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To cite this article: U Nuraini *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **496** 012043

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IOP Conf. Series: Materials Science and Engineering **496** (2019) 012043 doi:10.1088/1757-899X/496/1/012043

Characterization of relaxor ferroelectrics from $BiFeO_3$ doped $(K_{0.5}Na_{0.5})NbO_3$ systems

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Abstract. The additon of $BiFeO_3$ (BFO) to $(K_{0.5}Na_{0.5})NbO_3$ (KNN) systems and termed as (1-x)KNN-xBFO for x=0 and x=0.075 were successfully synthesised using a combination of solid-state reaction and auto-combustion methods. The single phase of KNN-BFO was formed by two step of heat threatments; it is calcined at 575 °C for 6h then sintered at 1100 °C for 6h. The phase structure of KNN material changes from the orthorombic symmetry to tetragonal symmetry after the addition of BFO. The relaxor ferroelectric properties were carried out using impedance analyzer at various temperature and frequency. The pure KNN shows a typical ferroelecrics that has two Curie temperature at 220 °C (orthorombic-tetragonal transition) and 440 °C (tetragonal-cubic transition). After the 7.5%mol.BFO doped in the KNN system, the maxima peak around Tc becomes broader and its transition temperature becomes invisible then has a relaxor behaviours. The Currie-Weiss law is used to prove the ferroelectric of KNN ($\gamma \leq 1$) and relaxor of KNN-BFO ($\gamma \geq 1$).

Keywords: KNN-BFO, relaxor, ferroelectric,

1. Introduction

$(K_{0.5}Na_{0.5})NbO_3$ (KNN) is one of the best candidates capable of replacing the role of $Pb(Zr,Ti)O_3$ (PZT) as a ferroelectric material. KNN has a good relative permittivity value, high Curie temperature, and environmental friendliness [1]. Zhou *et al.* [2] stated that pure KNN has an orthorhombic structure at room temperature and turn into a tetragonal symmetry structure at 200 °C then becomes a cubic symmetry structure at 400 °C. While Kumar *et al.* [3] revealed that this material can produce a dielectric constant of 648 at room temperature and the critical temperature of 372 °C. The transition of the phase structure in the material is marked by the change in the value of the dielectric constant at a certain temperature [4]. Pure KNN ceramics behave a good ferroelectric with Pr ~20 $\mu C/cm^2$ besides piezo ceramics with $d_{33} \approx 90$ pC/N [5].

Dopant that substituted into the KNN structure will affect the performance of the material either from its electrical value or piezoelectric constant. Agustinawati *et al.* [6] revealed that Li^{2+} ions that substitute on KNN system shifts the critical temperature from 440 °C to 510 °C. While Du *et al.* [7] reported that the 10% mol $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) doped KNN indicates the dielectric loss value less than 4% (which is relatively low) for the temperature region of 100-250 °C and a broader dielectric peak with maximum permittivity close to 2500. The result also ensures that doped BST will modify KNN's dielectric properties from a normal ferroelectric to become a relaxor typical after x>0.05. $BiFeO_3$ (BFO) recently have attracted much attention for its high Neel temperature T_N of 643 K and its high Curie temperature T_c of 1103 K [8]. The amount of BFO doped into KNN structure is expected to provide better dielectric performance. In this study, addition of BFO with variation x=0.075 was used to substitute KNN materials. The influence of BFO on phase structure and electrical properties of KNN ceramics was investigated.

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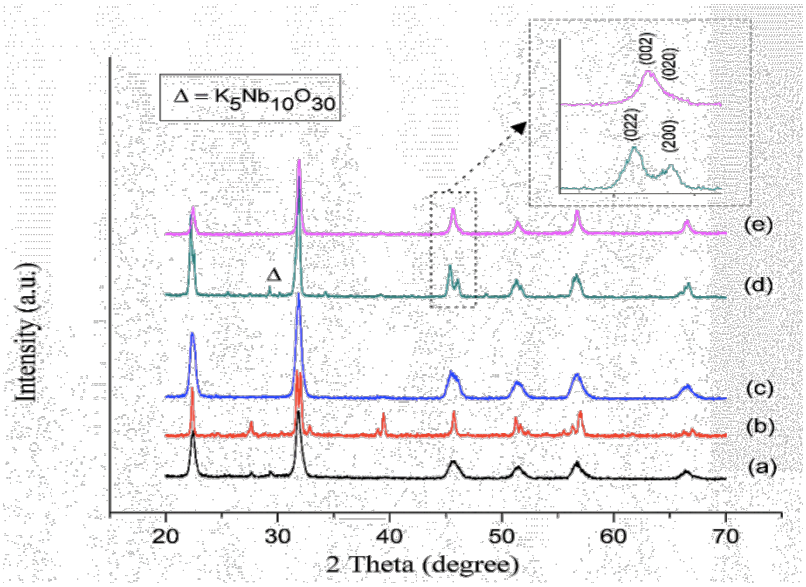


