

# PHYSICAL AND ELECTRICAL PROPERTIES ENHANCEMENT OF RARE-EARTH DOPED-POTASSIUM SODIUM NIOBATE (KNN): A REVIEW

MAZIATI AKMAL MAT HARTTAR\*, #MOHD WARIKH ABD RASHID\*, UMAR AL AMANI AZLAN\*\*

\*Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM),  
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

\*\*Faculty of Engineering Technology, Universiti Teknikal Malaysia Melaka (UTeM),  
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

#E-mail: warikh@utem.edu.my

Submitted February 4, 2015; accepted June 21, 2015

**Keywords:** Potassium sodium niobate, Piezoelectric, Volatility, Intrinsic defects, Rare earths

*Alkaline niobate mainly potassium sodium niobate, ( $K_xNa_{1-x}$ ) NbO<sub>3</sub> (abbreviated as KNN) has long attracted attention as piezoelectric materials as its high Curie temperature ( $T_c$ ) and piezoelectric properties. The volatility of alkaline element (K, Na) is, however detrimental to the stoichiometry of KNN, contributing to the failure to achieve high-density structure and lead to the formation of intrinsic defects. By partially doping of several rare-earth elements, the inherent defects could be improved significantly. Therefore, considerable attempts have been made to develop doped-KNN based ceramic materials with high electrical properties. In this paper, these research activities are reviewed, including dopants type and doping role in KNN perovskite structure.*

## INTRODUCTION

Recently, a significant worldwide attention has been paid on the lead-free materials instead of lead-based materials. In the last decades, lead zirconia titanate or PZT have attracted much attention due to excellent ferroelectric and piezoelectric properties. However, PZT is believed to ruin the green house's effect due to the existence of toxic lead [1]. In order to circumvent this drawback, extensive research is focused on the quest for alternate piezoelectric materials. In that respect, the most promising lead-free piezoelectric material are potassium sodium niobate (K, Na)NbO<sub>3</sub> (abbreviated as KNN). KNN derived from a combination of ABO<sub>3</sub> perovskite structure of KNbO<sub>3</sub> (KN) and NaNbO<sub>3</sub> (NN). A site is referring to K and Na ions while B is corresponding to Nb ion. It exhibited a high Curie temperature (420°C), high dielectric constant (~700), high remanent polarization (14  $\mu\text{C}\cdot\text{cm}^{-2}$ ), low coercive field (~140  $\text{kV}\cdot\text{cm}^{-1}$ ) and high piezoelectric constant [2-4].

Lead-Free KNN has been prepared in the form of bulk ceramics, thin and thick films [5-9]. KNN based ceramic is predominantly studied due to ease of sample preparation. However, it was reported that the proportion of K, Na, and Nb is likely to deviate from stoichiometry due to the volatilization of K and Na at elevated temperature. This occurrence might be attributed to defects and oxygen vacancies [10]. Generally, the intrinsic defects resulted from volatility issues led to

poor electrical properties of KNN due to high leakage current density [11-13]. Additionally, divergence of KNN from stoichiometry promotes the formation of secondary phases and the difficulty to obtain dense KNN ceramics [14-15]. To overcome these problems, several approaches have been studied. This could be achieved by modifying the base compound of KNN or substitutions of several cations at A-site or B-site of KNN structure [16].

The doping technique is believed to be an effective way to improve ferroelectric and piezoelectric properties of KNN. Through this approach, KNN based materials have chemical stability by equilibrating the ions charge which would reduce local stress and reduces the concentration of oxygen vacancies [17]. Thus, the study of different dopants to obtain dense KNN and good electrical properties is extremely favorable.

Rare-earth elements (i.e. CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>) were dominant dopants to be substituted for KNN-based materials. It was stated that rare-earth elements are known to demonstrate useful functions of stabilizing and lowering dissipation factor in dielectric ceramics [18]. In previous work on barium titanate (BaTiO<sub>3</sub> or BT) with ABO<sub>3</sub> structure, it is known that the appropriate amount of CeO<sub>2</sub> could enhance piezoelectric and dielectric constant of lead-free piezoelectric ceramics. CeO<sub>2</sub> also revealed "soft effect" and "hard effect" of piezoelectric properties [19-20]. Similar technique could be used to compensate the volatility of K and Na in KNN. However,

best to our knowledge little study has been done on doping rare earths in KNN (Figure 1). Therefore, this paper is dedicated to integrate what is known today about the effects of rare-earth dopants on piezoelectric lead-free materials with similar perovskite structure to those KNN. Later, this review will exclusively focus on rare earths doping in KNN as it is believed that the rare earths would enhance the quality of KNN.

