SYNTHESIS AND CHARACTERIZATION OF LEAD FREE $(K_{0.465}Na_{0.465}Li_{0.07})NbO_3$-$SrZrO_3$ PIEZOCERAMICS.

Mostafa, S. A. I.*; Ewais, E. M. M.† and Mohamed, A. A.§

* *Tabbin Institute for Metallurgical Studies (TIMS), P.O. 109 Helwan, 11421 Cairo, Egypt.*

† *Refractory and Ceramic Materials Division (RCMD), Central Metallurgical R&D Institute (CMRDI), P.O. 87 Helwan, 11421 Cairo, Egypt.*

§ *Chemistry Department, Faculty of Science, Helwan University.*

ABSTRACT

Lead-free piezoelectric ceramics composition: (1-x) $(K_{0.465}Na_{0.465}Li_{0.07})$ NbO_3-x$SrZrO_3$ (x = 0, 0.005, 0.050, 0.095, 0.140 and 0.185) have been synthesized by the conventional solid-state method. The effect of $SrZrO_3$ content on their phase structure and dielectric properties was studied. Phase composition, microstructure and dielectric constant also were investigated. It was found that $SrZrO_3$ diffuses into the $K_{0.465}Na_{0.465}Li_{0.07}NbO_3$ lattice to form a solid solution during sintering. With increasing the $SrZrO_3$ content, the grain size becomes smaller. The dielectric properties of investigated ceramics were measured at room temperature and 1 kHz and 0.95 $(K_{0.465}Na_{0.465}Li_{0.07})$ NbO_3-0.05$SrZrO_3$ ceramic posses high dielectric constant.

Keywords: Lead-free ceramics; KNN; dielectric properties.

1. INTRODUCTION

Lead-based ceramics Pb(Zr, Ti)O_3 (PZT) are widely used in many fields such as actuators, sensors, transformers and transducers due to their excellent piezoelectric properties [1, 2]. However, the environmental and health hazards of lead are well known and recycling and disposal of devices containing lead-based piezoelectric materials is of great concern. Throughout the world, demand is growing for materials that are benign to the environment and human health [3]. So that, much attention for lead-free piezoelectric ceramics has been paid to $(K_{0.5}Na_{0.5})NbO_3$ (KNN) based piezoelectric ceramics for its good electrical properties and high Curie temperature [4-16].

The (K,Na)NbO_3 (KNN)-based ceramics have been regarded as one of the most potential lead-free candidates since the breakthrough made by Saito et al[4].But the pure KNN ceramic is difficult to obtain the dense KNN ceramics because of the volatilization of the potassium element during their sintering.

For improving the density and electrical properties of the KNN ceramics, there are some research results have shown that the sintering as well as electrical properties of KNN ceramics can be improved by ABO_3- type addition, for example, $BaTiO_3$, $SrTiO_3$, $CaTiO_3$, $LiSbO_3$, $LiTaO_3$, $LiNbO_3$ and $SrTiO_3$[17]. A study of 0.5% alkali earth doping showed that strontium and calcium improve sintering and magnesium oxide hinders it, and Zirconia impedes grain growth [3].

In the present work, novel addition of SZ to modified KNN system by Li^+(KNLN). (1-x)($K_{0.465}Na_{0.465}Li_{0.07}$)$NbO_3$-x$SrZrO_3$ ceramics were prepared by the conventional solid-state method and the effect of SZ content on their phase structure dielectric properties was investigated.