Figure 1. XRD spectra of samples calcined *ff*powders: (a) KNN, (b) BFO, (c) 0.925KNN-0.075BFO, and sintered pellet of (d) KNN, (e) 0.925KNN–0.075BFO

2. Methods

(1-x) $K_{0.5}Na_{0.5}NbO_3$ – $xBiFeO_3$ (KNN-BFO) materials (with variation x = 0 and 0.075) were prepared through two-step powder synthesis method. The first step was separately synthesized $K_{0.5}Na_{0.5}NbO_3$ (KNN) and $BiFeO_3$ (BFO) powders. The KNN powder was synthesized being similar from our work [9] while BFO powders was prepared by auto-combustion method by using $Bi(NO_3)_3.5H_2O$, $Fe(NO_3)_3.9H_2O$, and $C_6H_8O_7$ as raw materials [10]. The second step was mixed KNN and BFO powders in ethanol media and ball milled for 6 hours then evaporated to remove the alcohol content in the samples. After calcined at 575 °C for 6 hours, the mixture is placed a 13 mm diameter of disk then pressed at 55 MPa and sintered in air at 1100 °C for 6 hours.

X-Ray diffraction (XRD) characterization with monochromatic Cu Kα radiation (X'Pert Diffractometer, Philips) was used to determine the crystal structure of the samples. Then the phases exist in the samples were analysed using Match II software. The further analysis of structure was exploited using Rietvel's refinement method of Rietica software [11]. SI 1260 Impedance/Gain-Phase Analyzer (0.1 Hz-32 MHz) is used in electrical characterization as a function of temperature from room temperature to 500 °C). Silver paste was printed as electrodes on the pellet sample that has been sintered then it fired at 925 °C for 20 min. The relative permittivity that measured at 1.27 kHz, 12.7 kHz, and 127 kHz as function of temperature was used to obtain the dielectric properties from the samples. While, the characterization of relaxor was determined by using the modified of Curie-Weiss law.

3. Results and discussion

X-Ray Diffraction of sintered samples of (1-x) $K_{0.5}Na_{0.5}NbO_3$ -$xBiFeO_3$ (KNN-BFO) (with x = 0 and 0.075) in the range of 2θ (from 20° to 70°) is showed in figure 1. Similar with previous study [9], the minor phase which identified as $K_5Nb_{10}O_{30}$ was exist because alkali metals such as Na and K can volatile during the sintering process [12,13]. All ceramics poses typical perovskite (ABO_3) spectra while the peak intensity varies depending on the x value. At x=0, the XRD pattern shows orthorhombic symmetry at room temperature which can be evidenced by the (022/200) splitting of the diffraction peaks around $2\theta \approx 45°$, as reported Zhou *et al.* [2]. When x=0.075, the split difraction peaks seem to merge into a single peak (002/020), indicating that the crystal structure was succesfully modified after BFO doped. The change of peak diffraction is explained by Xu *et al.* [14] as the success of BFO diffusion process to substitute KNN lattice. For complete this suggestion, the quantitative

Table 1. Lattice parameter of (1-x)KNN-xBFO analysed by Rietveld refinement using Rietica software

Material	Lattice Parameter (Å)			Crystal Structure
	a	b	c	
KNN	3.95523 ± 0.00148	5.63766 ± 0.00226	5.67845 ± 0.00215	Orthorhombic
0.925KNN-0.075BFO	3.97813 ± 0.00048	3.97813 ± 0.00048	3.99989 ± 0.00047	Tetragonal

Table 2. Density of KNN and KNN-BFO by Archimedes method.

No.	Sample	Density		
		Archimedes (g/cm^3)	Theoretic (g/cm^3)	Relative (%)
1	KNN	3,78	4,48	84,37
2	0.925KNN-0.075BFO	4,19	4,75	87.31