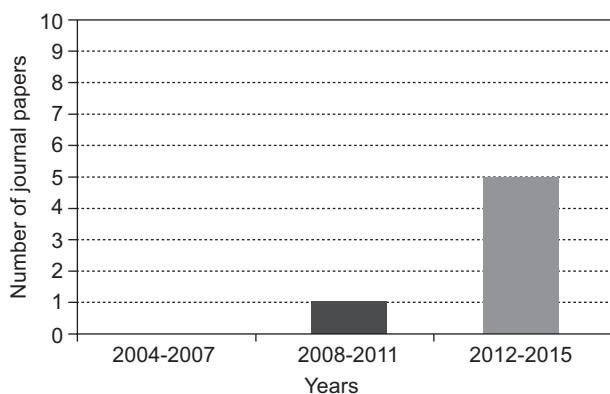


Figure 1. Graphical illustration on rare earths-doped KNN.

## RESULTS AND DISCUSSION

### The effects of rare earth elements on morphology and electrical properties of lead-free piezoelectric materials

Numerous studies have attempted to observe the effects of rare earths integration to lead-free piezoelectric ceramics. Guo et al. depicted that piezoelectric ceramics doped with rare earths resulted in a significant increase in piezoelectric properties [21]. In the same vein, Zhu et al. asserted that 0.02 mol ytterbium (Yb)-doped samples increased the degree of “soft” characteristics of piezoelectric that significantly improved the piezoelectric and dielectric properties of the ceramics. Additionally, author found that,  $\text{Yb}^{3+}$  substituent tends to enter A site structure and acts a donor dopant. Consequently,  $\text{Yb}^{3+}$  donor dopant reduces the concentration of the intrinsic oxygen vacancies created during sintering and retains the charge neutrality. This phenomenon led to deformation of crystal structure, reduce the inner stress and increase the mobility of domain wall subsequently increase the piezoelectric properties of ceramics [22].

Analogous to KNN,  $\text{BaTiO}_3$  or BT with  $\text{ABO}_3$  perovskite structure is the first discovered ferroelectric oxide. A pioneer work on rare earth doped- $\text{BaTiO}_3$  did by Park et al. Author observed that doping behaviors of various rare-earths in  $\text{BaTiO}_3$  lattice were different. Incorporation of dysprosium ion (Dy) into BT lattice could improve the densification rate of BT due to its high solubility. Furthermore, Dy doped samples showed the grain growth with an increasing temperature (Figure 2). This event implied that Dy substitution for

A-site continued until BT fully densified. Contrary to Dy, yttrium (Y) and holmium (Ho) revealed almost no grain growth over the whole temperature range, attributed to decreased tetragonality and densification [23]. Kim et al. reported similar observation. Author found that the addition of Y ions inhibited the growth of dielectric grain resulted in reduced density and sinterability of BT samples [24]. Among lists of investigated dopants, dysprosium was found to be effective in boosting the grain growth and densification rather than dissolved in the core region and makes the domains disappear. However, the measurement of ferroelectric properties was not reported.

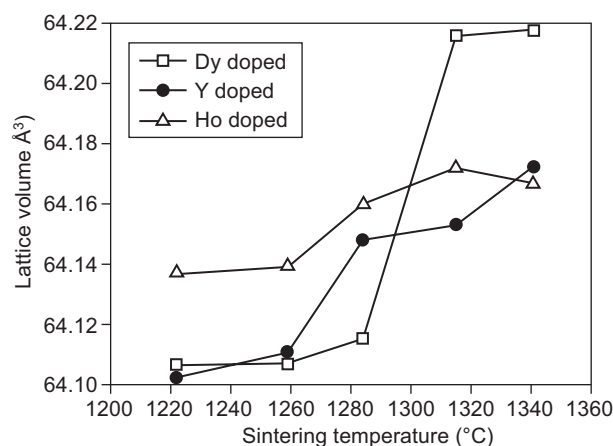


Figure 2. Lattice volume of various rare-earth doped BT as a function of sintering temperature [23].

