Dielectric Spectroscopy of the (K_{0.44}Na_{0.52}Li_{0.04})_{0.97}La_{0.01}Nb_{0.9}Ta_{0.1}O₃ Ceramic Obtained by Sol-Gel

R. López-Noda

Instituto de Cibernética, Matemática y Física, Universidad de La Habana, La Habana, Cuba

J. Portelles

Instituto de Cibernética, Matemática y Física, Universidad de La Habana, La Habana, Cuba; Facultad de Física, Universidad de La Habana, San Lázaro y L, La Habana 10400, Cuba.; Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, B.C, México, 22860

G. Rojas-George

CONACYT - Centro de Investigación en Materiales Avanzados S.C. (CIMAV), Miguel de Cervantes 120, Complejo Industrial Chihuahua, Cd. de Chihuahua, Chihuahua, México

A. Reyes-Rojas

Centro de Investigación en Materiales Avanzados S.C. (CIMAV), Miguel de Cervantes 120, Complejo Industrial Chihuahua, Cd. de Chihuahua, Chihuahua, México.

J. Fuentes

Facultad de Física, Universidad de La Habana, San Lázaro y L, La Habana 10400, Cuba.; Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, B.C, México, 22860

J.F. Rebellon-Watson

Instituto de Cibernética Matemática y Física, Departamento de Física Aplicada, Cuba

H'Linh Hmök (✉ hlinh.hmok@tdtu.edu.vn)

Computational Laboratory for Advanced Materials and Structures, Advanced Institute of Materials Science, Ton Duc Thang University, Ho Chi Minh, Vietnam; Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh, Vietnam <https://orcid.org/0000-0001-6291-6047>

M.P. Cruz

Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, B.C, México, 22860

J.M. Siqueiros Beltrones

Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, B.C, México, 22860

Keywords: Sol-Gel, KNN ceramics, conductivity, spectroscopic, impedance

Posted Date: August 11th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-55576/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Ho Chi Minh City, Vietnam, August 05, 2020

Dear Prof. Longtu Li
General Editor
Journal of Advanced Ceramics

We are submitting via online, the original manuscript entitled: **“Dielectric Spectroscopy of the $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})_{0.97}\text{La}_{0.01}\text{Nb}_{0.9}\text{Ta}_{0.1}\text{O}_3$ ceramic obtained by Sol-Gel”** by René López Noda, Jorge Portelles, Gabriel Rojas George, Armando Reyes Rojas, Juan Fuentes, Julia Flavia Rebellon Watson, H'Linh Hmök, Ma. Paz Cruz, Jesús M. Siqueiros Beltrones, for publication in *Journal of Advanced Ceramics*.

All authors have contributed intellectually to the work and have approved its final version of it. In their name, I declare that the work is original and has not been previously published or is in the process of being reviewed by any other journal.

Lead-free piezoelectric ceramics that could substitute the traditional $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and the health hazard inherent to its synthesis, use and disposal are of great interest in the materials science community. One of the most promising substitutes is $(\text{K,Na})\text{NbO}_3$. In this work, $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})_{0.97}\text{La}_{0.01}\text{Nb}_{0.9}\text{Ta}_{0.1}\text{O}_3$ lead free ceramics were synthesized by sol-gel. This compound only presents an analog synthesized by us by the RTGG method; it has not yet been homologated internationally. Among the interesting results reported in this paper is that using the sol-gel method we obtain a compound with values of the maximum relative permittivity (ϵ_{max}) at $T_{\text{T-C}}$ is 3000, which is larger than those of samples grown by the traditional solid-state technique although lower than those obtained by the RTGG method which is a considerably more elaborate method. We also find that La and Li doping induces shifts of the orthorhombic-to-tetragonal and tetragonal-to-cubic transition temperatures toward lower temperatures, which is also beneficial for applications. The conductivity of the compound shows lower values than those of the corresponding compound grown by the RTGG method, as a consequence of better composition homogeneity leading to lower dissipation losses. The mechanisms behind the measured properties of the compound are discussed at length along with the text. Taking into account the reported results and the ensuing discussion based on rigorous experiments, we hope to convince you and the reviewers that our paper deserves publication in your prestigious journal.

