (100 - 10^5 Hz) for x = 0.025 and x = 0.075 samples. Three anomalies related to the phase transitions (rhombohedral - orthorhombic at T_2, orthorhombic-tetragonal at T_1 and tetragonal – cubic at T_C) for $BaTiO_3$ have been observed. From these figures, it is shown that the temperature of ferroelectric–paraelectric phase transition Tc is about 394K for x = 0.025 and 375K for x = 0.075. We noted from these results that the small substitution of barium by ytterbium and niobium in the A site of the general perovskite ABO_3 induce an important variation of the ferroelectric-paraelectric temperature. In the other hand, it is remarkable the absence of frequency dispersion above and below T_C, this behaviour is related to the absence of ionic and electronic conductivities in these compositions. It is remarquable that the maximum of permittivity decreases from 8000 for x = 0.025 to 4000 for x = 0.075. This result is in agreement with our interpretation from MEB measurements.

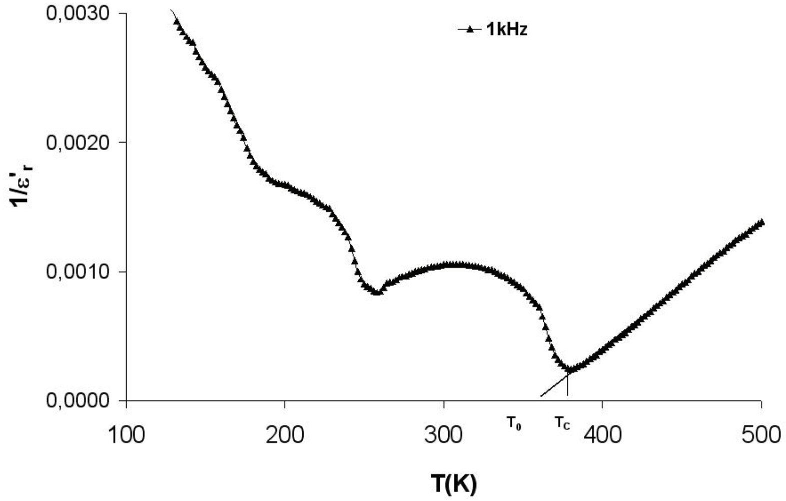


Fig. 7: The variation of 1/ε'r against temperature for x = 0.025

Figure 7, depicts the variation of $1/\varepsilon'_r$ against temperature at 10^3 Hz. The Curie-Weiss relation, $\varepsilon'_r = C/(T-T_0)$, holds at $T \geq 394$ K where C is the Curie constant. For classical ferroelectrics the order of the ferroelectric–paraelectric phase transition can be determined from the temperature dependence of $1/\varepsilon'_r$. When T_0 is less than T_c the phase transition is of the first order and when $T_C = T_0$ it is of second order type [20]. In our case Tc is equal to T0 which confirms the second order character of the ferroelectric-paraelectric phase transition. In the case of relaxor ferroelectric this hypothesis becomes invalid because of the diffuse character of this phase transition.

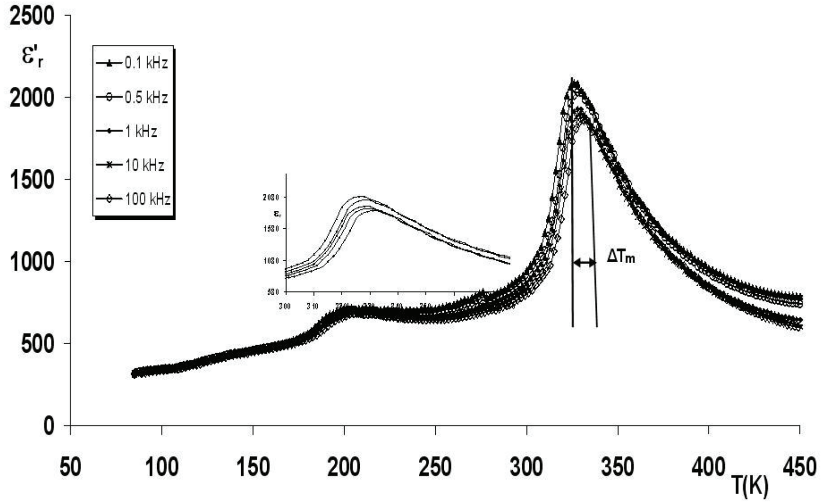


Fig. 8: Temperature dependence of the permittivity ε'_r for x = 0.1

For x = 0.1 (Figure 8), ε'_r presents an evolution in low temperature phase as a function of frequency which shows a relaxor behaviour but ΔT_m in this case is not very important, $\Delta T_m \approx 10$K and T_m is relatively higher ($T_m \approx 340$K). In spite of low value of ΔT_m this solid solution can be considered as promoter for relaxor applications.