Modifications of piezoelectric ceramics also have been done on bismuth titanate (BIT) by substitution of various dopants. Kim et al. studied the effect of neodymium (Nd) on the crystal structure, dielectric, ferroelectric and other electrical properties. Substitution of Nd permits the formation of BIT with small grain size, high dielectric constant, low dissipation factor and large remanent polarization [25]. These findings were supported by Mao et al. Author claimed that maximum remanent polarization achieved with a particular Nd substitution. The improved properties are associated to the reduction of the oxygen vacancy and the increase of mobility of domain wall [26]. However, the further increment of Nd content showed the increase in coercive field and decrease in Curie temperature ( $T_c$ ). Simões et al. reported the dielectric constant is Nd content independent. They found out that the increase in Nd content led to the narrowing of hysteresis loops due to an increase in the [27].

On the other hand, progress has been made in the addition of BT with various lanthanum (La) contents. Author observed the change in grain morphology with La-doped BIT. The remanent polarization of La substituted was found better than that of pure BIT. Moreover, author also reported that the La substitution improved the leakage current densities [28].

Bismuth sodium titanate  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  or BNT is another lead-free piezoelectric material with  $\text{ABO}_3$  perovskite structure. The further development on BNT has been done by doping some amount of rare earth oxides [29-31]. It was claimed that the incorporation of rare earth oxides has a prominent role in the structure and electrical properties of BNT ceramics. Fu et al. observed that no apparent change in the crystal structure of doped BNT, indicating that  $\text{Dy}^{3+}$  may have completely entered into a crystalline structure to form a solid solution. Moreover, the addition of appropriated Dy oxide improved piezoelectric and dielectric properties. But, the excessive amount of  $\text{Dy}_2\text{O}_3$  cause large crystal cell distortion and difficulty in increasing polarization [32].

By contrast, Zhou et al. investigated the effects of  $\text{Y}_2\text{O}_3$  on BNT properties [33]. Their results demonstrated that the average grain size decreased slightly with increase quantity of  $\text{Y}_2\text{O}_3$  (Figure 3). The samples with a 0.5 % doping amount of  $\text{Y}_2\text{O}_3$  revealed distinct piezoelectric coefficient,  $d_{33}$  and electromechanical coupling,  $k_p$  improvement with a maximum value  $137 \text{ pC}\cdot\text{N}^{-1}$  and 0.3 respectively.

Another study on doped BNT ceramics dealt with  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.15}\text{Zr}_{0.1}\text{O}_3$  (BCTZ) system with  $\text{CeO}_2$  dopant. Xinyou et al. found that piezoelectric constant ( $d_{33}$ ) and the planar electromechanical coupling ( $k_p$ ) of BCTZ ceramics increased markedly. It happened due to the number of pores decreased as  $\text{CeO}_2$  content increased. Though, further substitution of dopant material would cause bigger lattice distortion. As a result, domain wall movements of BCTZ are restrained, and the ions diffusion rate reduced [34].

Recently, europium (Eu) with trivalent ions was also considered as a substituent material in BNT ceramic. Ma et al. analyzed the significant of Eu integration into BNT by measuring the electrical properties of Eu-BNT [35]. Tangent loss ( $\tan \delta$ ), was observed to be minimized at  $\text{Eu} = 0.25 \%$ . Similarly, piezoelectric properties which

are piezoelectric coefficient, ( $d_{33} = 149 \text{ pC}\cdot\text{N}^{-1}$ ), and electrical permittivity, ( $\epsilon_r = 1658$ ) were recorded to be maximized at equivalent Eu content.

#### Rare earths doping on KNN perovskite structure

In comparison to other piezoelectric ceramics mentioned, KNN possesses a large piezoelectricity [36]. Moreover, other ceramics like pure BNT is hard to be poled in electrical fields which limit its application as piezoelectric materials [37]. As regards to the favorable outcomes of rare earths doping in piezoelectric materials, some researchers believed that KNN properties could be enhanced as well. Therefore, in recent years, emerging progresses have been carried out towards development of KNN with rare-earth dopants to obtain outstanding properties.

