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X-Ray Characterization of Lead Free Ferroelectric Material $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ Prepared by Solid State Reaction and Oxalate Coprecipitation Method

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Abstract

Lead free ferroelectric material behave ABO_3 structure ($A=K_{0.4}$, $Na_{0.4}$, $Ba_{0.16}$, $Sr_{0.04}$ and $B=Nb_{0.8}$, $Ti_{0.2}$) has been successfully synthesized using a combination of solid state reaction and oxalate coprecipitation method. A batch of $K_{0.5}Na_{0.5}NbO_3$ (KNN) synthesized through solid state reaction and a batch of $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) precurcor-calcined prepared via oxalate coprecipitation were mixed by 0.8 mol KNN and 0.2 mol BST for sample synthesis into two different routes: KNN(calcined)-BST(calcined) as first route and KNN(calcined)-BST (non calcined) as second route. $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ powders from each route were calcined based on thermal analysis. Single phase of $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ was formed by calcinations at 1100°C-2 hours for first route and at 700°C-2 hours for second route. The study of sintering was conducted by mean dilatometry. Sinter pellet sample shows good densification when sintering was took place at 1200°C for 2 hours. Due to volatility of alkaline element, K and Na were taken essesively by increasing 4% mol K-16% mol Na for first route and 2% mol K-8% mol Na for second route. Single phase of $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ pellet has been obtained successfully. After rietvield refinements, known that KNN powder behave perovskite tetragonal structure with a=b=3.9118 Å, c=3.9413 Å and BST powder behave perovskite tetragonal structure with a=b=3.9341 Å, c=3.9493 Å. It also known that $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ pellets from both routes behave perovskite tetragonal structure with lattice parameter a=b=3.9191 Å, c=3.9434 Å for first route and a=b=3.9062 Å, c=3.9263 Å for second route.

Key words: oxalate coprecipitation, solid state reaction, non lead ferroelectric, XRD analysis

INTRODUCTION

Ferroelectric material having high performance such as dielectric and piezoelectric properties has important applications in electronical devices such as capacitor, sensor, actuator, integrated circuit and electro-mechanic system (Fu, J.S., 2009 and Suasmoro, 2012). In the major case, ferroelectric material for piezoelectric application contains lead material up to 60 %Wt such as PZT. Unfortunately, lead based material is a dangerous material. That is the reason to find another material that can replace the function of lead based material as ferroelectric material.

Saito, et al (2004) reported that perovskite material has been synthesized using +1 cation such as Li, K, Na for A site and +5 cation such as Nb, Ta for B site. Saito prepared $(K_{0,44}Na_{0,52}Li_{0,04})(Nb_{0,84}Ta_{0,10}Sb_{0,08})O_3$ MPB (*morphotropic phase boundary*) with tetragonal and orthorhombic phase successfully and it behaves great piezoelectric properties similar to lead based material. This motivate other niobate based ferroelectric material. In literature, titanate based material $BaTiO_3$ has low Curie temperature but high relative permittivity. Contrary $KNaNbO_3$ has high Curie temperature but low dielectric property. Combining both type of above material should produce new composition of ferroelectric material with low Curie temperature and high performance of ferroelectric material. Li, Y., et al (2004) reported that $(Na_{0.5}Bi_{0.5})TiO_3$-$NaNbO_3$ as titanate and niobate based ferroelectric material exhibited excellent electrical properties, piezoelectric constant d_{33} = 80-88 pC/N and electromechanical planar coupling coefficient k_p = 17,92%.

Suasmoro, et al (2000) reported that $(Ba,Sr)TiO_3$ prepared through oxalate coprecipitation was formed after calcinations at 700°C for 2 hours. Beside, Rohmah, et al reported that $K_{0,5}Na_{0,5}NbO_3$ was formed after calcinations at 700°C for 2 hours from K_2CO_3, Na_2CO_3 and Nb_2O_3. The same calcinations temperature of both $K_{0,5}Na_{0,5}NbO_3$ and $(Ba,Sr)TiO_3$ motivate us to use this two combination method to synthesize $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$.

Recalling the ionic radius (table 1) of K, Na, Ba and Sr are close each other. Furthermore, ionic radius of Ti and Nb are close each other too. Therefore it is probable to perform $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$.

Table 1. Ionic Radius

Ion	Ionic Radius (Å)	Possible Site
K^+	0,138	A
Na^+	0,102	
Ba^{2+}	0,135	
Sr^{2+}	0,118	
Nb^{5+}	0,064	B
Ti^{4+}	0,086	

Main purpose of this research is to synthesize ferroelectric material with ABO_3 structure ($A=K_{0.4}$, $Na_{0.4}$, $Ba_{0.16}$, $Sr_{0.04}$ and $B=Nb_{0.8}$, $Ti_{0.2}$) by solid state reaction and oxalate coprecipitation method then perform ceramic pellet having single phase characterized by XRD.