We propose the following researchers who have extensive experiences on ferroelectric materials, piezoelectric ceramics, ceramic processing to evaluate the manuscript:

Prof. Dunmin Lin

College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610066, China

Key Laboratory of Information Materials of Sichuan Province & School of Electrical and Information Engineering, Southwest Minzu University, Chengdu 610041, China

E-mail: ddmd222@sicnu.edu.cn

Prof. Chan-Wong Lai Wa Helen

Chair Professor & Associate Dean of Faculty of Applied Science & Textiles

Office: CD627

Tel. : (852) 2766 5692

Fax.: (852) 2333 7629

Email: apahlcha@polyu.edu.hk

Dr. Yudong Hou

College of Materials Science and Engineering, Beijing University of Technology,
Beijing 100124, China

Email: ydhoul@bjut.edu.cn

We will be looking forward to your response.

Sincerely yours,

H'Linh Hmök

Corresponding author

E-mail: hlinh.hmok@tdtu.edu.vn

Dielectric Spectroscopy of the $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})_{0.97}\text{La}_{0.01}\text{Nb}_{0.9}\text{Ta}_{0.1}\text{O}_3$ ceramic obtained by Sol-Gel

R. López-Noda¹, J. Portelles^{1,2,3}, G. Rojas-George^{3,4}, A. Reyes-Rojas⁵, J. Fuentes^{2,3}, J.F. Rebellon-Watson⁶, H'Linh Hmök^{7,8,*}, M.P. Cruz³, J.M. Siqueiros Beltrones³.

¹*Instituto de Cibernética, Matemática y Física, Universidad de La Habana, La Habana, Cuba.*

²*Facultad de Física, Universidad de La Habana, San Lázaro y L, La Habana 10400, Cuba.*

³*Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, B.C, México, 22860*

⁴*CONACYT – Centro de Investigación en Materiales Avanzados S.C. (CIMAV), Miguel de Cervantes 120, Complejo Industrial Chihuahua, Cd. de Chihuahua, Chihuahua, México.*

⁵*Centro de Investigación en Materiales Avanzados S.C. (CIMAV), Miguel de Cervantes 120, Complejo Industrial Chihuahua, Cd. de Chihuahua, Chihuahua, México.*

⁶*Instituto de Cibernética, Matemática y Física, Departamento de Física Aplicada, Cuba*

⁷*Computational Laboratory for Advanced Materials and Structures, Advanced Institute of Materials Science, Ton Duc Thang University, Ho Chi Minh City, Vietnam*

⁸*Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam*

*E-mail address of the corresponding author: hlinh.hmok@tdtu.edu.vn

Abstract

$(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})_{0.97}\text{La}_{0.01}\text{Nb}_{0.9}\text{Ta}_{0.1}\text{O}_3$ lead free ceramics were synthesized by sol-gel method. Their morphology, crystal structure and spectroscopic dielectric properties were analyzed by the appropriate techniques. The co-existence of an orthorhombic and a tetragonal ferroelectric phase at room temperature is confirmed by Rietveld analysis. La and Li cations are effective in shifting down the ferroelectric transition temperatures. The tetragonal to cubic transition, ($T_{\text{T-C}}$), takes place at 371 °C while the orthorhombic to tetragonal, ($T_{\text{O-T}}$), occurs at 110 °C, and the maximum relative permittivity (ϵ_{max}) at $T_{\text{T-C}}$ is 3000, which is among the highest for KNN-based ceramics obtained by different methods. Conductivity behaves according to Jonscher's law in the frequency and temperature range of this study. The activation energy values corresponding to the different conduction mechanisms were obtained. The results were compared with those for the same composition obtained by combining the reactive template grain growth (RTGG) technique and the solid-state method.