In 2011, light and heavy rare earths which are praseo-dymium (Pr) and ytterbium (Yb) were proposed for dope in KNN-based ceramics by Wang et al. [38]. Author found that the ferroelectric properties of KNN

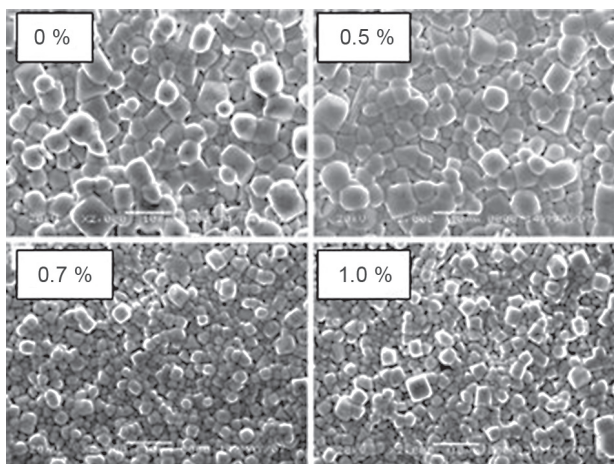


Figure 3. SEM micrographs of  $\text{Y}_2\text{O}_3$  doped-BNT [33].

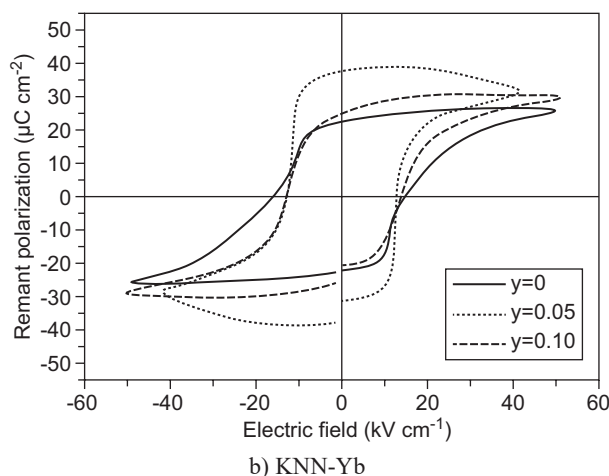
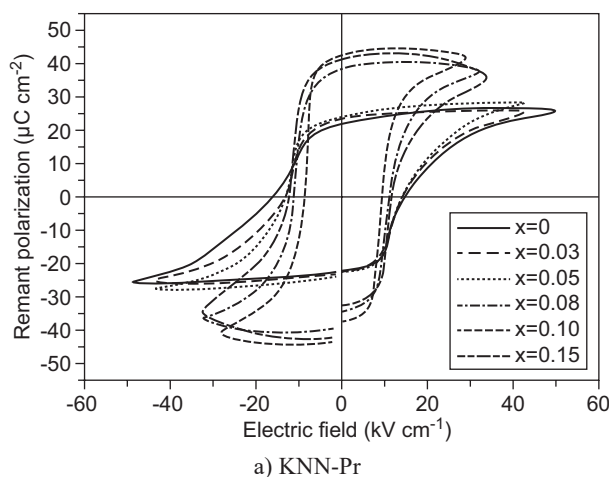


Figure 4. P-E Hysteresis loops of a) KNN-Pr, b) KNN-Yb with various content [38].

are significantly affected by dopants substitution. Based on the hysteresis loops (Figure 4), remanent polarization, of both substituent ceramics were observed to be highest at 0.1 % mol content. Though, Pr-doped KNN more efficiently provide optimal piezoelectric conditions ( $P_r = 2.8 \mu\text{C}\cdot\text{cm}^{-2}$  and  $E_c = 7.2 \text{ kV}$ ) than Yb-doped KNN.