RESEARCH METHOD

Niobate and titanate based material with composition $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ was prepared through solid state reaction and oxalate coprecipitation method. $K_{0.5}Na_{0.5}NbO_3$ (KNN) were prepared by solid state reaction using raw material K_2CO_3, Na_2CO_3 and Nb_2O_5 powders. Raw material then weighted properly to make stoichiometric $K_{0.5}Na_{0.5}NbO_3$ and milled using planetary milling 150 rpm for 2 hours before calcinations. Reagent grade raw material $TiCl_4$, $BaCl_2.2H_2O$, $SrCl_2.2H_2O$ and $H_2C_2O_2$ were used to prepared $(Ba/Sr)TiO(C_2O_4)_2.4H_2O$ precursor through oxalate coprecipitation method as describe elsewhere (Bernier, J.C., et al., 1986). $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ powder was prepared by solid state reaction using two different routes:

1. KNN(calcined)-BST(calcined), abbreviated C-C
2. KNN(calcined)-BST (non calcined), abbreviated C-NC

Experimental studies of reactions to form $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ have been conducted by differential thermal analyses (DTA) and thermo gravimetric analysis (TGA). To find out the sintering temperature, dilatometry test was taken from room temperature up to 1300°C. Ceramic pellets after sintering then studied using XRD. Formed phase identified by crystalline data match.

RESULTS AND DISCUSSION

This research was started with definite crystalline phase of KNN and BST. These phase were formed after calcinations at 700°C for 2 hours (Suasmoro, et al., 2000 and Rohmah, N.A., 2014). XRD pattern of both sample can be seen in figure 1. It can be noted that in both samples the undetected trace phase still exist (2θ = 27,6° and 29,3° for KNN and 2θ=24,1 for BST). After rietvield refinements, it was known that KNN and BST behave tetragonal perovskite structure with lattice parameter as described in table 2.

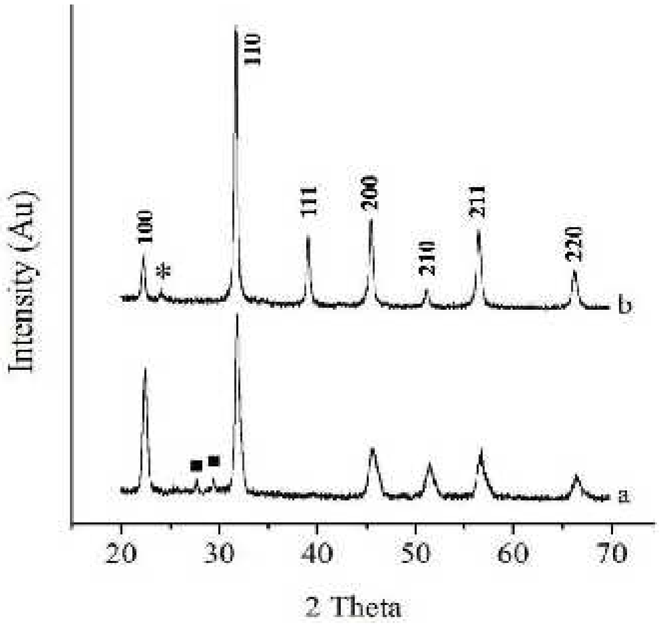

Figure 1. XRD difraction of KNN (a) and BST (b) after calcinations
(*) trace phase in BST and (■) trace phase in KNN

Table 2. Lattice parameter of KNN and BST

No	Material	Lattice Parameter (Å)			Crystal System
		a	b	c	
1	KNN	3.9118	3.9118	3.9413	perovskite tetragonal
2	BST	3.9341	3.9341	3.9493	perovskite tetragonal

