

Microstructural, dielectric and optical properties of $[\text{KNbO}_3]_{0.9} - [\text{BaNi}_{0.5}\text{Nb}_{0.5}\text{O}_3]_{0.1}$ perovskite ceramics

S Sriphan^{1,2*}, N Vittayakorn¹, S Kiravittaya^{2,3,4} and T Bongkarn^{3,4}

¹ Advanced Material Research Unit, Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand.

² Advanced Optical Technology Laboratory, Department of Electrical and Computer Engineering, Faculty of Engineering, Naresuan University, Phitsanulok 65000, Thailand.

³ Research Center for Academic Excellence in Applied Physics, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand.

⁴ Research Center for Academic Excellence in the Petroleum, Petrochemicals and Advanced Materials, Naresuan University, Phitsanulok 65000, Thailand.

Corresponding author's e-mail address : Saichon_Sriphan@hotmail.com

Abstract. In this work, $[\text{KNbO}_3]_{0.9} - [\text{BaNi}_{0.5}\text{Nb}_{0.5}\text{O}_3]_{0.1}$ (KBNNO) perovskite ceramics are synthesized under various conditions by using the solid-state combustion technique. Their microstructural, Raman, dielectric, optical, and photovoltaic properties are investigated. X-ray diffraction spectroscopy reveals that the synthesized ceramics have a cubic structure. A high purity KBNNO sample is obtained at the sintering temperature of 1100°C with the dwell time of 3 h. Raman spectroscopy of these ceramics shows a broadening of vibrational peaks for the sample sintered at 1130°C, which implies an existence of impurity phases. The dielectric constant of ~3000 at room temperature is obtained. The optical absorption of light in visible range as well as the photovoltaic response are observed in this ceramic. This work demonstrates the potential usages of KBNNO in electrical and opto-electronic applications.

1. Introduction

Since the application of ferroelectric (FE) material as a photovoltaic (PV) cell has been emerged, low band gap ceramic materials have been developed to absorb more photons in light spectrum [1-3]. An interesting material is $[\text{KNbO}_3]_{1-x} - [\text{BaNi}_{0.5}\text{Nb}_{0.5}\text{O}_{3-\delta}]_x$ (KBNNO_x), where δ is the oxygen deficiency [3], due to the tunable band gap property (1.1 – 3.8 eV) by varying the x content. The optimal material properties for FE-PV application have been found in KBNNO_{0.1} with $\delta = 0.25$. Previous works have reported several related properties of KBNNO_x ceramics [3-5]. However, the modification of this material to improve a certain property has not been reported yet.

In this work, we focus on enhancing the dielectric properties of KBNNO_x while preserving the PV response. KBNNO_{0.1} is designed to enhance the dielectric properties by setting $\delta = 0$. The solid-state combustion technique is applied to fabricate the samples. The microstructural, dielectric, optical and PV properties of this ceramic are investigated.

2. Experimental Details

2.1. Sample Preparation

The starting materials, which are KNO_3 , $\text{Ba}(\text{NO}_3)_2$, NiO and Nb_2O_5 were weighed to their stoichiometric proportions. The mixed powders were then ball-milled for 24 h. Solid-state combustion were used to synthesize powders/ceramics with low firing temperature and short dwell time. Glycine ($\text{C}_2\text{H}_5\text{NO}_2$), acted as a fuel, was mixed with the dried powders (1:0.61 ratio) and then the mixture was calcined at 650°C for 1.5 h. More detail description can be found in our previous report [6]. A 1.2-g of each calcined powder was then pressed into a pellet with a diameter of 1.5 cm. The KBNNO pellets were then sintered at various sintering temperatures T_{sin} ranging from 1070°C to 1130°C for 3 h.

2.2. Characterizations

Samples were examined by a field emission scanning electron microscope (FESEM, JSM-7001F). The ceramic densities were measured by the Archimedes method. X-ray diffraction (XRD, PANalytical X'Pert PRO) spectroscopy was used to indicate the phase purity and to find the optimal sintering temperature T_{sin} . Raman spectroscopy (Renishaw Invia Reflex) was applied to confirm the purity of ceramics. The dielectric properties at various temperature were collected using LCR meter (Agilent 4263B) and a heater. The optical absorption data was recorded with an ultraviolet-visible-near-infrared (UV-Vis-NIR) spectrophotometer (PerkinElmer Lambda 1050). After depositing gold electrode contacts, the current-voltage characteristics under dark and illumination conditions were measured. The setup consists of Keithley 6485 picoammeter as the ammeter, Agilent 34401A digital multimeter as the voltmeter, Agilent E3633A DC power supply as the voltage source, and 12-V 5-W white LED light bulb as the light source with a fixed optical power of $\sim 1000 \text{ mW/cm}^2$.