Modified KNN-based ceramics also showed prominent orthorhombic-tetragonal phases near room temperature ( $T_{oc}$ ). Therefore, the enhanced piezoelectric properties could be attributed to the polymorphic phase transition (PPT). This result matches those observed in the earlier study. Noheda et al. asserted that the improvement of properties is believed due to the coexistence of orthorhombic-tetragonal phases at room temperature. This nature could be explained in term of a rising number of polarization occur at this phase [39].

Later, Wei et al. gave the a brief explanation on enhancement mechanism of Pr-doped KNN [40]. As known, the doped  $\text{Pr}^{3+}$  ions can be integrated into the univalent ion site ( $\text{K}^+\text{Na}^+$ ) in KNN base compound (Figure 5a). Ions substitution would lead to the polarization of dipoles in a way that the positive charge ions (+) would displace along the electric field whilst negative charge ions would shift towards the opposite direction (Figure 5b). Hence, dipoles polarization would induce lattice distortion and yield to improvement in piezoelectric performances [41].

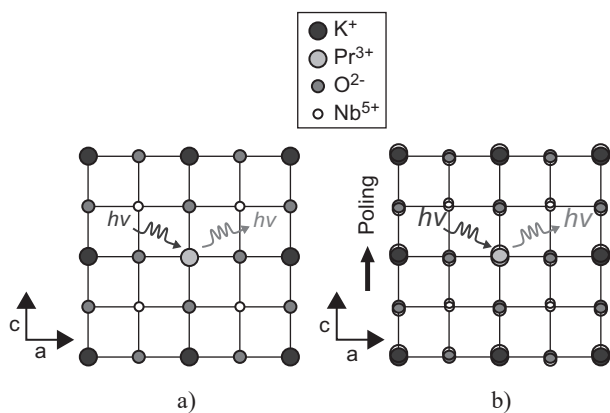


Figure 5. Polarization phenomenon a) KNN-Pr before polarization, b) KNN-Pr after polarization [40].

Similar densifications in BIT have been applied to KNN by Bathelt et al. [25-26]. The incorporation of Nd on A-site is well defined as its ionic radius is 127 pm which is smaller than  $\text{K} = 164 \text{ pm}$  and  $\text{Na} = 139 \text{ pm}$ . The dilatometric result depicted that sintering is stimulated by reducing the onset temperature from  $1150^\circ\text{C}$  to  $1125^\circ\text{C}$  with integration of 0.25 mol Nd (Figure 6) [42]. The finding supports the idea of Guanming et al., who suggested that rare earths could act as a sintering aid by lowering the sintering temperature, as well as improved densification [43]. However, higher levels of dopant impede densification caused by the presence of secondary phase and/or solubility limit. Interestingly, the

highest piezoelectric response coincides well with the inflection point of the permittivity curve in the transition region (PPT).

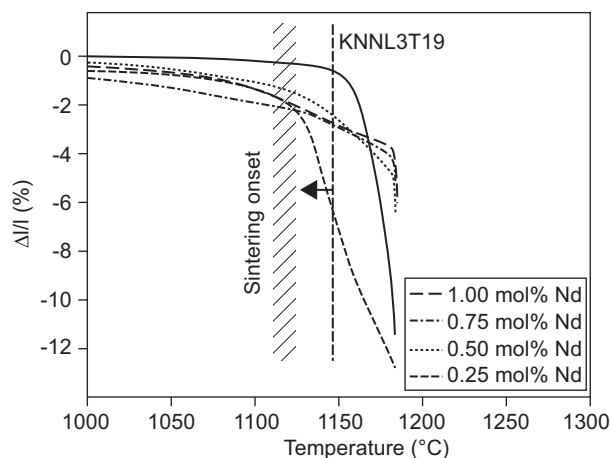


Figure 6. Influence of Nd-doping on densification behavior [42].

In parallel with the development of rare earths-doped BT [23], Zhou et al. attempted to succeed in developing rare earths doped-KNN [44]. As stated by Pires et al., an acceptable percentage difference between host ion and substituent should not exceed 30 % [45]. Hence, on the basis of ionic radii closeness,  $\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Ho}^{3+}$  were selected to compensate the ionic imbalance in A-site of KNN structure. In this study, Zhou and co-researchers employed Raman spectroscopy to identify phase transitions and structural changes of KNN ceramics. Phase transitions occurred in rare-earths-doped KNN samples had comparable shifting. It was revealed that the shoulders at low frequency near  $618 \text{ cm}^{-1}$  enlarged and the intensities became weak as rare-earths substitution is increased (Figure 7). The changes in these spectra implied a clear signal of disorder resulting from tetragonal distortion.