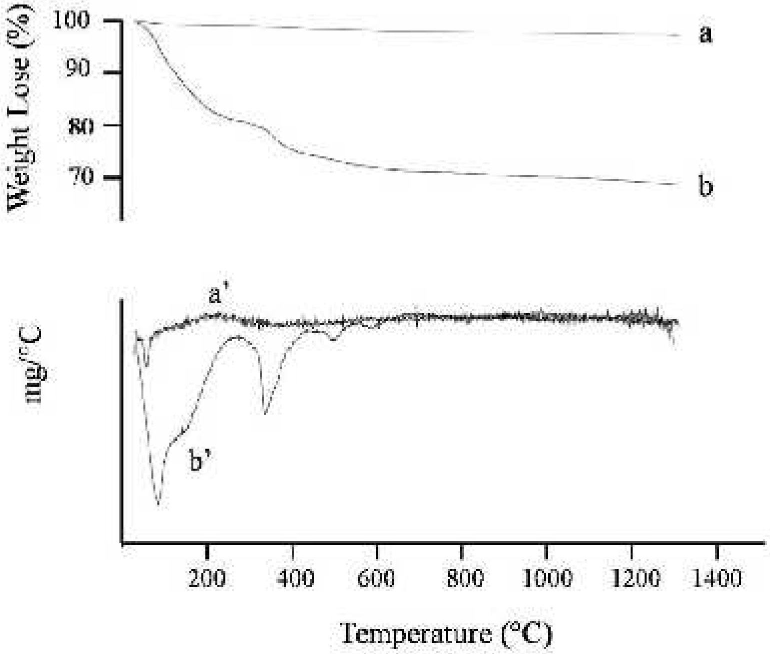

Figure 2. TGA and DTG of calcined KNN-calcined BST (aa')
and calcined KNN-precursor BST (bb')

Thermogravimetry analysis DTA-TGA of powder mixture through route 1 and route 2 are displayed in figure 2. In calcined - calcined route, weight loss were not detected. Because of that, samples were calcined for 2 hours at some temperatures: 700°C, 900°C and 1100°C. Optimum calcinations temperature to form $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ was 1100°C. Unfortunately, secondary phase still detected. The secondary phase should be caused by volatility of K and Na as reported by Wang, Y.L, et al, 2011. Therefore, K^+ and Na^+ number must be taken excessively. Single phase of $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ powder can be obtained practically by excess 2 mol % K and 8 mol % Na (figure 3d)

In other side, calcined - non calcined route shows three thermal events. First thermal event under 250°C is due to evaporation of trapped water in cavity and dehydration process to form $Ba/SrTi(C_2O_4)_2$ was formed. Second thermal event is due to breaking-off oxalate bonding and released CO gas. Last thermal event is due to decarbonation. Thermal events finished after 700°C. Because of that, the calcination was carried out at 700°C for 2 hours and it was successfully form $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ (figure 3e)

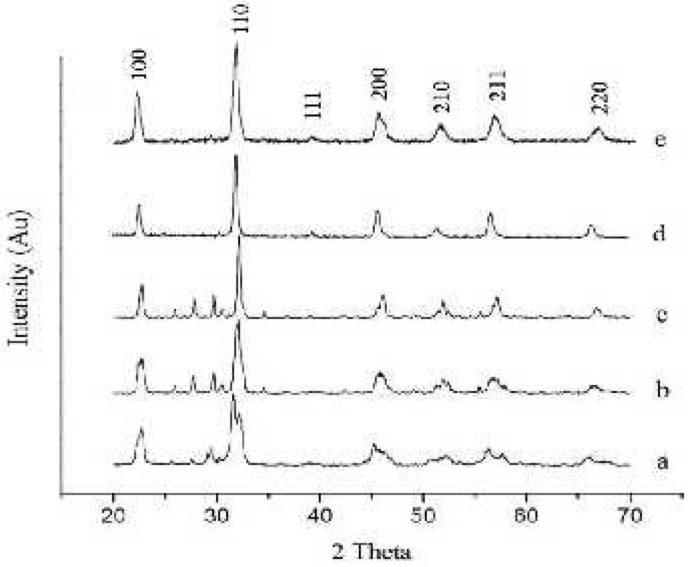

Figure 3. XRD Pattern of calcined $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ from both route a. C-C at 700°C; b.C-C at 900°C; c.C-C at 1100°C; d. C-C at 1100°C by excess 2 mol % K and 8 mol % Na; e. C-NC at 700°C

This XRD result shows that ions Ba^{2+}, Sr^{2+}, K^{+}, Na^{+} incorporated in A site and ions Ti^{4+}, Nb^{5+} incorporated in B site to form perovskite structure ABO_3. After rietvield refinements, it was known that $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ powder from both routes behave tetragonal perovskite structure with lattice parameter described in table 3.