2. Experimental Procedure

The lead-free ceramic compositions: (1-x) ($K_{0.465}Na_{0.465}Li_{0.07}$) NbO_3 – x $SrZrO_3$ (x =0.0, 0.005, 0.05, 0.095, 0.14 and 0.185 mol.) were prepared via conventional mixed – oxide method. Pure reagent powders of K_2CO_3 (99%), Na_2CO_3 (99%), Li_2CO_3 (99%), Nb_2O_5 (99.5%), $Sr(NO_3)_2$ (99%) and ZrO_2 (97%) were used as starting materials. A ($K_{0.465}Na_{0.465}Li_{0.07}$) NbO_3 (KNLN) powder was prepared before addition $SrZrO_3$ (SZ) reagent. The starting powders were weighed according to the stoichiometric formula and ball-milled with zirconia grinding ball and ethanol for 24 hrs. The same method procedure was applied to ball mill $Sr(NO_3)_2$ and ZrO_2 powders. Then the slurries were separately dried and calcined at 800°C for 6 hrs, respectively. After pulverization, the powder batches were weighed according to the stoichiometric formula and ball- milled together for 8 hrs to obtain compositions (1-x) KNLN – x SZ. The result slurry was then dried and pulverized sequentially. These powders, milled with 1 wt, % PVA (5% aqueous solution), then were uni-axially pressed into a disk of 13 mm diameter, at pressure of 300 MPa and subsequently sintered in air at 1100-1250°C, depending on the $SrZrO_3$ content.

The phase composition was analyzed by X-ray diffraction (XRD) analysis obtained by using CuKα radiation (X' Pert, PANalytical). Bulk density of the sintered samples was determined by the Archimedes method. The surface microstructure of the samples was observed using scanning electron microscopy SEM (FEI INSPECT 50 S).

The dielectric properties of ceramics were measured using a high precision LCR meter (GW Instek; LCR 821) by measuring the capacitance (C) and dielectric loss ($\tan\delta$) were measured at room temperature and 1 kHz. The relative permittivity was calculated according to the formula:

$$\varepsilon_r = \frac{Ct}{As_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where ε_r is the relative permittivity, C is the capacitance, t is the thickness of the sample, A is the area and ε_0 is the permittivity of air and is equal to 8.854×10^{-12} F/m.

3. Results and Discussion

All samples sintered at optimum sintering temperatures are given in table 1. It is commonly known that adding alkaline earth (AE) to substitute perovskite structure by creating A site vacancies in case of KNN leads to increase the density due to enhancement of promote densification [18]. The addition of SZ to KNN also can promote densification.

Figure 1 shows bulk density of (1-x) KNLN-xSZ ceramics and their relative density. The obtained densities of the investigated doped ceramics are in range of 4.22-4.33

g/cm^3, equivalent to the relative density 94-96%, where the theoretical density is 4.51 g/cm^3.

Table (1): Sintering temperature and characterization of lead-free (1-x) [$K_{0.465}Na_{0.465}Li_{0.07}$] NbO_3 – xSZ ceramics

X content of SZ	Sintering temp. (°C)	Bulk density g/cm^3	Relative density (%)	ε_r 1 kHz	tan δ 1 kHz
0	1100	4.127	91.5	1378	0.93
0.005	1100	4.248	94.2	1561	0.46
0.050	1200	4.258	94.4	2448	0.61
0.095	1200	4.228	93.7	1864	0.04
0.140	1250	4.288	95.1	1744	0.46
0.180	1250	4.330	96.0	1619	0.32

