

Effects of Copper Oxide Doping on the Properties of Sodium Potassium Niobate (Na_{0.5}K_{0.5}) NbO₃ Piezoelectric Single Crystals Grown by Flux Method

R. Saravanan, D. Rajesh, S. V. Rajasekaran, R. Peurmal, M. Chitra, and R. Jayavel

Abstract—Lead free piezoelectric single crystals of sodium potassium niobate (K_{0.5}Na_{0.5})NbO₃ and 0.5wt%, 1wt%, 1.5wt% of copper oxide CuO doped sodium potassium niobate (K_{0.5}Na_{0.5})NbO₃ (KNN) single crystals were grown by high-temperature solution method and the dielectric properties, morphology and domain pattern were investigated. The flux used during crystal growth is eutectic mixture of potassium carbonate K₂CO₃ and sodium carbonate Na₂CO₃. Additions of small amounts of boron oxide B₂O₃ further lower the melting temperature of the eutectic mixture. It was found that 1.5wt% CuO doped single crystals of sodium potassium niobate exhibits excellent dielectric properties. XRD results showed sharp peaks indicating good crystalline behavior of both pure and CuO doped KNN crystals. Phase analysis showed that all samples crystallized in pure orthorhombic perovskite phase. A slight decrease in the diffraction angles has been observed with increase in doping concentration. This is due to the replacement of Nb⁵⁺ ions by Cu²⁺ ions, leading to the formation of higher oxygen vacancies with the doping concentrations.

Index Terms—Dielectric, domain, KNN, piezoelectric, single crystal etc.

I. INTRODUCTION

Recently, lead-free piezoelectric single crystals have been widely studied to find alternative for (Pb, Zr)TiO₃ (PZT) [1], [2], because lead oxide affects both human health and the environment. Lead-free piezoelectric Na_{0.5}K_{0.5}NbO₃ (KNN) system has been attracted interest because of their excellent dielectric property and biocompatibility [1], [3]. The dielectric losses are minimized at their equimolar composition of sodium niobate and potassium niobate that has a morphotropic phase boundary (MPB) when compared to other compositions with different ratios [4]. However, there are difficulties due to the volatilization of K and Na at temperatures above 850°C [5], [6]. One of the methods to improve the electric property of KNN single crystal is to do elemental substitution that is well established [7], [8]. The

ionic radius of the acceptor dopant Cu²⁺ is 0.73Å. Upon doping, it may substitute the B-site ions Nb⁵⁺ as its' ionic radius of 0.68Å, is approximately the same value. As the doubly ionized Cu²⁺ ions substitute the Nb⁵⁺ ions, charge imbalance will be created in the sites that will force the adjacent oxygen O²⁻ ions to vacate its place thereby producing oxygen vacancies in the crystal thus maintaining the charge neutrality. This phenomenon will transform the doped KNN into a hard piezoelectric single crystal.

Textured CuO-doped (K_{0.5}Na_{0.5}) NbO₃ material was grown using Reactive-Templated Grain Growth (RTGG) and the microstructural evolution and texture development were investigated in this system by Y. Kizaki Et al. [8]. Li et al. [9] directly added CuO to the calcined KNN powders and observed a significant change in the microstructure. In the above two cases, Cu addition led to drastic changes in the structure and microstructure as well as the electrical properties of the KNN powder and ceramic material. Powders and Ceramic materials do not have homogenous microstructures when compared to single crystals which may have better electrical properties. In the current study, the single crystals of KNN in both pure and doped form are grown by High temperature Solution growth method. The CuO-added KNN single crystal was expected to be a good and hard piezoelectric material. It is used in high power applications such as ultrasonic motors and transformers. High-intensity ultrasound transducers with piezoelectric materials require "Hard" piezoelectric property with low dielectric loss to deliver a high acoustic power without excessive heat generation. In order to attain the piezoelectric hardness, CuO is used as a dopant in this study.

II. EXPERIMENT

In recent years, high temperature flux method has been successfully used to grow high-quality pure single crystals for a wide range of electronic materials. The main advantage of this method is that the crystals are grown below the melting temperature of the oxide material making this process particularly suitable for the growth of crystals.