Table 3. lattice parameter of $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ powder

No	Routes	Lattice Parameter (Å)			Crystal System
		a	b	c	
1	calcined KNN-calcined BST	3.9321	3.9321	3.9373	perovskite tetragonal
2	calcined KNN-non calcined BST	3.9196	3.9196	3.9474	perovskite tetragonal

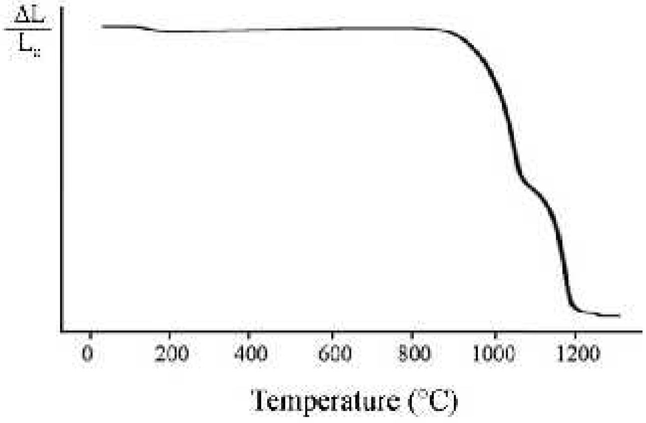

Figure 4. Dilatometry test result of $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$
from calcined-calcined route

Dilatometry curve shows that maximum shrinkage has been performed after 1200°C. Therefore $(K_{0.4}Na_{0.4}Ba_{0.16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ pellets were sintered at 1200°C for 2 hours. Due to volatility of alkaline element (Wang, Y.L., et al. 2011) , the mol fraction of K and Na was increased by 2 mol % K and 8 mol % Na refered to Rohmah, N.A., 2014.

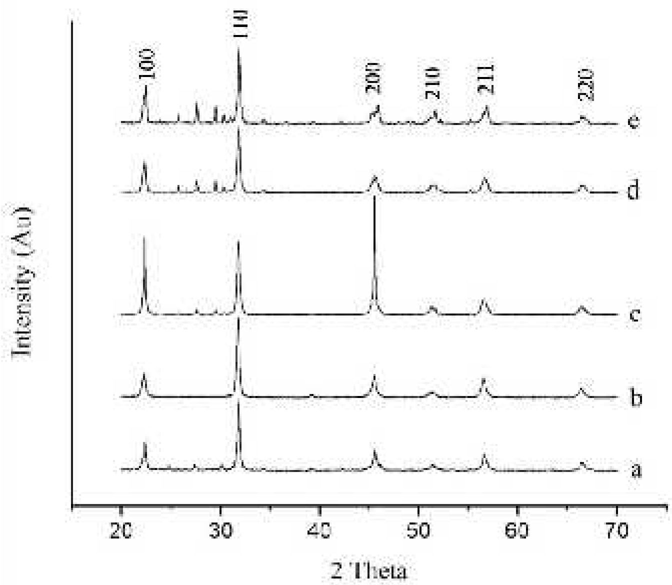

Figure 5. XRD Pattern of Sintered $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$
a. C-C excess 2%K-8%Na; b. C-C excess 4%K-16%Na; c. C-NC excess 2%K-8%Na; d. C-NC excess 3%K-12%Na; e. C-NC excess 1%K-4%Na

By excess 2 mol % Na and 8 mol % K, undetected trace phase still exist. Then the number of excess was taken to be 4 mol % Na and 16 mol % K for first route. Increasing this excessive to first route was successfully form single phase perovskite $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ (figure 5b). The optimum excess for second route is 2 mol % K and 8 mol % Na (figure 5c). After rietvield refinement, structure of sintered $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ was known as described in table 4. Comparing this two routes, known that second route (calcined-non calcined) is better in degree of packing.

Table 4. Lattice parameter of sintered $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$

No	Routes	Lattice Parameter (Å)			Crystal System
		a	b	c	
1	calcined KNN-calcined BST	3.9191	3.9191	3.9434	perovskite tetragonal
2	calcined KNN-non calcined BST	3.9062	3.9062	3.9263	perovskite tetragonal

CONCLUSION

Single phase of $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ has been obtained successfully using the combination of solid state reaction and oxalate coprecipitation method with two routes: calcined KNN - calcined BST and calcined KNN - non calcined BST. For first route, single phase $(K_{0.4}Na_{0.4}Ba_{0,16}Sr_{0.04})(Nb_{0.8}Ti_{0.2})O_3$ was obtained successfully by calcination at 1100°C for 2 hours with excess 2 mol % K and 8 mol % Na. However for second route, the same result was obtained by calcinations at 700°C for 2 hours.

Due to volatility of K and Na, to preserve single phase of sintered pellet samples, more excessive K and Na was required. For first route, it needs 4 mol % K and 16 mol % Na. However for second route required 2 mol % K and 8 mol % Na. Both calcined powder and sintered pellet show that cell parameter from second route was more compact than the first route.

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