It was believed that at both, A1 and A2 modes a diffusion phase transition occurred from tetragonal to orthorhombic until tetragonal phase is dominant. Nevertheless, it was presented that the weaker line near  $863 \text{ cm}^{-1}$  referred to the tetragonal phase existence up to 4 wt. %. Apparently, rare-earths preference to enter the A-site of KNN is significant as a peak position of A1 and A2 modes showed very slight differences. As expected, the piezoelectric constant was enhanced from  $87 \text{ pC}\cdot\text{N}^{-1}$  up to  $128 \text{ pC}\cdot\text{N}^{-1}$  considering the effect on tetragonal-orthorhombic phase [39].

Up to date, the study on lanthanum oxide ( $\text{La}_2\text{O}_3$ ) and cerium oxide ( $\text{CeO}_2$ ) dope in KNN were undertaken by Zhao et al. [46]. Detailed examination on morphology showed the reduction in the grain size of doped KNN. Zhao et al. claimed that rare earth cations reduced the diffusion coefficient of vacancies. Consequently, mass transportation in the lattice KNN is weakened and grain



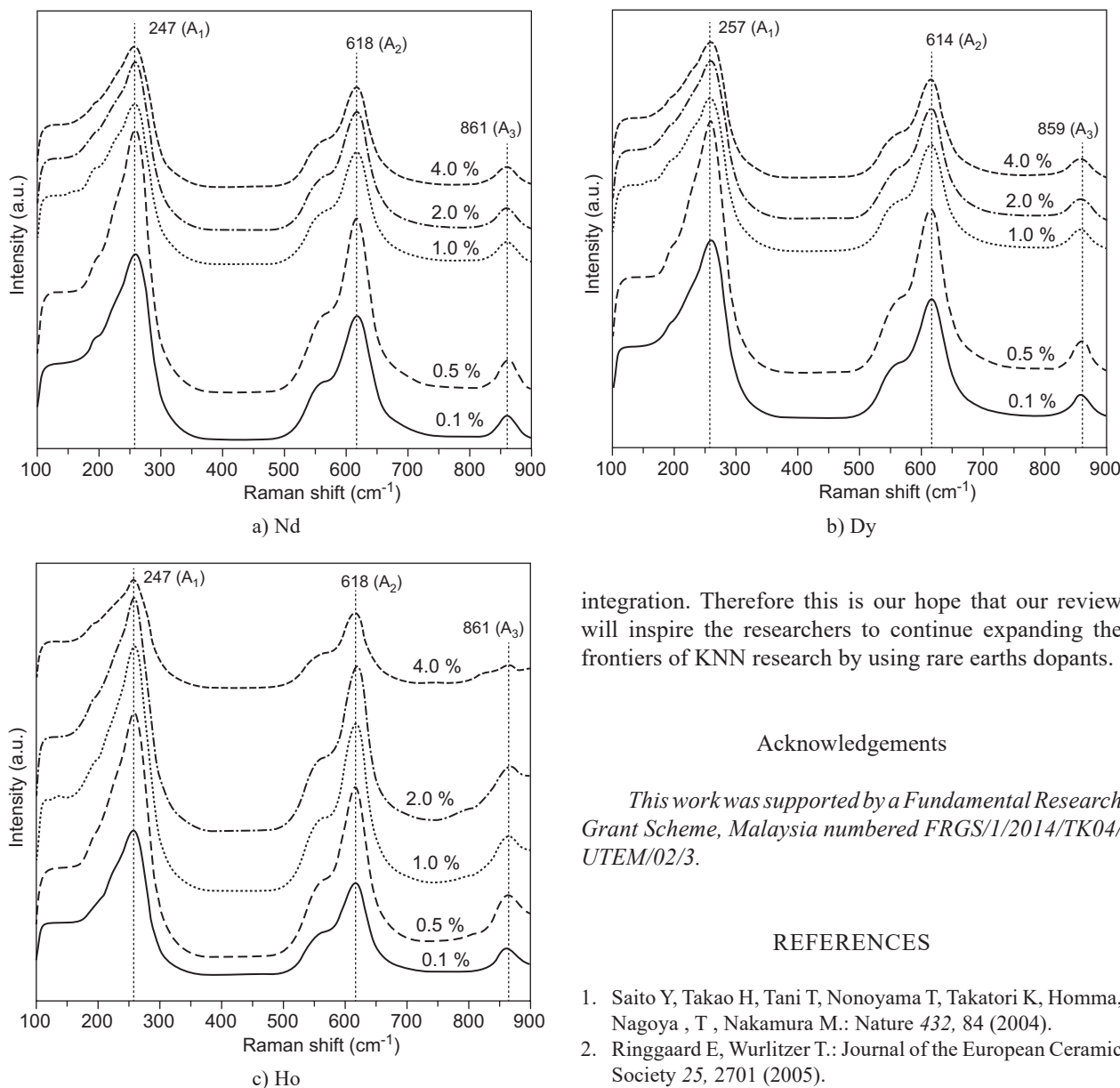


Figure 7. Raman spectra of a) Nd, b) Dy and c) Ho doped KNN at room temperature [45].

growth is inhibited. The finding of the present student is consistent with those of Qiu et al. who reported that rare earth oxides hindered the grain growth and create homogenous microstructure [47]. As expected, electrical properties of doped KNN were enhanced with the incorporation of those substituent.