Keywords: Sol-Gel, KNN ceramics, conductivity, spectroscopic, impedance

1 Introduction

Lead-free piezoelectric ceramics that could substitute the traditional $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) and the health hazard inherent to its synthesis, use and disposal are of great interest in the materials science community. One of the most promising substitutes is $(\text{K,Na})\text{NbO}_3$ (KNN) [1], whose properties have been improved by the addition of dopants such as Li and Ta to reduce the orthorhombic to tetragonal ($T_{\text{O-T}}$) [2-3], and La to reduce the tetragonal to cubic ($T_{\text{T-C}}$) ferroelectric phase transition temperatures [4-5]. One of the first and more widely used methods to prepare KNN-based compounds is the solid-state reaction (SSR) procedure, but long processing times and high calcination and sintering temperatures are needed to produce high quality and dense ceramics. A different approach was taken by combining SSR with the reactive template grain growth (RTGG) method, producing thus not only dense but also textured ceramics, particularly of the composition $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})(\text{Nb}_{0.84}\text{Ta}_{0.10}\text{Sb}_{0.06})\text{O}_3$ [1]. Unfortunately, the process is comparatively complicated, time-consuming and difficult to master. Efforts have been done to reproduce it as was reported by Portelles *et al.* [6] who also improved its properties by adding La to stabilize the compound obtaining better results for the $(\text{K}_{0.5}\text{Na}_{0.5})_{0.94}\text{Li}_{0.06}]_{0.97}\text{La}_{0.01}(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_3$, $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ doped 5 at% of La and Ti, $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})_{0.97}\text{La}_{0.01}\text{Nb}_{0.9}\text{Ta}_{0.1}\text{O}_3$ composition [5, 7-9]. On the other hand, using sol-gel, the $(1-x)(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-x\text{LiNbO}_3$ composition, as well as other KNN-based compounds, are easy to synthesize [10] resulting in good composition, stability, higher density, morphology control, and high reproducibility.

In previous studies, we have characterized the influence of La substitution in the KNN perovskite's A-site obtained by the ceramic method [9]. In this work, we report a similar study where a trivalent ion (La^{3+}) is doped into site-A of $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})_{0.97}\text{La}_{0.01}\text{Nb}_{0.9}\text{Ta}_{0.1}\text{O}_3$ (KNNLiTaLa0.01) ceramic samples obtained by the sol-gel technique. Li, La and Ta were substituted in the crystal structure to reduce the orthorhombic to tetragonal and tetragonal to cubic transition temperatures. It is found that Li and La doping of a polymorphic KNN compound generates oxygen vacancies strongly affecting its electric and dielectric properties. The characterization of

its dielectric properties, ac conductivity as functions of temperature and frequency in the neighborhood of its ferroelectric-paraelectric phase transition is reported. The results are compared with those obtained for samples of a similar composition obtained by a combined SSR-RTGG method [4]

2 Experimental

Ceramics of $(K_{0.44}Na_{0.52}Li_{0.04})_{0.97}La_{0.01}Nb_{0.9}Ta_{0.1}O_3$ were synthesized by sol-gel using Nb_2O_5 (99.9%,) and La_2O_3 (99.99%) from Alfa Aesar; Ta_2O_5 (99.993%), Na_2CO_3 (99%), K_2CO_3 (99%) and oxalic acid $C_2H_2O_4$ (97%) from Sigma Aldrich; as well as Li_2CO_3 (99%, Fraga Labs) and nitric acid (HNO_3 , 64%, Jalmek). 40 mol of nitric and 2.5 mol of oxalic acid per mol of the resultant KNNLLT were used as dissolvent and chelating agents. The working solution was prepared in a glass beaker covered with a watch glass. As a first step Nb_2O_5 and nitric acid were mixed, then Ta_2O_5 and La_2O_3 were incorporated, and finally Na_2CO_3 , K_2CO_3 , Li_2CO_3 , and oxalic acid were also added and mixed; afterward the beaker was uncovered letting the gel formation to begin. This process was conducted with continuous stirring at 900 rpm and a temperature of 80 °C. The obtained gel was heated at 250-300 °C to remove it from the beaker leaving a powder that was ground and then annealed at 800 °C. The powder was pressed to form 6 mm diameter, 0.5 mm thick pellets that were sintered at 1200 °C for 2h.

The crystal structure of the samples was determined by X-ray diffraction (XRD) using a PAN analytical XPert PRO diffractometer, with a $CuK\alpha$ ($\lambda_{01} = 1.5406 \text{ \AA}$) radiation, from 20° $\square$ 2 θ $\square$ 90°, using a step-scanning mode with a step size of 0.05° and 100 s of step counting time. Rietveld refinement was performed to the x-ray diffraction data until a $\chi^2 < 2$ was reached, using a Thompson–Cox–Hasting pseudo-Voigt function profile (TCHZ) for all the peaks. For morphology, a JEOL JSM 5300 Scanning Electron Microscope (SEM) was used on fractured samples.