3. Results and Discussion

Figure 1 shows the surface of KBNNO sintered at various T_{sin} . The pores were found for all sintered ceramics. The percentage of theoretical density (%T.D.) data can be calculated using the percentage of the measured density D and the theoretical density. In figure 1(a), the calculated %T.D. of KBNNO ceramics sintered at 1070°C was 94.06% with $D = 4.59 \text{ g/cm}^3$. By increasing T_{sin} up to 1100°C , good grain growth was achieved, and a compact structure was formed (see figure 1(b)). The highest D and %T.D. were obtained (4.80 g/cm^3 and 98.36%) at this temperature. This density is higher than the value reported for KNO-based ceramics such as $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ [7]. One of the key steps to achieve the high D is attributed to the applied ball milling technique. Another key factor is the fulfilment of oxygen atoms (by setting $\delta = 0$) in the unit cell structure. However, larger grain sizes and the disappearance of small grains were observed at higher sintering temperature. The grain boundaries melted while the porosity increased. Hence, the obtained D for high temperature was lower for example $D = 3.51 \text{ g/cm}^3$ with %T.D. = 71.93% for the ceramic sintering at 1130°C (see figure 1(c)).

Figure 2 shows the room temperature XRD and Raman spectra obtained from KBNNO ceramics sintered at various temperatures (1070°C to 1130°C) for 3 h. For XRD results (see figure 2(a)), main diffraction peaks of (001), (110), (200), (210) and (211) were found in the 2θ range of $10^\circ - 60^\circ$. These

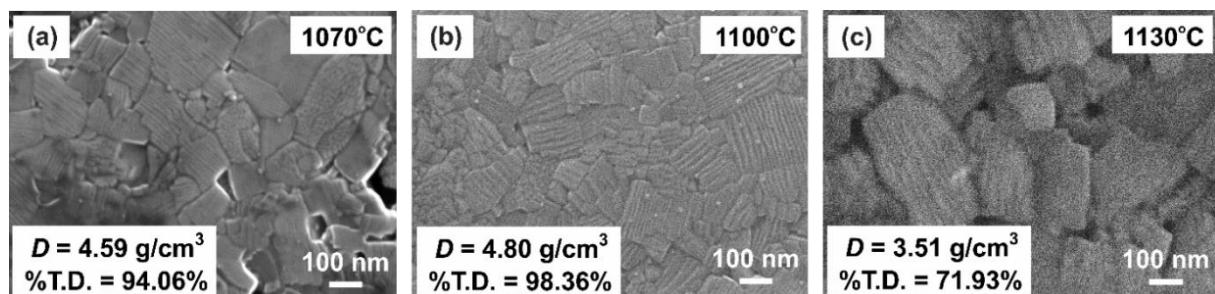


Figure 1. FESEM images of KBNNO ceramic sintered at (a) 1070°C , (b) 1100°C and (c) 1130°C .

major peaks indicate a single-phase perovskite structure [3-6]. The obtained XRD results matched well with the standard cubic KNbO_3 (KNO) (JCPDS file No. 08-0212). For T_{sin} below 1100°C , small unidentified impurity peaks were observed (marked downward triangles in figure 2(a)). They tended to decrease continuously with increasing T_{sin} . This indicates that $\text{BaNi}_{0.5}\text{Nb}_{0.5}\text{O}_3$ composition has diffused well into the KNO lattice to form KBNNO. However, new impurity peaks (marked by stars) were detected in the sample sintered at 1130°C . According to this result, the highest purity KBNNO ceramic is found at 1100°C . In figure 2(b), Raman spectroscopy, measured in the range of $150 - 1000 \text{ cm}^{-1}$, was used to confirm the presence of ceramic impurities. The KBNNO ceramics sintered at 1070°C , 1100°C and 1130°C are chosen for representing low, middle and high temperature regions. The fingerprint of the KNO family could be observed as shown in the peaks of the $(\text{B}_1, \text{B}_2)(\text{TO}_2)$ mode at $\sim 180 \text{ cm}^{-1}$, the $\text{A}_1(\text{TO}_1)$ mode at $\sim 260 \text{ cm}^{-1}$ and the $\text{A}_1(\text{TO}_4, \text{TO}_4)$ mode at $\sim 290 \text{ cm}^{-1}$ [4]. As T_{sin} increases to 1100°C , the overall spectral feature does not alter much. However, obvious changes of the spectrum with lower intensity at mode 3 and broader peak at mode 4 were observed for the sample sintered at 1130°C . These might be caused by re-formed impurities in the furnace due to a high firing temperature. This result is consistent with the XRD result shown in figure 2(a).