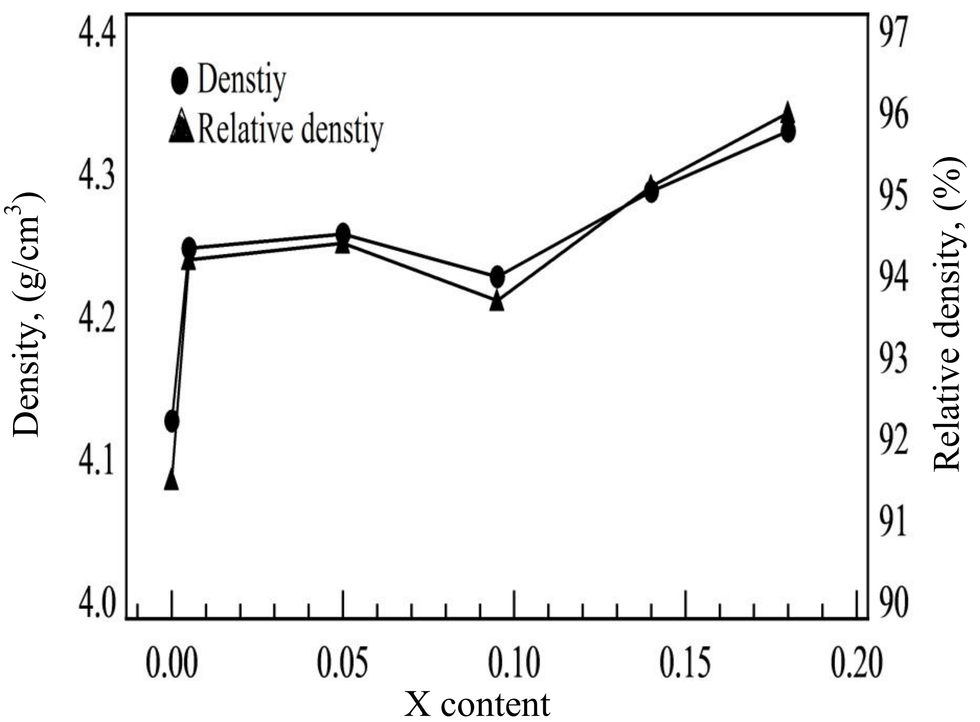

Fig. 1: Bulk density of the (1-x) [$K_{0.465}Na_{0.465}Li_{0.07}$]$NbO_3$ – x $SrZrO_3$ as a function of x sintered at 1100°C to 1250°C.

Figure 1(a) shows the XRD patterns at room temperature with the 2θ range from 20° to 70° of (1-x) KNLN-xSZ ceramic samples sintered at optimum sintering temperatures. It can be seen that samples with phase structure of perovskite ABO_3 type, SZ have diffused in to the KNLN lattice to form new solid solutions, while a trace amount of secondary phase lithium potassium niobium oxide, $K_3LiNb_6O_{17}$ (PDF card # 36-0533) with the tetragonal tungsten bronze structure was detected. Thesis result agrees with Tanaka et al. [19]. The appearance of second phase may be due to different crystal structures between KNN (orthorhombic perovskite structure) and LN (triagonal ilmenite structure) [20]. At high $LiNbO_3$ concentrations more than 0.06, the solubility of Li into

A sites of the KNN lattice becomes difficult [6], leading to the formation a $K_3LiNb_6O_{17}$ second phase.

Figure 2(b) shows the enlarged XRD patterns of the ceramics in the ranges of 2θ from 44° to 54°. It can be seen that the specimens have orthorhombic perovskite phases, which agree with the pure KNN ceramic (at x=0). However, with the increase of the SZ content, the crystalline system of the ceramics changes abnormally. When x<0.05, the ceramic display the coexistence of orthorhombic and tetragonal phases, and three specimens show no evidence of peak splitting at about 45° and is labeled as pseudo-cubic at x = 0.095-0.185.