After silver paint electrodes were thermally diffused on the samples' flat surfaces, relative permittivity, and dielectric loss, as functions of temperature were evaluated in a custom-made stage using an HP 3238 LCR. The samples were heated at a rate of 1 °C/min while applying a voltage of 1 V; measurements were taken in the 100 Hz to 1 MHz range in a 30-500 $\pm$ 1 °C interval.

3.2 Morphology

Fig. 2 shows an SEM micrograph of the KNNLiTaLa0.01 ceramic sample fracture surface. The observed grain size is $1.6 \mu\text{m}$ with a $\sigma = 0.8 \mu\text{m}$ standard deviation, with a predominantly cubic-like microstructure. The low porosity appreciated in the sample gives rise to a relatively high density, 4.2 g/cm^3 , as compared to the theoretical density value of 4.51 g/cm^3 [12], that favors the good dielectric-piezoelectric properties discussed below. Nevertheless, the density is lower than that obtained by the RTGG preparation method [6, 9].

Fig. 2. SEM image of the fracture surface of a $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})_{0.97}\text{La}_{0.01}\text{Nb}_{0.9}\text{Ta}_{0.1}\text{O}_3$ sample sintered at 1200°C .

3.3 Dielectric properties

Fig. 3a) and 3b), show the relative dielectric permittivity (ϵ) and dielectric loss ($\tan \delta$) as functions of temperature, for frequencies at 0.1, 0.5, 1.0, 5.0, 10, 50, 100, 500 kHz and 1 MHz, in the $30\text{--}500^\circ\text{C}$ range. The comparison with other similar KNN and KNN doped compounds shows significantly lower transition temperatures, a fact that confirms the incorporation of La into the structure [7]. The maximum permittivity of $\epsilon_{\text{max}} = 3000$ is obtained at $T_{\text{T-C}} = 371^\circ\text{C}$, the tetragonal-to-cubic transition temperature. The maximum permittivity obtained is larger than those of other KNN compounds obtained by the conventional ceramic method [7] and comparable to that of any other similar ceramics obtained by the sol-gel method [10]. The downshift in temperature for the tetragonal-to-cubic transition is even higher for the ceramics of the same

composition obtained by the RTGG method ($T_{T-C} = 214\text{ }^{\circ}\text{C}$) [9] highlighting the effect of density and texture associated to such preparation method. The orthorhombic-to-tetragonal transition, on the other hand, occurred at $T_{O-T} = 110\text{ }^{\circ}\text{C}$. Both transitions take place at lower temperatures as compared with those corresponding to undoped KNN [13]. The shift of the orthorhombic-to-tetragonal and tetragonal-to-cubic toward lower temperatures is with respect to the corresponding ones in undoped KNN and $\text{La}_{0.05}$, $\text{Li}_{0.05}$ doped KNN obtained via conventional solid-state processing, is notable and is assumed to be related to the $\text{Li}_{0.04}$ and $\text{La}_{0.01}$ doping and the sol-gel processing of the samples [10]. The permittivity (ϵ) analysis shows no dispersion with frequency at T_{T-C} (see Fig. 3a)), meaning a *normal*-type transition. In contrast, the dispersion at T_{O-T} indicates the existence of polymorphic phases, generated by La doping [9]. Table 2 shows the comparison of the transition temperatures and ϵ_{max} with those of similar compounds. The obtained compound presents similar values of the temperature for the permittivity maxima for the tetragonal-to-cubic polymorphic transition than similar compounds obtained by sol-gel but somewhat lower than those in other reports obtained by the same method, due to the La doping.

Fig. 3. (color online) a) The relative dielectric permittivity (ϵ) and b) dielectric loss ($\tan \delta$) at different frequencies, as functions of temperature, for the KNNLiTaLa0.01 ceramic showing the orthogona-to-tetragonal and the tetragona-to-cubic critical temperatures.