The raw materials are high-purity (99.9%) powders of Na₂CO₃, K₂CO₃, Nb₂O₅ and CuO. The powders were weighed to obtain the compositions according to the formula of (Na_{0.5}K_{0.5}) (Nb_(1-x)Cu_x) O₃ where $x = 0.5, 1, 1.5$. The weighed powder was mixed and grinded for 1 h using mortar and calcined at 950 °C. The pure and CuO doped KNN calcined powders were mixed in a KF–NaF eutectic

Manuscript received April 15, 2012; revised May 26, 2012.

R. Saravanan and M. Chitra are with Crystal Growth Centre, Anna University, Chennai

D. Rajesh is with G.T. Sollar Cell, China

S. V. Rajasekaran is with Government Arts and Science College, Dharmapuri

R. Peurmal is with KTH, Sweden

R. Jayavel is with Crystal Growth Centre, Anna University, Chennai and Centre for Nanoscience and Technology, Anna University, Chennai (Corresponding author. Tel.: + 91-44-2235 8328, fax: +91-44-2230 1656, e-mail address: rjvel@annuni.edu).

composition to get the lowest possible melting point. The weight ratio of the calcined powders, KF, NaF and B₂O₃ was taken as 5: 2: 1:0.5 and were mixed and grinded for 4 h using mortar. Then, the mixture was put into a Pt-crucible and heat treated using the following heat cycles: (1) heating from room temperature to 1000 °C at a rate of 100 °C /h, (2) heating from 1000 °C to 1150 °C at a rate of 50 °C /h to get the molten form (3) The molten mixture was given a soaking temperature of 1150 °C for a period of 24 h to get it in homogenized form. (4) Then it was cooled slowly from 1150 °C to 1000 °C at 0.5 °C /h to initiate nucleation and solidification. (5) The solid solution was cooled down to 600 °C at the rate of 50 °C /h to obtain the crystal (6) Finally, the crystal was given a soaking temperature of 600 °C for a period of 2 h to favor the growth of the ferroelectric domains and slow cooled to room temperature.

The components of the crystal, sodium carbonate and potassium carbonate are volatile at around 850°C but the composition of the KNN crystal is highly refractory. The morphologies of the single crystal were confirmed using scanning electron microscopy and atomic force microscopy. The temperature dependence of the dielectric permittivity and dielectric loss of pure and CuO doped KNN single crystals were measured using a LCR meter.

III. RESULT AND DISCUSSION

A. X-Ray Diffraction Studies

The powder XRD results show that the diffraction peaks of CuO doped KNN crystal slightly shift towards lower angles when compared to those of pure KNN crystal. There is no significant difference between the XRD patterns of the pure and the CuO doped KNN crystal. This implies that all samples are crystallized in pure orthorhombic perovskite phase. The observed shift in the diffraction peaks (2θ values) towards lower angles implies that the lattice parameters become lower with increasing concentration of the dopant CuO. This is attributed to the substitution of B-site Nb⁵⁺ ions of sodium potassium niobate (K_{0.5}Na_{0.5}) NbO₃ by the smaller Cu²⁺ ions of the dopant CuO. Further, a charge imbalance has been locally created around the substituted sites making the adjacent oxygen O²⁻ atoms to vacate its place creating oxygen vacancies.

The above inference has been verified and confirmed using single crystal XRD analysis. Here also, a small change in the lattice parameters has been observed for the doped crystals. For pure KNN crystal, the lattice parameters are found to be $a=5.6398$ Å, $b=3.9444$ Å, and $c=5.6709$ Å, whereas for the 1.5wt% of CuO doped KNN crystal, the lattice parameters are found to be $a=5.6355$ Å, $b=3.9411$ Å, and $c=5.6678$ Å. This confirms that Cu²⁺ ion has entered the lattices of KNN crystal in the form of substitutional impurity. The smaller Cu²⁺ ion replaces the larger Nb⁵⁺ ions of the crystal lattice thereby giving rise to slight decrease in the lattice parameters.