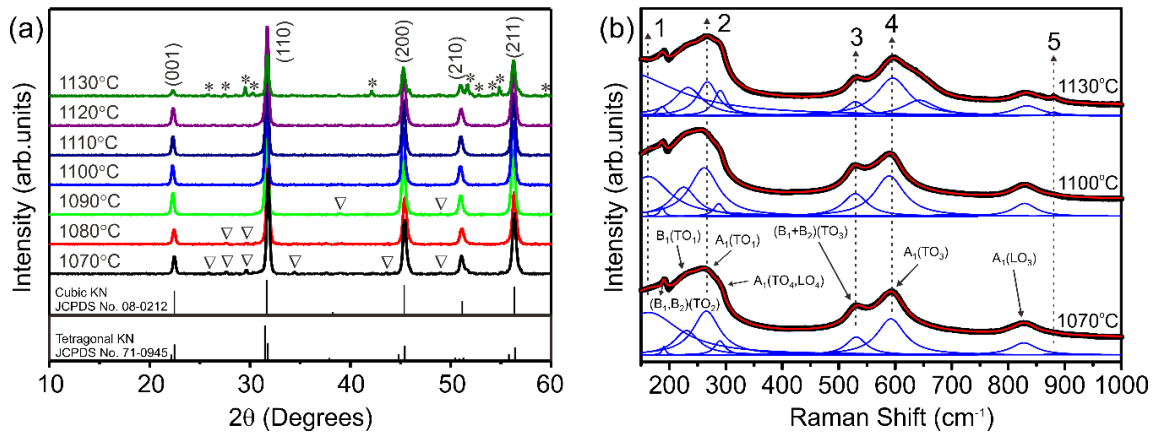


Figure 2. (a) XRD patterns of KBNNO ceramic at various T_{sin} . (b) Raman spectra of KBNNO ceramic samples (black solid lines) at different T_{sin} between $1070^\circ\text{C} - 1130^\circ\text{C}$ plotted with the fitted spectra (red solid lines) and the decomposed fitted peaks (blue solid lines).

Figure 3(a) shows the variation of the dielectric constant ϵ_r and the loss tangent $\tan \delta$ for the unpoled KBNNO samples sintered at 1080°C , 1100°C and 1120°C . These sintering temperatures are chosen because they provide the ceramics, which their dielectric properties can be measured without the breaking (due to low material density) during the measurement. All data was recorded at the temperatures T ranging from 25°C to 100°C with a probe signal frequency of 1 kHz . The highest ϵ_r of 3033 was obtained from the sample sintered at 1100°C . This T_{sin} is consistent with the occurrence of the highest D observed by FESEM shown in figure 1(b). The obtained ϵ_r was higher than the typical KBNNO_x by ~ 5 times [3] and it showed the maximum value at room temperature. The values of $\tan \delta$ for each T_{sin} tended to decrease as T increased (inset of figure 3(a)). The highest loss behavior was found for the sample sintered at 1080°C ($\tan \delta = 6.62$) and it was higher than that of the 1100°C sample.

Room temperature absorbance α spectra of KBNNO and KNO ceramics are shown in figure 3(b). Both samples had high absorbances in the UV region (wavelength $< 400 \text{ nm}$). However, the KBNNO had three broad anomalous absorption peaks at the violet ($\sim 410 \text{ nm}$), red ($\sim 700 \text{ nm}$) and near-infrared ($\sim 1200 \text{ nm}$) regions. The additional absorption peaks can therefore be a key factor for enhancing the optical property of KBNNO for PV application. To investigate the PV effect, the current-voltage (J - V) characteristics of unpoled KBNNO and KNO samples under dark and illumination conditions were

measured and they are shown as the inset of figure 3(b). No PV response was observed for the typical KNO sample. On the other hand, the PV behavior of KBNNO was observable under illumination condition. The short-circuit current density and open-circuit voltage were about $0.9 \mu\text{A}/\text{cm}^2$ and 0.7 V , respectively. This PV response relates to the appearance of additional absorption peaks, in the visible light wavelength.