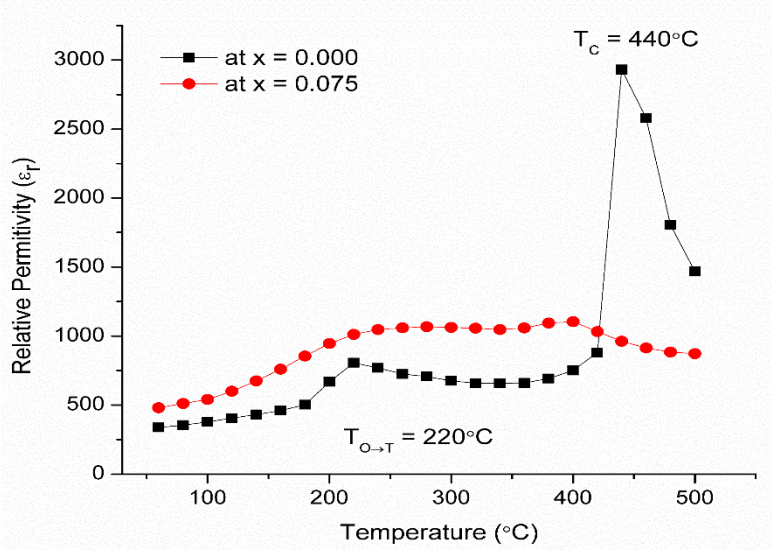


Figure 2. Temperature dependence of the relative permittivity for (1-x)KNNxBFO ceramics with x = 0 and 0.075 at 127 kHz

analysis is done by Rietveld's Refinement method using Rietica software. The result of refinement from all samples is described in table 1. It is presented that orthorhombic symmetry crystal structure is the initial structure of KNN. With the addition of BFO, its crystal structure begins to transform into a tetragonal symmetry (a=b≠c). The existance of minor phase ($K_3Nb_{10}O_{30}$) that appears in KNN caused the highest reliability factor, similar from our previous work [9]. The difference in the radius of the dopant and the main atom (Fe^{3+} on Nb^{5+} sites and Bi^{3+} on K^+/Na^+ sites) results in a rearrangement of the lattice where the a-axis becomes extended while c-axis will shrink. The radius of the Bi^{3+} (103 pm) ion is about the Na^+ (102 pm) and not far from the K^+ (138 pm) ions radii, while the radius of the Fe^{3+} (64.5 pm) ion is just about the Nb^{5+} (64 pm) ion radius, therefore it would be reasonable to speculate that both ions (Bi^{3+} and Fe^{3+}) could be easily substituted into KNN lattice, on site A and site B. The density of pellet samples is measured using Archimedes method and its result is written in table 2. BFO doped increase the density of KNN so it can be mean that BFO doped made the shrinkage process more optimal than pure KNN. The shrinkage process will influence the dielectric properties of materials.

Figure 2 presents the relative permittivity (ε_r) of (1-x) KNN- x BFO samples as a function of temperature measured at 127 kHz during heating process. When x=0, the material shows two-phase transition temperature, at 220 °C associated with the tetragonal-cubic (T_c) transition and the orthorhombic-tetragonal transition (T_{o-t}) at 440 °C. It is also have reported in previous study [9] which

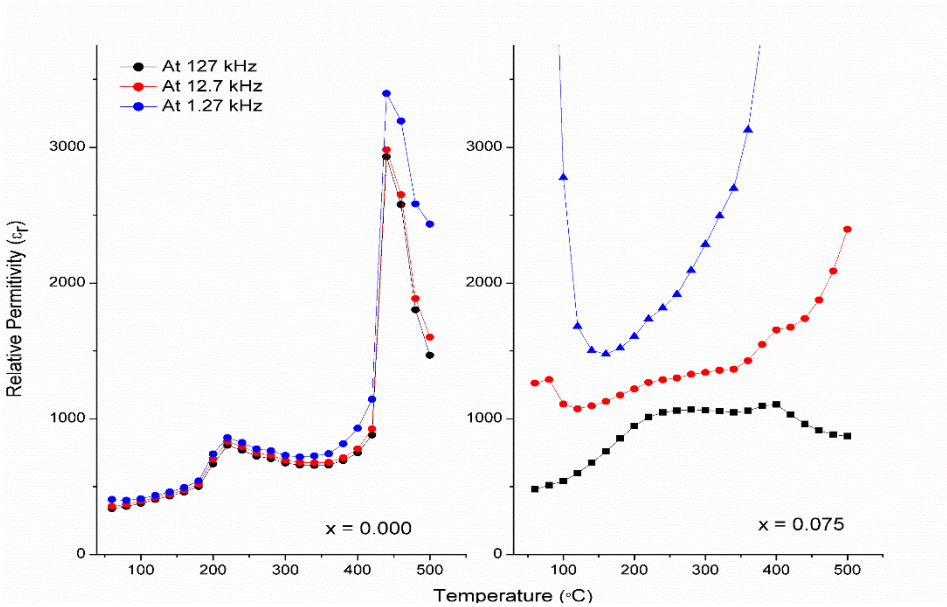


Figure 3. Temperature dependence of the relative permitivity for (1-x)KNN – xBFO ceramics with x 0 and 0.075 measured at different frequencies

corresponds to the result of Ahtee and Glazer project [4]. When x=0.075 mol.% BFO, no peaks that indicate the temperature of (T_{o-t}) or tetragonal-cubic (T_c) transition can be observed evidently. Xu *et al.* [14] has stated about the boundary between tetragonal phase and orthorhombic which called as MPB (morphotropic phase boundary). It appears when 0.01 mol.% BFO added into KNN. Moreover, a MPB also can be expected in the system through transition point for the structure (by diffraction pattern) when the split (022/200) peaks from an orthorhombic symmetry are gradually merged into a single peak [15].

