

Crystal Growth and Dielectric Property of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ and Mn-Doped $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ Single Crystal Grown by Flux Method

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Abstract—Lead free piezoelectric single crystals of $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ and 0.5 wt%, 1.0 wt% and 1.5 wt% MnO_2 doped $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN) were grown by high-temperature solution method using K_2CO_3 – Na_2CO_3 eutectic composition as flux with addition of small amounts of boron oxide for lowering the melting temperature. The effect of the manganese dopant on the dielectric properties, surface morphology and the domain structure were investigated. The MnO_2 -doped KNN crystals were found to exhibit higher dielectric permittivity when compared with pure KNN single crystal. Mn doping increases the dielectric constant and decreases the dielectric loss. A slight decrease in the orthorhombic to tetragonal phase transition temperature $T_{(O-T)}$ and Curie temperature T_C has been observed in manganese-doped KNN single crystals. From SEM and AFM analysis, the domain size of KNN–Mn crystal was found to be of the order of 5–13 μm at room temperature which is smaller than that of the pure KNN crystal (20–30 μm).

Index Terms—Ferroelectric, defect, KNN, piezoelectric, single crystal etc.

I. INTRODUCTION

The mixed alkali niobate $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN) and its derivatives have recently been receiving a great deal of attention as effective lead-free replacement material for $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) single crystal. The KNbO_3 – NaNbO_3 system has a morphotropic phase boundary close to the $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ composition and it has to replace PZT, then the electrical properties of KNN have to be improved. Piezoelectric single crystals have attracted much for their varied applications such as medical transducers and sonar, as they possess high piezoelectric constants and high electromechanical coupling factors [1,2]. In this work, we have studied the lead-free $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (KNN) piezoelectric single crystals [3,4] as most of the lead based piezoelectric materials are toxic. The KNN has a high Curie temperature and a large piezoelectric coefficient [5]. KNN crystallizes in perovskite structure, which undergoes two phase transitions, when the crystal polarizes along the [001] direction. The first transition is from tetragonal to orthorhombic phase that happens at the temperature 180 °C.

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The second transition is from paraelectric cubic phase to tetragonal phase, which is called the ferroelectric transition temperature or the Curie temperature, T_C that happens at 405 °C. The recent studies show that ultrasonic wire bonding transducer has been successfully prepared using KNN based lead-free piezoelectric ceramics [6]. Several different methods have been used to improve the dielectric properties. Dopants [7] have been added to improve the dielectric properties of KNN single crystals. Recently Lin *et al.* [8] have shown the improvement in dielectric properties of KNN single crystals by doping Manganese that reduces the domain size of the crystal. The components of the crystal sodium and potassium have lower melting points and hence volatile at higher temperatures. Therefore, the growth process of the pure and Mn doped KNN crystals have to be carried out at lower temperatures and the growth process itself is challenging [9,10]. Hence addition boron oxide as flux reduces the growth temperature. While doping, A-site and B-site substitution of NbO_3 happens. In this paper, pure and 0.5 wt%, 1 wt%, 1.5 wt% of MnO_2 doped KNN single crystals were grown by high-temperature solution method using small amounts of boron oxide flux. The effect of the manganese dopant in Curie temperature, structure and dielectric properties of KNN single crystals were studied. Different domains of pure and Mn doped KNN crystals were investigated.

II. EXPERIMENTAL METHODS

The raw materials of high-purity (99.9%) powders of Na_2CO_3 , K_2CO_3 , Nb_2O_5 and Mn_2O_3 were weighed to obtain the compositions according to the formula of $(\text{Na}_{0.5}\text{K}_{0.5})(\text{Nb}_{(1-x)}\text{Mn}_x)\text{O}_3$ 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 Mn doped KNN calcined powders were mixed in a KF–NaF eutectic composition to get the lowest possible melting point. The weight ratio of the calcined powders, KF, NaF and B_2O_3 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 as-grown crystals were washed repeatedly in water and hot dilute nitric acid and the obtained crystals are white in color. The Manganese doped KNN crystals exhibits darker brown color as shown in Fig (1).