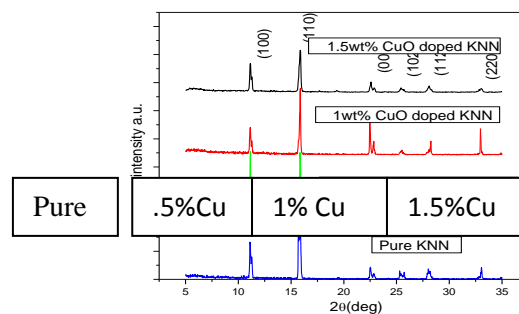
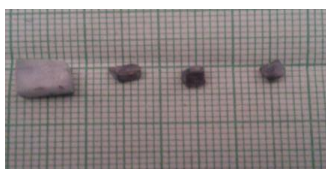


Fig. (1) and (2). Photographs and XRD patterns of pure and cu doped KNN single crystals grown by Flux method.

B. Dielectric Studies

Dielectric permittivity and loss parameters have been measured at 100 KHz for all the pure and doped crystals by varying the temperature from RT to about 450°C. The pure KNN crystal has orthorhombic perovskite phase from RT to 210°C. There exists a small kink at around 210°C indicating an orthorhombic–tetragonal phase transition. The pure KNN single crystal showed a strong peak at around 429°C (Curie Temperature- T_c) that corresponds to tetragonal cubic phase transition.

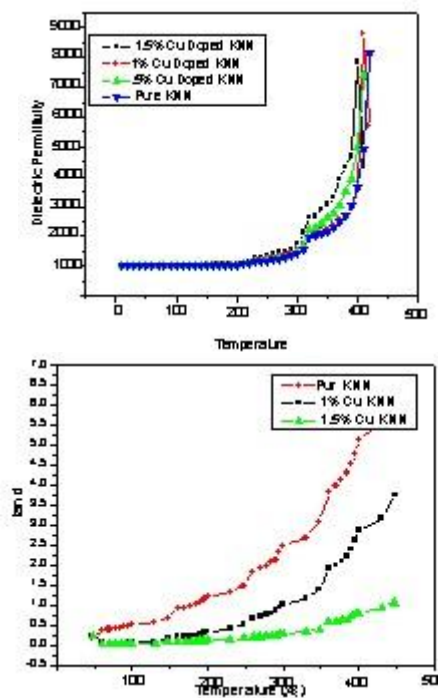


Fig. (3) and (4). The temperature dependence of dielectric permittivity and dielectric loss ($\tan \delta$) of Pure and Cu doped KNN single crystal.

The peaks of all the three doped single crystals at the Curie temperature are sharp, indicating that the single crystals are showing a normal ferroelectric behavior and that the addition of the dopant CuO does not change this character. The doped crystals show a downshift in the Curie temperature value. The highest doped crystal in the present study has shown a shift from 429°C to 408°C. The orthorhombic to tetragonal phase transition temperature also has decreased from 210 to 198°C with increasing dopant CuO ratio. The decrease in the phase transition temperatures and T_c values may be attributed to the slightly induced lattice distortion of the doped crystal due to Cu substitution

on the Nb-sites of the perovskite structure which in turn creates oxygen vacancies.

The variation in loss parameter with increase in temperature shows a wavy pattern and is high near the Curie temperature indicating maximum power dissipation at around T_c . A significant decrease in the loss factor $\tan \delta$ has been observed for all the doped crystals and is least for the highest doped crystal in the study.

C. SEM-EDS and AFM Studies

AFM morphological studies show that the root mean square (rms) roughness of the pure KNN single crystal is found to be 6.96nm. The roughnesses of the doped crystals have increased considerably with increasing percentage of doping and are found to be about 9, 10.8, and 14 nm respectively for the 0.5wt%, 1.0 wt%, and 1.5wt% of CuO doping in KNN crystals. The pure KNN single crystal possesses a very smooth surface shown in AFM image in Fig (6). CuO doped KNN single crystals appear to have less population of domains since the surface roughnesses of the CuO doped KNN single crystals are higher than that of the pure crystal.