## CONCLUSION

Despite the progresses that have been made in the modification of KNN by doping approaches, much work remains to be accomplished. The numerous study of rare earths in lead-free piezoelectric materials has resulted in increasing demand for more efficient means of rare earths

integration. Therefore this is our hope that our review will inspire the researchers to continue expanding the frontiers of KNN research by using rare earths dopants.

## Acknowledgements

This work was supported by a Fundamental Research Grant Scheme, Malaysia numbered FRGS/1/2014/TK04/UTEM/02/3.

## REFERENCES

1. Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma, Nagoya, T, Nakamura M.: *Nature* 432, 84 (2004).
2. Ringgaard E, Wurlitzer T.: *Journal of the European Ceramic Society* 25, 2701 (2005).
3. Jaffe B., Cook Jr.W.R, Jaffe H.: *Piezoelectric Ceramics*, p. 185-212. Academic Press, London, New York 1971.
4. Kumar P, Pattanaik M, Sonia.: *Ceramics International* 39, 65 (2013).
5. Feizpour M., Bafrooe H.B., Hayati R., Ebadzadeh T.: *Ceramics International* 40, 871 (2014).
6. Matsubara M, Kikuta K, Hirano S. *Journal of Applied Physics* 97, 105 (2005).
7. Amini M.M., Mirzae M.: *Ceramics International* 35, 2367 (2009).
8. Li G., Wu X., Ren R., Shi P.: *Thin Solid Films* 548, 556 (2013).
9. Rubio-Marcos F., Ochoa P., Fernandez J.: *Journal of the European Ceramic Society* 27, 4125 (2000).
10. Wang L., Shi P., Wu X.: *Journal of Alloys and Compund* 608, 202 (2014).
11. Matsubara M., Kikuta K., Hirano S.:
12. Wada S., Seike A., Tsurumi T.: *Jpn. J. Applied Physic* 40, (2001)
13. Lin D., Kwok K.W., Chan H.L.W.: *Journal of Applied Physics* 102, 034102 (2007).