III. RESULT AND DISCUSSION

A. X-Ray Diffraction Analysis

XRD analysis confirmed the grown KNN single crystals belong to orthorhombic systems shown in Fig(2). It has been observed that all the grown crystals have pure perovskite phase with lattice parameters $a = 3.950\text{\AA}$, $b = 3.946\text{\AA}$ and $c = 3.448\text{\AA}$ respectively without any impurity phases. The orthorhombic phase was characterized by two peak splitting process which are (110)/(001) and (220)/(002) that is shown in the XRD spectra of the crystals. Compared with pure KNN, the peaks of Mn doped crystals were found to slightly shift to lower 2θ values. This indicates that the lattice parameters are decreased slightly for Mn doped KNN single crystals.

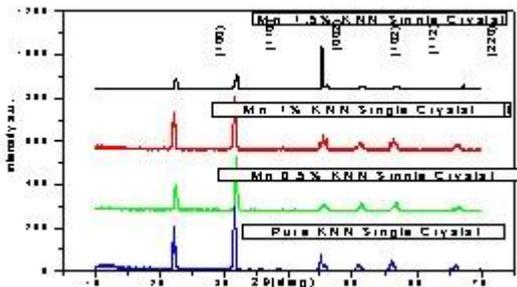


Fig. (1) and (2). Photographs of obtained Pure and Mn doped KNN single crystals grown and XRD patterns of pure and Mn doped KNN single crystals.

B. Dielectric Studies

Dielectric measurements are carried out at various temperatures ranging from room temperature to a high temperature of 500 °C for the KNN single crystals. Fig.(3) and Fig.(4) shows the temperature dependence of the dielectric permittivity and dielectric loss for pure and Mn doped ($K_{0.5}Na_{0.5}$) NbO_3 single crystals. Dielectric permittivity increases with temperature for both pure and Mn doped KNN crystals. The dielectric loss has decreased significantly for the doped crystals. It increases with temperature and the rate of variation falls significantly for doped crystals. Higher the doping concentration, smaller is the variation in dielectric loss with temperature. Above 300 °C, a sharp and steep increase in dielectric permittivity is

observed. The peak coincides with a loss peak around the same temperature indicating a dielectric dispersion phenomenon. The dielectric permittivity increases nonlinearly beyond 300 °C whereas the loss factor is significantly lower for the doped crystals at higher temperatures. Thus, the addition of Mn improves the dielectric behaviour of KNN crystals, which can be explored for potential applications.

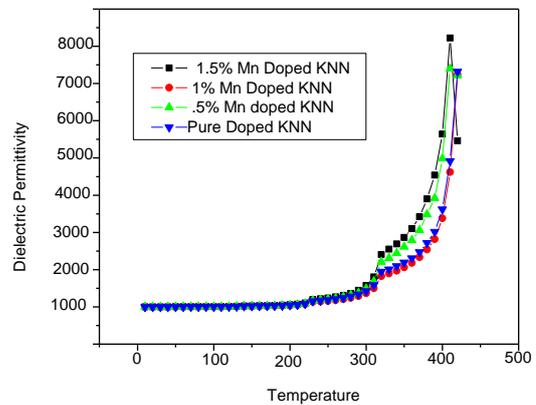
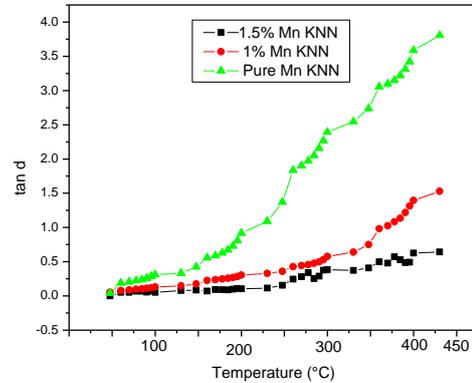


Fig. (3) and (4). The temperature dependence of dielectric permittivity of pure and Mn doped KNN single crystal and loss ($\tan \delta$) measured pure and Mn doped KNN single crystals.