Table 2. Dielectric and transition temperatures magnitudes

System/[Reference]	Method	T _{O-T} (°C)	T _{T-C} (°C)	ε _{max}	Tanδ
(K _{0.5} Na _{0.5})NbO ₃ [3]	SSR	200	420	~5800	~17
(K _{0.44} Na _{0.52} Li _{0.04}) _{0.97} La _{0.01} Nb _{0.9} Ta _{0.1} O ₃ [8]	SSR	~175	400	~3100	N/A
(K _{0.44} Na _{0.52} Li _{0.04}) _{0.97} La _{0.01} Nb _{0.9} Ta _{0.1} O ₃ [9]	RTGG	90	214	7500	0.15

3.4 Conductivity

Electric conductivity and dielectric properties are related in a ferroelectric system. The conductivity is affected by impurities, defects, changes in the polarization, and free charge transport. One way of analyzing the conductivity behavior is by following Jonscher's formalism [14]. Here, the electric conductivity as a function of frequency (ω) is given by Jonscher's universal law:

$$\sigma(\omega) = \sigma_{dc} \left[1 + \left(\frac{\omega}{\omega_H} \right)^n \right] + A\omega \quad (1)$$

Where σ_{dc} , ω_H , are the dc conductivity (long range), hopping frequency respectively and n and A are fitting exponent and coefficient. All terms are temperature dependent. The first term in Eq. (1) refers to the Universal Dielectric Response (UDR) and the second to the Near Constant Loss (NCL). [15]

As is well known, the temperature dependence of the dc conductivity and the hopping frequency expressed by an Arrhenius law:

$$\sigma_{dc} T = \sigma_0 \exp \left(-\frac{U_{dc}}{k_B T} \right) \quad (2)$$

$$\omega_H = \omega_0 \exp \left(-\frac{U_H}{k_B T} \right) \quad (3)$$

Where U_{dc} and U_H are the activation energies of the dc conductivity and the hopping conduction mechanism, respectively, σ_0 and ω_0 are pre-exponential factors and $k_B = 8.617 \times 10^{-5} \text{ eV K}^{-1}$ is Boltzmann's constant.

Fig. 4 shows the frequency dependence of *ac* conductivity. It can be seen that it follows Jonscher's law in the 100Hz-1MHz frequency and the 250-500 °C temperature intervals. The obtained conductivity values are significantly lower concerning those of the samples obtained by the RTGG method [9]. This fact, together with the XRD results presented in Fig. 1, shows the effectiveness of the homogenization of the KNNLiTaLa0.01 compound by Sol-Gel method as compared with that obtained via RTGG method [9]. Fig. 5a) shows the behavior of the hopping frequency obtained using Jonscher's law with temperature. It can be seen that it obeys an Arrhenius law in intervals below and above the critical temperature T_{T-C} . Similarly, Fig. 5b) shows the behavior of the *dc* conductivity obtained from Jonscher's law, and it also obeys an Arrhenius law below and above the critical temperature T_{T-C} . The change in the value of the activation energy around the critical temperature $T_{T-C} = 361$ °C in both hopping and *dc* conductivity processes has been demonstrated before by many researchers [6, 15-16]. In Fig. 5a), the change in the hopping activation energy value is registered while passing the tetragonal-to-cubic phase transition from 0.54 eV to 1.12 eV. This is attributed to a change in charge carrier type in the hopping mechanism as the transition of the sample from ferroelectric to paraelectric takes place. These activation energy values are associated to single and double ionized oxygen vacancies [17-18]. The activation energy jump of the hopping mechanism from the ferroelectric to the paraelectric behavior suggests that, in the ferroelectric state, the electric dipole ordering with the external field direction. The associated transport short distance hopping mechanism is by single ionized oxygen transport. In the paraelectric state, dipoles disappear and thermal energy ($k_B T$) enhances the probability of the existence of double-ionized oxygen ions ($V_O = V_O'' + 2e'$) that would be responsible now for the hopping conduction process. Thermal energy would reduce the mobility of these ions [6]. Fig. 5b) shows the change in activation energy at the tetragonal-to-cubic phase transition from 0.86 to 1.00 eV for the *dc* conductivity mechanism. This is an indication that for the long-range conduction mechanism, double ionized oxygen atoms are the responsible ions according to $V_O = V_O'' + 2e'$ [6]. and the energy jump signals the transition from ferroelectric to paraelectric state. The enhancement of the activation energy corresponding to the *dc* conductivity mechanism in the ferroelectric-paraelectric phase transition suggests that in the ferroelectric state, the dipole moments align with the external field direction while the long-range transport of charge carriers (double-ionized oxygen) behave according to the calculated *dc* activation energy. It is interesting

to see that, in the paraelectric state, double-ionized oxygen is responsible for both *dc* conductivity and hopping conductivity. The obtained values for the activation energies for both mechanisms are similar to those reported by other authors for the KNN systems [15-18]. The values of the exponent in Jonscher's law are shown in Fig. 6. The values in the graph are comparable to those reported for different ferroelectric systems [6, 17-18]

Fig. 4. (color online) The conductivity behavior as function of frequency at several temperatures. Discrete points (squares) are experimental; continuous lines are Jonscher's law fittings.