The relative permittivity for (1-x)KNN-xBFO samples measured at different frequencies as a function of temperature is shown in figure 3. Increasing frequencies doesn't change the phase transition temperature for pure KNN, besides the fact that pure KNN ceramics are known to have two phase transition temperature, both orthorhombic-tetragonal and tetragonal to cubic [16]. These results indicate that pure KNN act as a normal ferroelectric which does not affected by frequencies changes. When x=0.075 the T_c point changed for those frequencies and at 1.27 and 12.7 kHz there are "tail curve" for high temperature. Our previous work [17] explained that there are two possible explanation; the existence of multiple ferroelectric structure and effect of defect dipoles. In this case, the defect dipole that created when BFO doped KNN should be:

On A sites,

$$Bi_2O_3 \xrightarrow{KNN} 2Bi_{K/Na}^{\bullet\bullet} + 4e' + O_O^X$$

On B sites,

$$Fe_2O_3 \xrightarrow{KNN} 2Fe_{Nb}'' + 2V_O^{\bullet\bullet} + O_O^X$$

The defect dipole creates an imbalance and produces local electric field in the KNN-BFO structure. Local electric fields and elastic fields will induce relaxor behaviour with the emerging of polar nanoregions (PNRs) [7].

The characteristic of ferroelectric-relaxor behavior can be proved with obey a modified Curie-Weiss law,

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C}$$

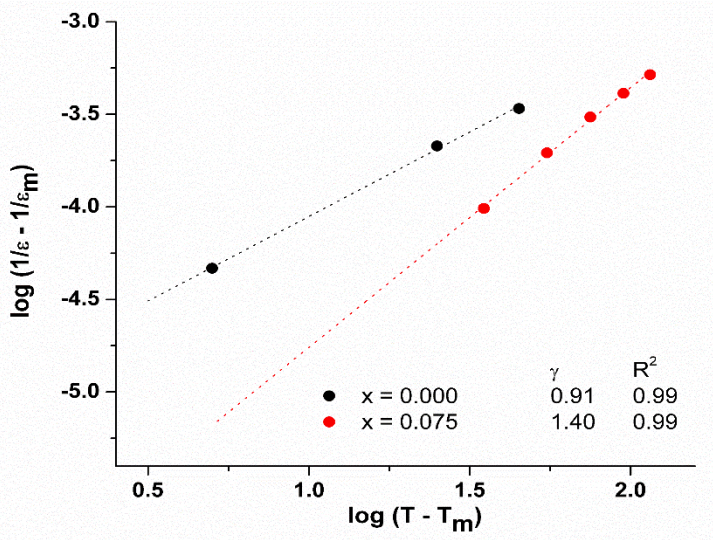


Figure 4. The plot of log (1/ε-1/ε_m) as function of log (T-T_m) at 127 kHz for (1-x) KNN–xBFO ceramics.

where ε and ε_m are relative permittivity and its maxima, T and T_m are temperature and its maxima. The value of γ is in the range between 1 and 2 which will indicates the normal ferroelectrics if its value approaches 1 and 2 for ideal relaxor. The value of γ can be determined from the results of fitting the logarithmic plots of the reciprocal permittivity versus temperature. Ignoring the influence of space charges at high temperature during frequency of 127 kHz results the γ value as shown in figure 4. The results confirms that KNN act as a normal ferroelectric with γ≈1, while BFO doped has a relaxor characteristic. It also means that the BFO doped modified the behaviour of KNN which initially pure ferroelectric to become relaxor.

4. Conclusions

The effect of $BiFeO_3$ (BFO) doping in the $K_{0.5}Na_{0.5}NbO_3$ (KNN) system has been investigated for its dielectric properties and its phase structures. The pure KNN that have orthorhombic symmetry transforms to a tetragonal symmetry after 0.075 mol.% BFO doped on the system. It is not also confirmed by quantitative analysis using Rietveld's refinement but also be compared to electrical analysis by cole-cole plot to obtain conductivity. The dielectric properties of KNN was successfully modified which initially act as a normal ferroelectric to become relaxor. The value of γ that be determined using modified Curie-Weiss law is approaches 1 (normal ferroelectric) for KNN and 2 (ideal relaxor) for KNN-BFO.

Acknowledgements

The research supported by Ministry of Research Technology and Higher Education of the Republic of Indonesia and LPPM ITS through program PMDSU 2017 No.489/PKS/ITS/2017.

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