14. Flückiger U., Arend H.: *Journal of Crystal Growth* *43*, 406 (1977).
  15. Hao J., Chu R., Xu Z., Zhang G., Li G.: *Journal of Alloys and Compound* *479*, 376 (2009).
  16. Wakasa Y., Kanno I., Yokokawa R., Kotera H., Shibata K., Mishima T.: *Sensors and Actuators A* *171*, 223 (2011).
  17. Taub J., Ramajo L., Castro M.S.: *Ceramics International* *39*, 3555 (2013).
  18. Kim J.H., Yoon S.H., Han Y.H.: *Journal of the European Ceramic Society* *27*, 1113 (2007).
  19. Chen M., Xu Q., Kim B.H., Ahn B.K., Chen W.: *Mater. Res. Bull.* *43*, 1420 (2008)
  20. Li Y.M., Chen W., Xu Q., Zhou J., Wang Y., Sun H.J.: *Ceramics International* *33*, 95 (2007).
  21. Gao Y.K., Chen Y.H., Ryu J.G., Uchino K., Viehland D.: *Jpn. J. Appl. Phys.* *40*, 687 (2001).
  22. Zhu Z., Li G., Li B., Yin Q., Jiang K.: *Ceramics International* *34*, 2067 (2008).
  23. Park K.J., Kim C.H., Yoon Y.J.: *Journal of the European Ceramic Society* *29*, 1735 (2009).
  24. Kim C.H., Park K.H., Yoon Y.J., Hong M.H., Hong J.O., Hur K.H.: *Journal of the European Ceramic Society* *28*, 1213 (2008).
  25. Kim J.S., Lee Y.S., Lee H J, Ahn C.W., Kim I.W., Jang M.S.: *Journal of Electroceramics* *21*, 633 (2008).
  26. Mao X.Y., Mao F.W., Chen X.B.: *Integrated Ferroelectrics* *79*, 155 (2006).
  27. Simões A.Z., Aguiar E., Ries A., Longo E., Varela J.: *Materials Letters* *61*, 588 (2007).
  28. Simões A.Z., Riccardi C.S., Moura F., Ries A., Junior N.L.A., Zaghete M.A., Stojanovic B., Longo E., Varela J.A.: *Materials Letters* *5*, 2842 (2004).
  29. Fu P., Xu Z., Chu R., Li W., Zhang G., Hao J.: *Materials Chemistry and Physics* *124*, 1065 (2010).
  30. Fu P., Xu Z., Chu R., Li W., Zhang G., Hao J.: *Materials Science and Engineering: B* *167*, 161 (2010).
  31. Fu P., Xu Z., Chu R., Li W., Zhang G., Hao H.: *Materials Chemistry and Physics* *31*, 796 (2010).
  32. Fu P., Xu Z., Chu R., Li W., Zhang G., Hao J.: *Journal of Alloys and Compounds* *508*, 546 (2010).
  33. Zhou C., Liu X., Li W., Yuan C.: *Materials Research Bulletin* *44*, 724 (2009).
  34. Xinyou H., Renke X., Chunhua G., Zhigang C.: *Journal of rare earths* *32*, 733 (2014).
  35. Mao X., Yin J., Zhou Q., Xue L., Yan Y.: *Ceramics International* *40*, 7007 (2014).
  36. Zhengfa L., Yongxiang L., Jiwei Z.: *Current Applied Physics* *11*, S2 (2010).
  37. Noheda B., Cox D.E.: *Phase Transit* *79*, 20 (2006).
  38. Wang Z., Zhuo Y., Xiao D., Wu W., Zhang C., Huang X., Zhu J.: *Current Applied Physics* *11*, S143 (2011).
  39. Noheda B., Cox D.E., Shirane G., Gonzalo J.A., Cross L.E.: *Applied Physics Letter* *74*, 2059 (1999).
  40. Wei Y., Wu Z., Jia Y., Wu J., Shen Y., Luo H.: *Applied Physics Letter* *105*, 42902 (2014).
  41. Takahashi M.: *Japanese Journal of Applied Physics* *7*, 1236 (1970).
  42. Bathelt R., Soller T., Benkert K., Schuh C., Roosen A.: *Journal of the European Ceramic Society* *32*, 3767 (2012).
  43. Guanming Q, Xi.kun L., Tai Q., Haitao Z., Hanghao Y., Ruiting M.: *Journal of Rare Earth* *25*, 281 (2007).
  44. Zhou J., Ma Q., Wang P., Cheng L., Liu S.: *Ceramics International* *40*, 2451 (2014).
  45. Pires A.M., Davolos M.R.: *Ceramics International* *40*, 7007 (2014).
  46. Zhao Y., Wang L., Huang R., Liu R., Zhou H.: *Ceramics International* *40*, 2505 (2014).
  47. Houabes M., Metz R.: *Ceramics International* *33*, 1191 (2007).
-