Fig. 5. (color online) Arrhenius plots for (a) hopping frequency and (b) *dc* conductivity versus temperature behavior with their corresponding activation energies.

Fig. 6. The n parameter of Jonscher relaxation law for different temperatures obtained from fitting of the experimental ac conductivity values.

4 Conclusions

The fabrication of the $\text{KNNLiTaLa}_{0.01}$ compound seems to be not only dependent on the preparation conditions but also on the preparation method. In this work, we show that the sol-gel method renders a compound with values of the maximum dielectric permittivity larger than those of samples grown by the traditional solid-state technique but lower than those obtained by the RTGG method for similar compositions. For our samples, grown by sol-gel, we find that La doping induces shifts of the orthorhombic-to-tetragonal and tetragonal-to-cubic transition temperatures toward lower temperatures. The conductivity of the compound obeys Jonscher's Universal Law in the studied temperature and frequency intervals showing lower values than the corresponding compound grown by the RTGG method, suggesting better composition homogeneity because of lower free ion mobile species. The studied compound shows a sharp change in the dc conductivity and hopping activation energies at the tetragonal-to-cubic phase transition. The calculated values of the activation energies for dc conductivity and hopping mechanisms allowed us to conclude that the corresponding charge carriers responsible for both processes were single and double ionized oxygen ions.

Authors' contributions

Conceptualization: R. López-Noda, J. Portelles, J. Fuentes, G. Rojas-George, H'Linh Hmök; Methodology: R. López-Noda, J. Portelles, J.F. Rebellon-Watson; Formal analysis and investigación: R. López-Noda, J. Portelles, J. Fuentes, G. Rojas-George, A. Reyes-Rojas, H'Linh Hmök; Writing – original draft preparation: R. López-Noda, J. Portelles, J. Fuentes, G. Rojas-George, H'Linh Hmök, J.M. Siqueiros Beltrones; Writing – review and editing: R. López-Noda, J. Portelles, J. Fuentes, G. Rojas-George, H'Linh Hmök, M.P. Cruz, J.M. Siqueiros Beltrones; Funding acquisition: J.M. Siqueiros Beltrones; Resources: R. López-Noda, J. Portelles, J. Fuentes, G. Rojas-George, J.M. Siqueiros Beltrones; Supervision: R. López-Noda, J. Portelles, J. Fuentes, G. Rojas-George, H'Linh Hmök, J.M. Siqueiros Beltrones;

Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Thanks are due to DGAPA-UNAM for financial support through grants No. IN104320 and IN109016. H'Linh Hmök thanks PRODEP-SEP, Mexico for scholarship grant No. 511-6/2019.-15551.

References

- [1] Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, Nagaya T, Nakamura M. Lead-free piezoceramics. *Nature* 2004, **432**: 84.
- [2] Wang K, Li J, Liu N. Piezoelectric properties of low-temperature sintered Li-modified (Na, K)NbO₃ lead-free ceramics. *Appl Phys Lett* 2008, **93**: 092904.
- [3] Long C, Li T, Fan H, Wu Y, Zhou L, Li Y, Xiao L, Li Y. Li-substituted K_{0.5}Na_{0.5}NbO₃-based piezoelectric ceramics: Crystal structures and the effect of atmosphere on electrical properties. *J Alloys Compd* 2016, **658**: 839-847.
- [4] Gao D, Kwok KW, Lin D, Chan HLW. Microstructure and electrical properties of La-modified K_{0.5}Na_{0.5}NbO₃ lead-free piezoelectric ceramics. *J Phys D: Appl Phys* 2009, **42**:035411.