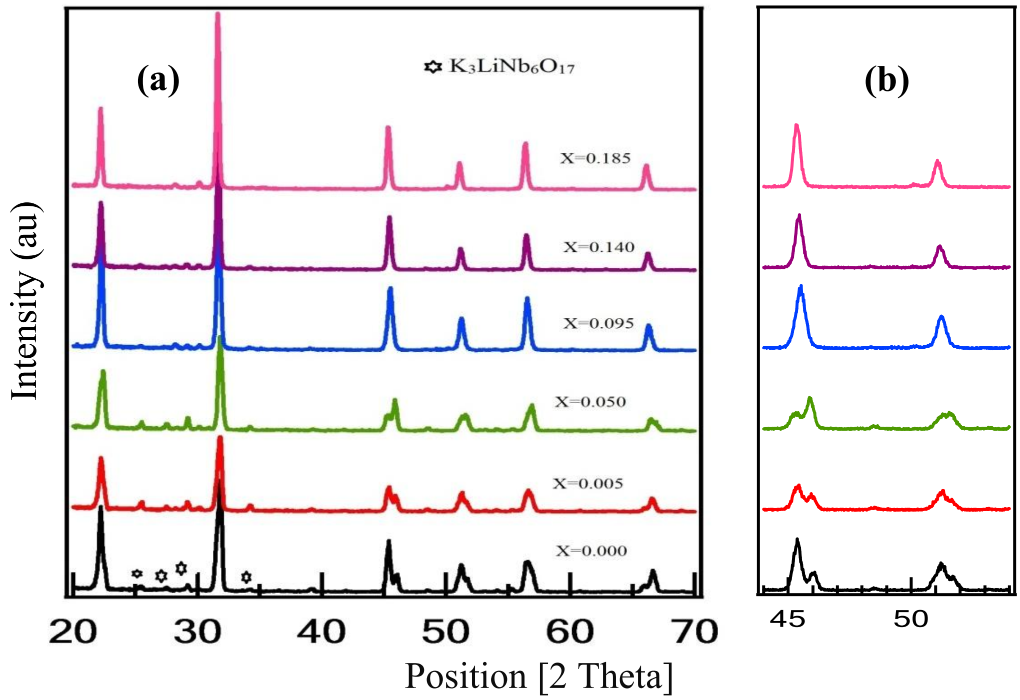

Fig. 2: X-ray diffraction patterns of the (1-x) [$K_{0.465}Na_{0.465}Li_{0.07}$] NbO_3 – x $SrZrO_3$ ceramics in the range of 2*θ* (*a*) from 20° to 70° and (*b*) from 44° to 54°.

Figure 3 shows the surface SEM pictures of (1-x) KNLN-xSZ ceramics. Seen from figure 3, with the increase of the SZ content, the grain size of the ceramics refines and becomes more homogeneous. This indicates that the addition of SZ promotes the nucleation but inhibits the growth of KNN grains. This is due to the addition of SZ into the KNLN, Sr^{2+} and Zr^{4+} ions distribute evenly in the KNLN ceramics and form nucleation points.

Figure 4 shows the dependence of ε_r and of the (1-x)KNLN-xSZ specimens on x. At figure 4, with the increase of x, the dielectric constant ε_r of the ceramics first increases evidently and then decreases slightly, and at x=0.05, ε_r reaches its maximum value (2448). The piezoelectric coefficient (d_{33}) and dielectric constant ε_r are interrelated (i.e., a ceramic with high piezoelectric coefficient also exhibits a large dielectric constant). According to phenomenological theory, piezoelectric coefficient (d_{33}) is related to ε_r via a general equation $d_{33} = 2\ \varepsilon_o\varepsilon_r Q_{11}Ps$ [21]. Where d_{33} is the piezoelectric coefficient, P_s

the remnant polarization on poling, ε_r the dielectric constant, ε_o the permittivity of free space, and Q_{11} the electrostriction coefficient.