Two types of domains were observed in all the pure and doped samples which are the twinned domain and the stripped domains. The domain width and length were found to be about 0.7 μm and 10 μm respectively. The domain-wall width of the doped crystals was observed to be 0.7 μm which is the same as pure KNN crystals. The domain lengths in the doped crystals were found to be longer with increase in doping percentages when compared to the pure KNN crystal. The differences in the domain structures between the pure and the doped crystals have arisen due to the intra-granular stresses. The intra-granular stresses may arise due to the substitution of the larger Nb^{5+} ions by the smaller Cu^{2+} ions in the B-site of the perovskite-type crystal structure. This substitution also creates a charge imbalance locally that gives rise to oxygen vacancies. SEM image also shows existence of few steps or terraces on the surface of the pure crystal.

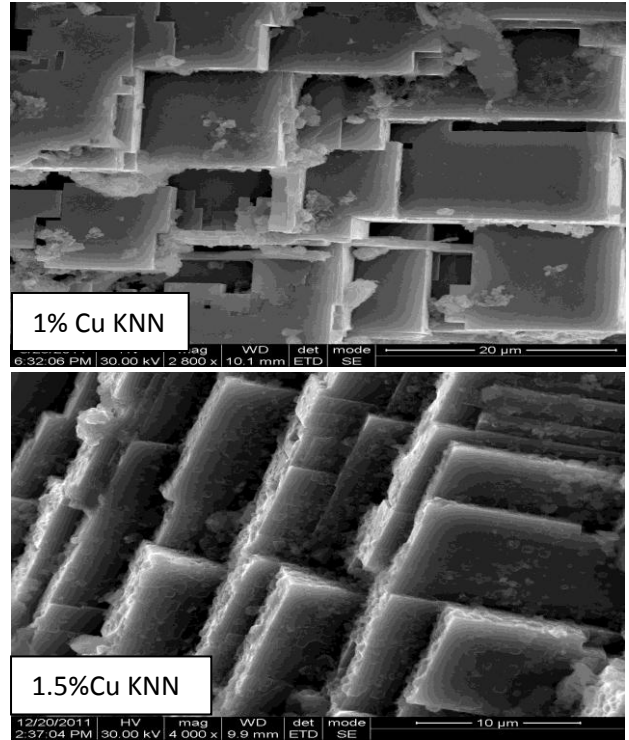
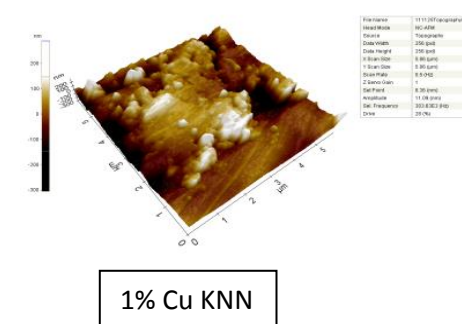
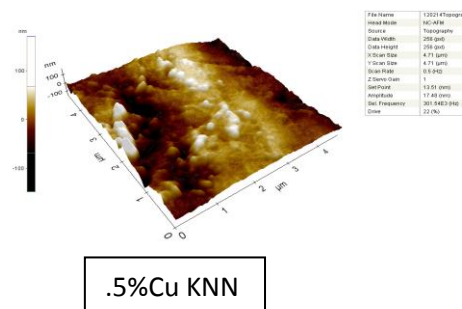
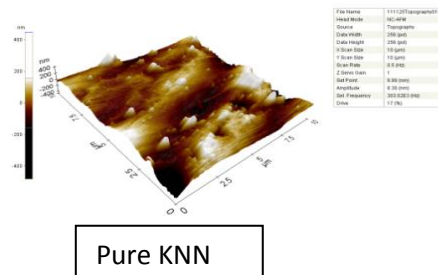
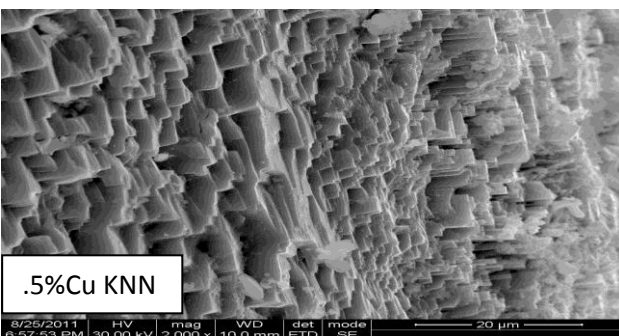
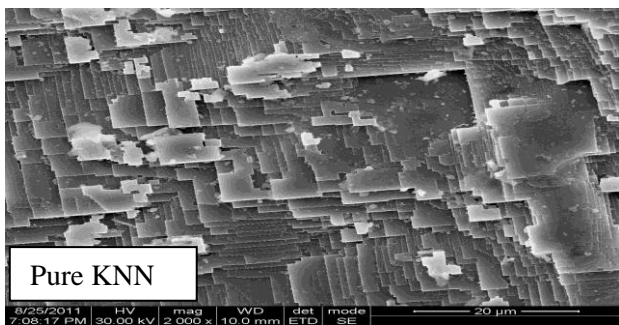