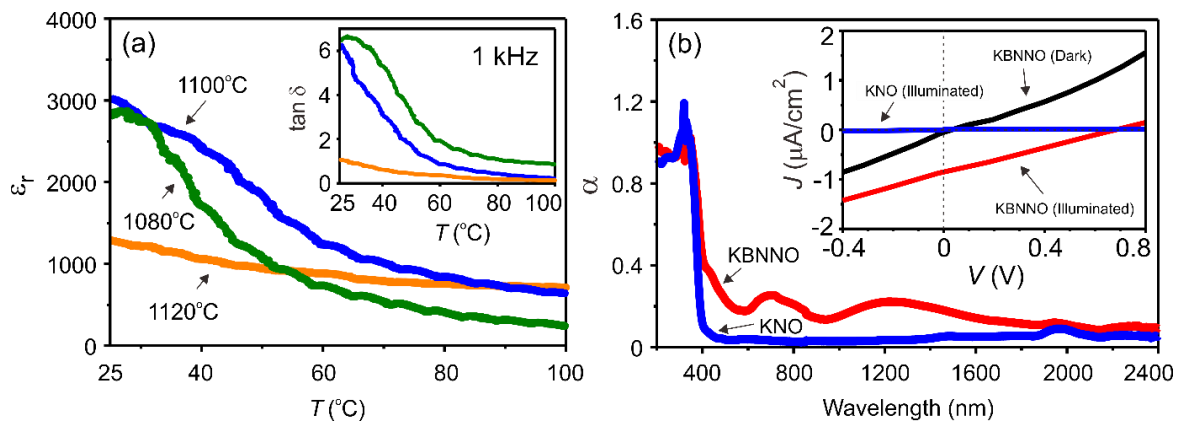


Figure 3. (a) Temperature-dependent of ϵ_r and $\tan \delta$ (inset) at 1 kHz for KBNNO ceramic sintered various T_{sin} . (b) UV-Vis-NIR absorption spectra for KBNNO and KNO ceramics. The inset of (b) shows the room temperature J - V characteristics under dark and illumination conditions.

4. Conclusions

In this work, KBNNO ceramics were synthesized by the solid-state combustion technique with the variation of sintering temperature T_{sin} from 1070°C to 1130°C . FESEM reveals the high density of KBNNO sintered at 1100°C . XRD technique showed that KBNNO sintered at 1100°C for 3 h provides a high purity ceramic. Raman and XRD techniques could detect the impurity phases. The highest obtained density is $4.80 \text{ g}/\text{cm}^3$. A high dielectric constant ϵ_r of ~ 3000 with high dissipation loss ($\tan \delta = 6.62$) are observed. The designed KBNNO ceramic also has a PV response. The obtained short-circuit current density and open-circuit voltage are $0.9 \mu\text{A}/\text{cm}^2$ and 0.7 V under LED illumination condition. Hence, the present KBNNO material has attractive features for developing devices such as hybrid energy harvesters/sensors.

Acknowledgements

This work is financially supported by Naresuan University and Faculty of Engineering, Naresuan University. We would like to thank Dr. Noppadon Nuntawong at National Electronics and Computer Technology Center (NECTEC), Thailand, for his comments and suggestions. We also would like to thank Miss Unchittha Prasatsap (PhD student) in Advanced Optical Technology Laboratory for the lab instrumental details.

References

- [1] Yuan Y, Xiao Z, Yang B and Huang J 2014 *J. Mater. Chem. A* **2** 6027–41
- [2] Zhang G, Wu H, Li G, Huang Q, Yang C, Huang F, Liao F and Lin J 2013 *Sci. Rep.* **3** 1265
- [3] Grinberg I, West D V, Torres M, Gou G, Stein D M, Wu L, Chen G, Gallo E M, Akbashev A R, Davies P K, Spanier J E and Rappe A M 2013 *Nature* **503** 509–13
- [4] Zhou W, Deng H, Yang P and Chu J 2014 *Appl. Phys. Lett.* **105** 111904
- [5] Bai Y, Siponkoski T, Peräntie J, Jantunen H and Juuti J 2017 *Appl. Phys. Lett.* **110** 063903
- [6] Sriphan S, Kiravittaya S and Bongkarn T 2017 *Integr. Ferroelectr.* **177** 112–20
- [7] Singh R, Kulkarni A R and Harendranath C S 2014 *Physica B* **434** 139–44