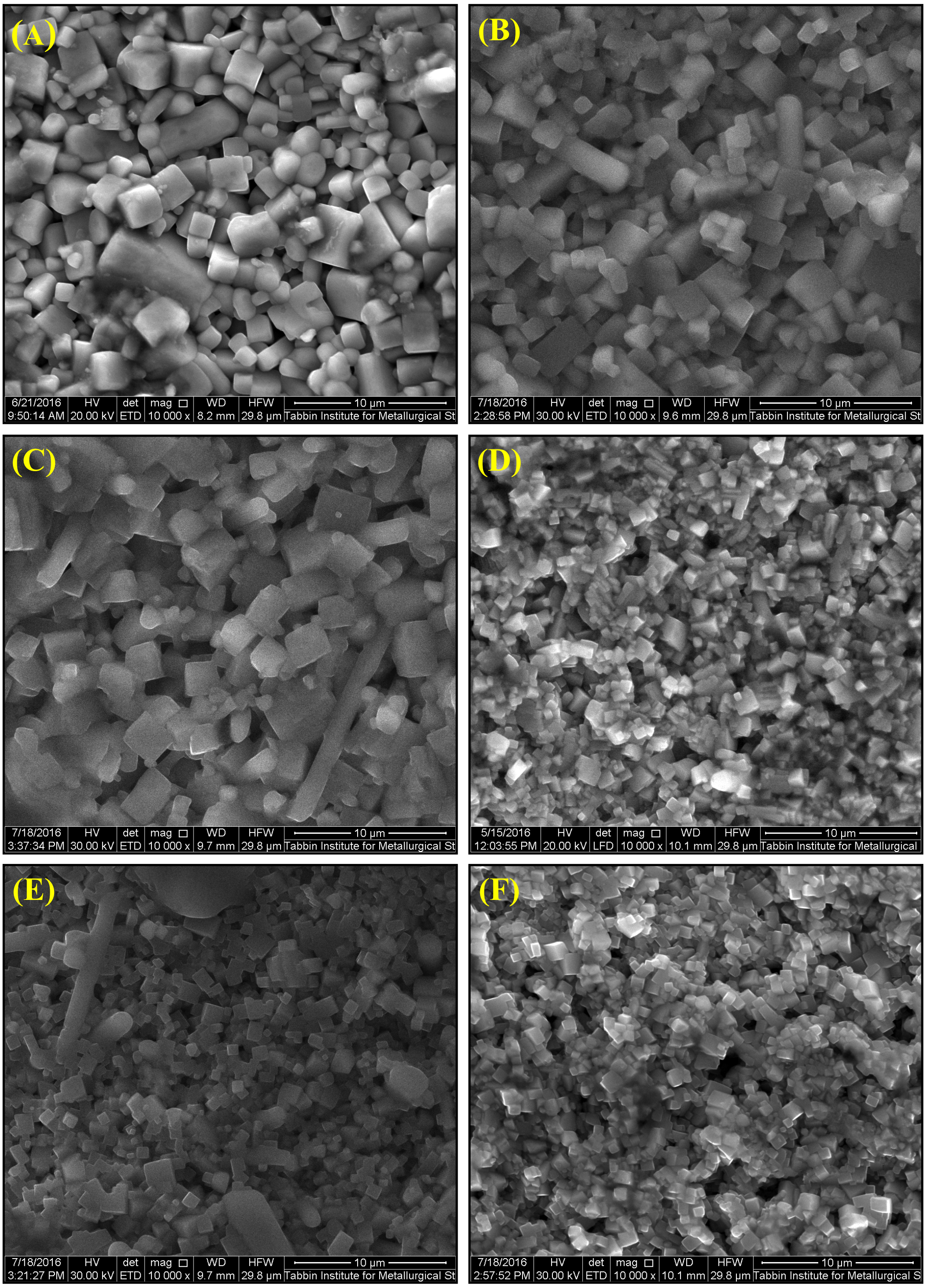

Fig. 3: SEM photographs of (1-x) $[K_{0.465}Na_{0.465}Li_{0.07}]$ NbO_3 – x $SrZrO_3$ ceramics surfaces: (a) *x*=0; (b) *x*=0.005; (c) *x*=0.05; (d) *x*=0.095; (e) *x*=0.14; (f) *x*=0.185.