C. Atomic Force Microscopy and Scanning Electron Microscopy

The Fig. (5) shows the SEM micrograph of the pure and Mn doped KNN single crystals. A remarkable cleavage behavior for Mn substituted KNN single crystal was observed with narrow strips appeared on the surface of the crystal. In Mn doped KNN single crystals, complicated ferroelectric domain morphology with irregularly shaped domain has been observed. As doping percentage increases, parallel lines started appearing as shown in Fig(5). Fig(6) shows domain patterns of KNN and Mn-doped KNN crystals grown by the flux method from the AFM analysis. The domain size was about 125 nm and domain width 12–15 nm, which were aligned in turn. The fine patterns were observed in each band-shaped domain structure. A domain size decrease with increase Mn concentration was observed in the surface of KNN crystals, whereas the domain decreased along the growth direction in the surface of Mn-doped KNN crystals. Additionally, the structures of the KNN and Mn-doped KNN crystals cut in parallel and perpendicular directions were quite similar. This is due to thin-layered grain growth as shown in Fig. (5). The Mn doped KNN single

crystals contain the alternation of broad and narrow sub-micron sized domains. There exist lots of nanodomains that were arranged within the micro domains. The domain wall energy decreases with increase in Mn substitution. According to the classical theory of ferroelectric domains, the domain size is proportional to the square root of domain wall

energy, since the domain size is determined by a balance between the energy of domain wall and the energies of the electric and elastic fields caused by the spontaneous polarization and strain. Therefore, the domain size decreases and the growth pattern become uniform with increasing doping concentration of Mn in KNN single crystal.