The degree of disorder of the $Ba_{1-x}(Yb_{0.5}Na_{0.5})_xTiO_3$ ceramic samples was evaluated using an empirical formula developed by Uchino and Nomura [21]:

$$\frac{1}{\varepsilon'_r} - \frac{1}{\varepsilon'_{r\max}} = \frac{(T - T\varepsilon'_{r\max})^\gamma}{C'} \qquad (1)$$

Where C is a constant and γ is a measure of diffuseness; γ value is between 1 and 2. The parameter γ gives information on the character of the phase transition and only depending on the composition of the specimens. The limiting values $\gamma = 1$ and $\gamma = 2$ reduce the equation to Curie-Weiss law for the case of normal ferroelectric and for ideal relaxor ferroelectric respectively [22].

The logarithmic plots related to this equation for all doped compositions x =0.025 and 0.1 are shown in figures 9 and 10 respectively.

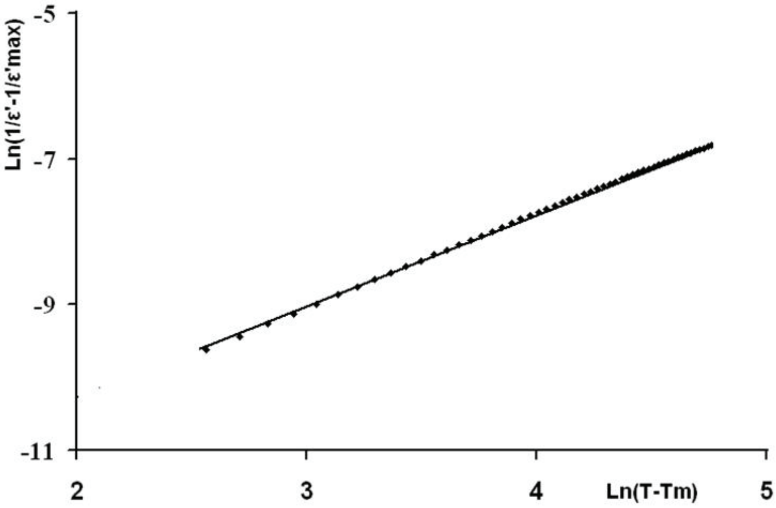


Fig. 9: Plot of *ln*(1/ε-1/ε_{max}) as a function *ln*(T-T_m) at 10 kHz for x = 0.025

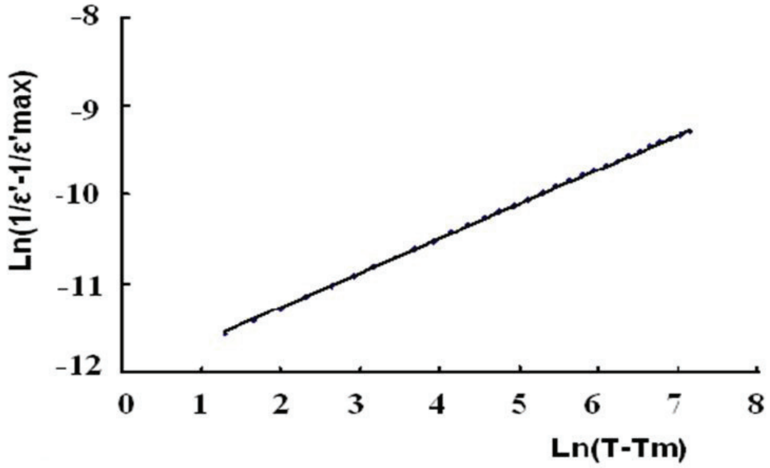


Fig. 10: Plot of *ln*(1/ε-1/ε_{max}) as a function *ln*(T-T_m) at 10 kHz for x = 0.1

The slope of the fitting is used to determine the value of γ at 10 kHz. These parameters are γ =1.126 and 1.975 respectively for x = 0.025 and x = 0.1. These results confirme the diffuse phase transition for compound with x = 0.1.

4. Conclusion

Ceramics of solid solution of $Ba_{1-x}(Yb_{0.5}Na_{0.5})_xTiO_3$ ($0 \le x \le 0.1$) have been synthesized and their structural and dielectric properties were investigated. From X-ray diffraction study, these compounds exist in a single phase at room temperature having a tetragonal structure for all studied compositions. Dielectric permittivity was measured in the temperature and frequency ranges 75 - 450 K and 100 Hz - 100 kHz respectively by changing x. It is remarkable that the maximum of permittivity at ferroelectric-paraelectric phase transition presents a fast decrease in its value in spite of the small percent of substitution. We noted that this evolution is linked to the decreasing of the average size of grains and increasing of the percent of defects with the increasing of the percent of substitution. The evolution from a classic ferroelectric to relaxor behaviour was observed with increasing x.

This study points out the preparation of lead-free relaxor ceramics, which promotes environmental protection.

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