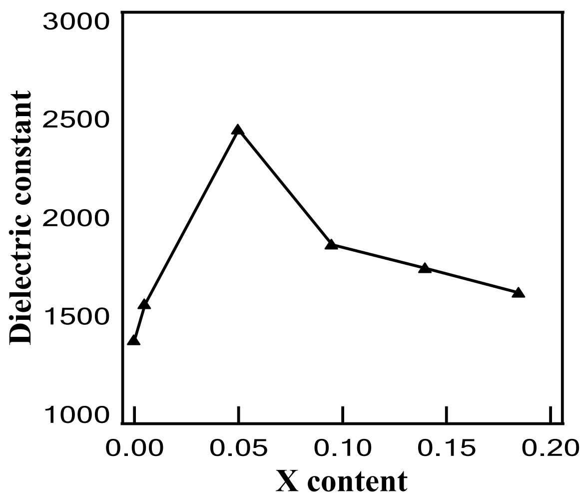

Fig. 4: Dielectric properties of (1-x) [$K_{0.465}Na_{0.465}Li_{0.07}$] NbO_3 – x ceramics as a function of x were measured at room temperature and 1 kHz.

4. CONCLUSIONS

- Lead-free ceramics (1-x) ($K_{0.465}Na_{0.465}Li_{0.07}$) NbO_3 – x $SrZrO_3$ (x = 0.005, 0.05, 0.095, 0.14 and 0.185) have been prepared by a conventional sintering technique, and their structure and dielectric properties have been studied. The ceramics possess a perovskite structure ABO_3 type. SZ have diffused in to the KNLN lattice to form new solid solutions. After the doping of SZ, the grain growth is inhibited and dielectric constant increases by doping of SZ until x = 0.50 where $\varepsilon_r \sim 2448$ and then decreased.

Acknowledgments

This work was supported by Tabbin Institute for Metallurgical Studies (TIMS), and Refractory and Ceramic Materials Division (RCMD), Central Metallurgical R&D Institute, Egypt.

5. REFERENCES

[1] Jaffe, B.; Cook, W. and Jaffe, H.: "Piezoelectric ceramics". Academic Press, NY, p. 92, (1971).

[2] Berlincourt, D. in: O. E. Mattiat (Ed.): "Ultrasonic transducer materials: Piezoelectric crystals and ceramics". Plenum Press, London, Chapter 2, (1971).

[3] Rödel, J.; Jo, W.; Seifert, K. T. P.; Anton, E. M.; Granzow, T. and Damjanovic, D.: "Perspective on the development of lead-free piezoceramics". Journal of the American Ceramic Society, 92, pp. 1153-1177, (2009).

[4] Saito, Y.; Takato, H.; Tani, T.; Nonoyama, T.; Takatori, K.; Homma, T.; Nagaya, T. and Nakamura, M.: "Lead-free piezoceramics". Nature, 432, pp. 84-87, (2004).

[5] Zhang, S.; Xia, R. and Shrout, T. R.: "Lead-free piezoelectric ceramics vs. PZT?". Journal of Electro ceramics, p. 19, 251-257, (2007).

[6] Guo, Y.; Kakimoto, K. and Ohsato, H.: "Phase transitional behavior and piezoelectric properties of ($Na_{0.5}K_{0.5}$)NbO_3-$LiNbO_3$ ceramics". Applied Physics Letters, 85, pp. 4121-4123, (2004).

[7] Zuo, R. Z.; Lv, D. Y.; Fu, J.; Liu, Y. and Li, L. T.: "Phase transition and electrical properties of lead free $(Na_{0.5}K_{0.5})NbO_3$-$BiAlO_3$ ceramics". Journal of Alloys and Compounds, 476, pp. 836-839, (2009).

[8] Zhao, Y.; Huang, R.; Liu, R.; Wang, X. and Zhou, H.: "Enhanced dielectric and piezoelectric properties in Li/Sb-modified $(Na,K)NbO_3$ ceramics by optimizing sintering temperature". Ceramic International, 39, pp. 425-429, (2013).

[9] Wattanawikkam, C.; Vittayakorn, N. and Bongkarn, T.: "Low temperature fabrication of lead free KNN-LS-BS ceramics via the combustion method". Ceramics International, 39, pp. 399-403, (2013).

[10] Rubio-Marcos, F.; Reinos, J. J.; Vendrell, X.; Romero, J. J.; Mestres, L.; Leret, P.; Fernández, J. F. and Marchet, P.: "Structure, microstructure and electrical properties of Cu^{+2} doped $(K,Na,Li)(Nb,Ta,Sb)O_3$ piezoelectric ceramics". Ceramics International, 39, pp. 4139-4149, (2013).