- [5] Fuentes J, Portelles J, Pérez A, Durruthy-Rodríguez MD, Ostos C, Raymond O, Heiras J, Cruz MP, Siqueiros JM. Structural and dielectric properties of La- and Ti-modified $K_{0.5}Na_{0.5}NbO_3$ ceramics. *Appl Phys A* 2012, **107**: 733–738.
- [6] Portelles J, Palmero N, Fuentes J, López Noda R, Raymond Herrera O, Cruz MP, Siqueiros JM. Dielectric spectroscopic study of $(K_{0.44}Na_{0.52}Li_{0.04})_{0.97}La_{0.01}Nb_{0.9}Ta_{0.103}$ ceramics. *J Appl Phys* 2017, **122**:234102.
- [7] HMok H, Duarte A, Portelles J, Fuentes J, Durruthy Rodriguez MD, Raymond O, Heiras J, Cruz MP, Siqueiros JM. Study of lead-free ceramics of the $[(K_{0.5}Na_{0.5})_{0.94}Li_{0.06}]_{0.97}La_{0.01}(Nb_{0.9}Ta_{0.1})O_3$ piezoelectric composite. *RCF* 2012, **29(1)**: 28-32
- [8] Fuentes J, Portelles J, Durruthy-Rodríguez MD, H'Mok H, Raymond O, Heiras J, Cruz MP, Siqueiros JM. Dielectric and piezoelectric properties of the KNN ceramic compound doped with Li, La and Ta. *Appl Phys A* 2015, **118**:709–715
- [9] Portelles J, Fuentes J, Gervacio J, Ostos C, Raymond O, Heiras J, Cruz MP, Siqueiros JM. Li, La, Ta doped KNN ceramics obtained by RTGG. *Ferroelectrics* 2018, **534**:175-182.
- [10] Hou Y, Wang C, Zhao J, Ge H, Zhu M, Yan H. The fine-grained KNN–LN ceramics densified from nanoparticles obtained by an economical sol–gel route. *Mater Chem and Phys* 2012, **134**: 518-522
- [11] Zhang W, Kumada N, Takei T, Yonesaki Y, Kinomura N. Crystal structures of $KBa_2Nb_5O_{15}$ and $LaK_2Nb_5O_{15}$ with the TTB-type structure. *Mater Res Bull* 2007, **42**: 844–850.
- [12] ICDD “ $K_{0.5}Na_{0.5}NbO_3$ ” crystallographic file (ICDD 61-0315) International Centre of Diffraction Data (2015)
- [13] Guo Y, Kakimoto K, Ohsato H. Phase transitional behavior and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$ – $LiNbO_3$ ceramics. *Appl Phys Lett* 2004, **85**: 4121.
- [14] James AR, Priya S, Uchino K, Srinivas K. Dielectric spectroscopy of $Pb(Mg_{1/3}Nb_{2/3})O_3$ – $PbTiO_3$ single crystals. *J Appl Phys* 2001, **90 (7)**: 3504-3508.
- [15] Peláiz A, López R. Dielectric relaxation and electrical conductivity in ferroelectric ceramic/polymer composite based on modified lead titanate. *J Appl Phys* 2007, **102**:14102.
- [16] Noda RL, Salas UA, Gaudisson T, Piñar FC, Ammar S, Valenzuela R. Magnetoelectric Coupling in $BaTiO_3$ – $CoFe_2O_4$ Nanocomposites Studied by

- Impedance Spectroscopy Under Magnetic Field. *IEEE Transactions on Magnetics* 2014, **50(11)**:1-4.
- [17] Ang C, Yu Z, Cross LE. Oxygen-vacancy-related low-frequency dielectric relaxation and electrical conduction in Bi:SrTiO₃. *Phys Rev B* 2000, **62**:228
- [18] Liu L, Huang Y, Su C, Fang L, Wu M, Hu C, Fan H. Space-charge relaxation and electrical conduction in K_{0.5}Na_{0.5}NbO₃ at high temperatures. *Appl Phys A* 2011, **104**: 1047-1051.

Figure 3

(color online) a) The relative dielectric permittivity (ϵ) and b) dielectric loss ($\tan \delta$) at different frequencies, as functions of temperature, for the KNNLiTaLa0.01 ceramic showing the orthogonal-to-tetragonal and the tetragona-to-cubic critical temperatures.

Figure 4

(color online) The conductivity behavior as function of frequency at several temperatures. Discrete points (squares) are experimental; continuous lines are Jonscher's law fittings.

Figure 5

(color online) Arrhenius plots for (a) hopping frequency and (b) dc conductivity versus temperature behavior with their corresponding activation energies.

Figure 6

Figure 6

Figure 7

The n parameter of Jonscher relaxation law for different temperatures obtained from fitting of the experimental ac conductivity values.