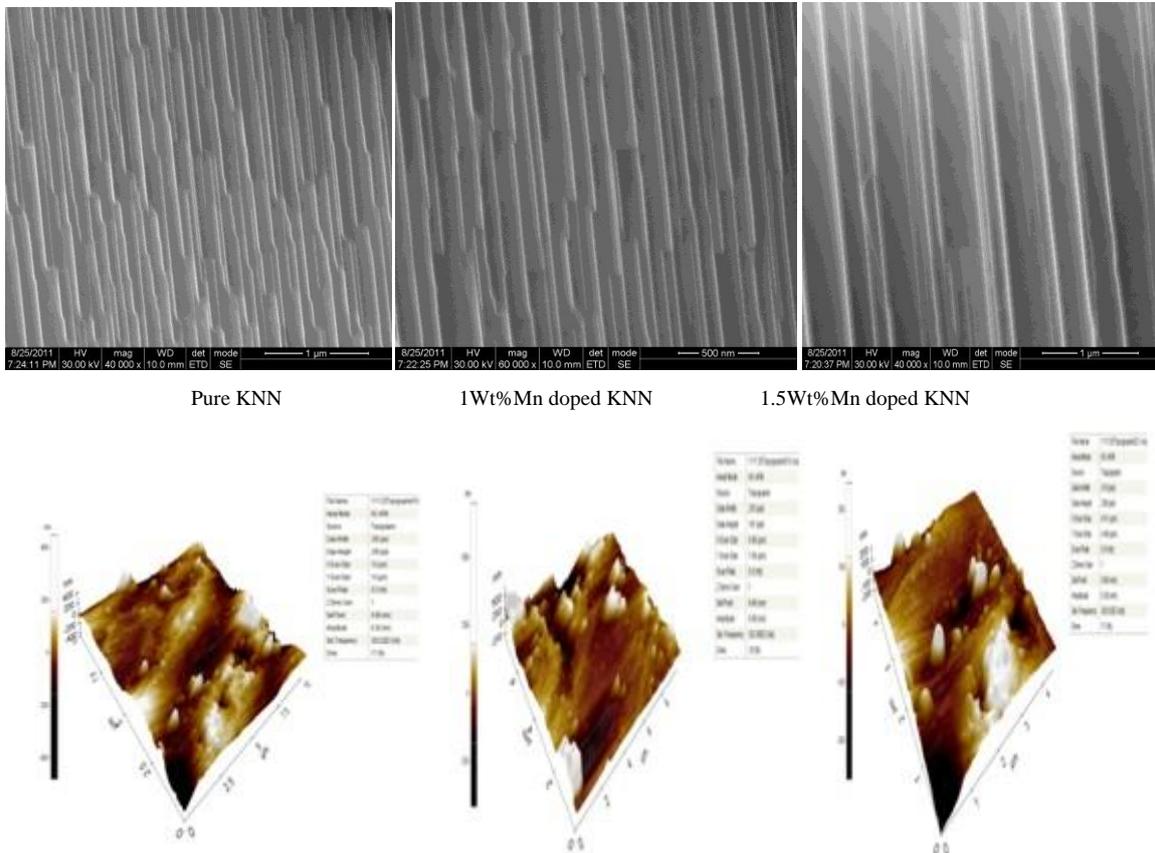


Fig. (5) and (6). Microstructure of pure and Mn doped KNN single crystal grown by Flux method and Domain structure of pure and Mn doped KNN.

D. Raman Studies

In order to investigate the bonds between Nb and O ions in the NbO_6 units the Raman analysis has been done for the grown crystals. The observation plane of the samples was an orthorhombic (110) face. In the KNN, Raman modes can be ascribed to the internal vibrational modes of NbO_6 units, i.e., n_1 (A_1g), n_2 (Eg), and n_5 ($F2g$). Of these vibrations, the first two modes are stretching and the last one is the bending mode. The Raman spectra for the crystals are shown in the Fig(7). The full-width at half maximum values (FWHM) and the center positions of the vibrational modes are noted. The stretching and bending modes were detected at $525\text{--}725$ and $175\text{--}375\text{ cm}^{-1}$ respectively. A broad scattering peak centered at around 615 cm^{-1} was observed. The FWHM of the samples was almost the same for all the crystals indicating that they have the same crystal structure. The centers of the n_1 and n_5 modes in 1.5Wt%Mn doped KNN single crystal were shifted to higher wavenumbers to that of the pure KNN single crystal. The n_1 mode has shifted from 620.4 to 637.5 cm^{-1} , and the n_5 mode has shifted from 257.1 to 284.3 cm^{-1} . This result indicates that the bonding strength in Mn doped single crystal has increased due to the shortening of the distance between Nb ions and the coordinated O ions in NbO_6 units. The Raman spectrum of Mn doped KNN single crystal show that n_1 mode at $621\text{--}642\text{ cm}^{-1}$ became sharp and the n_2 modes which possess different stretching vibrations from n_1 mode were detected around 574 cm^{-1} .

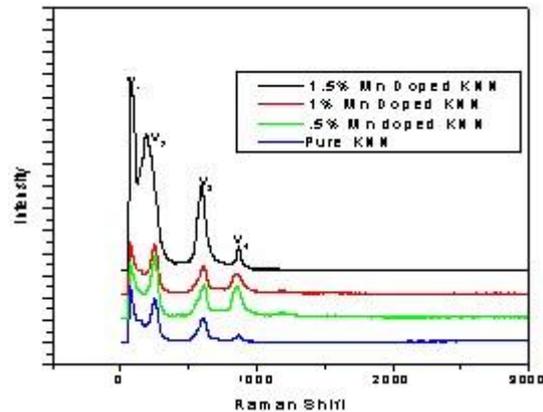


Fig. (7). Raman spectrum of Pure and Mn doped KNN single crystal

IV. CONCLUSION

Pure and Mn-doped KNN single crystals were grown by Flux method and improved dielectric properties were found. X-ray diffraction analysis confirms the crystal structure as orthorhombic system. The Raman spectral analysis shows the centers of the n_1 and n_5 modes in Mn doped KNN single crystal were shifted to a higher wavenumbers than pure KNN single crystal. The domain structures of the as grown crystal were investigated using AFM. In addition, it was found that the doped Mn was substituted in the perovskite type structure.

As a result, the size of the domains decreases and the dielectric properties have improved.

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