[11] Wu, J.; Xiao, D.; Wang, Y.; Zhu, J.; Shi, W.; Wu, W.; Zhang, B. and Li, J.: "Phase structure, microstructure and ferroelectric properties of $(1-x)[(K_{0.50}Na_{0.50})_{0.94}Li_{0.06}](Nb_{0.94}Sb_{0.06})O_3$-$xCaTiO_3$ lead-free ceramics". Journal of Alloys and Compounds, 476, pp. 782-786, (2009).

[12] Du, H.; Zhou, W.; Luo, F.; Zhu, D.; Qu, S.; Li, Y. and Pei, Z.: "Structure and electrical properties' investigation of $(K_{0.5}Na_{0.5})NbO_3$-$(Bi_{0.5}Na_{0.5})TiO_3$ lead-free piezoelectric ceramics". Journal of Physics D: Applied Physics, 85, p. 410-416, (2008).

[13] Cheng, X.; Wu, J.; Wang, X.; Zhang, B.; Zhu, J.; Xiao, D.; Wang, X. and Lou, X.: "Giant d_{33} in $(K,Na)(Nb,Sb)O_3$-$(Bi,Na,K,Li)ZrO_3$ based lead-free piezoelectrics with high T_c". Applied Physics Letters, 103, 052906, (2013).

[14] Gao, Y.; Zhang, J.; Qing, Y.; Tan, Y.; Zhang, Z. and Hao, X.: "Remark ably strong piezoelectricity of lead-free $(K_{0.45}Na_{0.55})_{0.98}Li_{0.02}(Nb_{0.77}Ta_{0.18}Sb_{0.05})O_3$ ceramic". Journal of the American Ceramic Society 94, pp. 2968-2973, (2011).

[15] Yang, Z. P.: "Effects of composition on phase structure, microstructure and electrical properties of $(K_{0.5}Na_{0.5})NbO_3$-$LiSbO_3$ ceramics". Materials Science and Engineering, A432, pp. 292-298, (2006).

[16] Rubio-Marcos, F.; Marchet, P.; Romero, J. J. and Fernandez, J. F.: "Structural, microstructural and electrical properties evolution of $(K,Na,Li)(Nb,Ta,Sb)O_3$ lead-free piezoceramics through NiO doping". Journal of the European Ceramic Society, 31, pp. 2309-2317, (2011).

[17] Chen, T.; Wang, H.; Zhang, T.; Wang, G.; Zhou, J.; Zhang, J. and Liu, Y.: "Enhanced piezoelectric coefficient of HfO_2-modified $(K_{0.44}Na_{0.56})_{0.94}Li_{0.06}(Nb_{0.94}Sb_{0.06})O_3$ lead-free ceramics". Journal of the Ceramics International, 40, pp. 3755-3759, (2014).

[18] Malic, B.; Bernard, J.; Holc, J.; Jeko, D. and Kosec, M.: "Alkaline-earth doping in $(K,Na)NbO_3$ based piezoceramics". Journal of the European Ceramic Society, 25, pp. 2707-2711, (2005).

[19] Tanaka, J.; Onoda, Y.; Tsukioka, M.; Shimazu, M. and Ehara, S.: "The RMN study of Li ion motion in $K_3LiNb_6O_{17}$ and K_3LiTaO_{17}". Japanese Journal of Applied Physics, 21, pp. 451-455, (1982).

[20] Inbar, I. and Cohen, R.: "Origin of ferroelectricity in $LiNbO_3$ and $LiTaO_3$". *Ferroelectrics,* 194, pp. 83-95, (1997).

[21] Shujun, Z.; Ru, X. and Thomas, R.: "Lead-free piezoelectric ceramic vs. PZT?". Journal of Electroceram, 19, pp. 251-257, (2007).