Fig. (5). Microstructure of pure and Cu doped KNN single crystal.



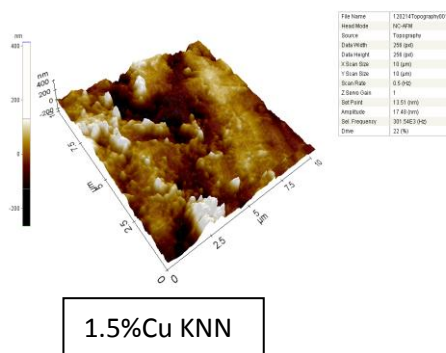


Fig. (6). Roughness of pure and Cu doped KNN single crystal using AFM analysis.

IV. CONCLUSION

The pure and CuO doped KNN single crystals were successfully grown by high temperature solution growth method. A change of color on the KNN single crystal has been observed as a function of CuO content. White color for pure crystal has changed to a pale greenish gray and then to a darker gray and finally to black color with increasing doping concentration of CuO. XRD patterns of pure and doped KNN single crystal confirms formation of orthorhombic perovskite phase for all the crystals grown. The observed shift in the diffraction peaks towards lower angles implies that the lattice constants decrease with increasing concentration of the dopant CuO. Further, it may be inferred that the smaller Cu^{2+} ions of the dopant is included in the pure KNN crystal as a substitutional impurity, replacing the larger Nb^{5+} ions which in turn

creates a local charge imbalance and hence oxygen vacancies in the crystal. This inference is supported by the improved dielectric properties of the doped crystals. The surface roughnesses of the doped crystals are observed to be higher than that of the pure crystal. This suggests that the doped crystals have less population of domains than the pure crystal. All the samples show two phase transitions in the temperature dependent dielectric measurements. The first transition is identified as the Orthorhombic to Tetragonal phase transition and the second is identified as the Tetragonal to Cubic phase transition at the Curie temperature T_c . It is observed that the phase transition temperatures and the T_c values have decreased with increasing dopant concentration. The dielectric peaks of pure and doped crystals at the Curie temperature are sharp indicating that all the samples have normal ferroelectric behavior.

REFERENCES

- [1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, and M. Nakamura *Nature*, 2004, pp. 432-84.
- [2] Y. Guo, K. Kakimoto, and H. Ohsato *Appl. Phys. Lett.* 2004, vol. 85, no. 18, pp. 4121.
- [3] R. Zuo, X. Fang, and C. Ye *Appl. Phys. Lett.* 2007, vol. 90, no. 092904.
- [4] L. Egerton and D. M. Dillon *J. Am. Ceram. Soc.* 1959, vol. 42, no. 438.
- [5] M. Ichiki, L. Zhang, M. Tanaka, and R. J. Maeda *Am. Ceram. Soc.* 2004, vol. 24, no. 1693.
- [6] H. Birol, and D. Damjanovic, N. J. Setter *Eur. Ceram. Soc.* 2006, vol. 26, no. 861
- [7] E. Hollenstein, M. Davis, D. Damjanovic, and N. Setter: *Appl. Phys. Lett.* 2005, vol. 87, no. 182905.
- [8] Y. Kizaki, Y. Noguchi, and M. Miyayama: *Appl. Phys. Lett.* 2006, vol. 89, no. 142910.
- [9] E. Li, H. Kakemato, S. Wada, and T. Tsurumi, "Enhancement of Qm by codoping of Li and Cu to potassium sodium niobate lead-free ceramics," *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* 2008, vol. 55, no. 5, pp. 980-987.