Crystal Growth and Dielectric Properties of $Na_{0.5}K_{0.5}NbO_3$ Single Crystal Grown by Flux Method Using B_2O_3 Flux

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

***Abstract*—Lead free piezoelectric single crystals of $(K_{0.5}Na_{0.5})NbO_3$ have been successfully grown by the high temperature flux solution method using B_2O_3 flux. Structure of the grown KNN single crystals was confirmed by powder X-ray diffraction analysis. The chemical composition of the as-grown single crystal was determined by Energy Dispersive X-ray analysis (EDS). Dielectric properties and the domain structure of KNN single crystals were investigated. The two phase transition temperatures of orthorhombic-to- tetragonal (O-to-T) and tetragonal-to-cubic (T-to-C) are found to be around 210 ℃ and 429 ℃ respectively for KNN single crystals as revealed from the dielectric measurements. The surface roughness was estimated to be about 6.96nm at room temperature using AFM studies. The Raman spectrum shows the characteristic peaks υ_1, υ_2 and υ_5 of KNN single crystals, which are correlated to the internal vibrations of the NbO_6 octahedron. The formation of single crystal of $(K_{0.5}Na_{0.5})NbO_3$ requires sintering below 1000 ℃ to avoid the problem of potassium volatilization.**

***Index Terms*—Dielectric properties, flux method, raman spectrum, single crystal etc.**

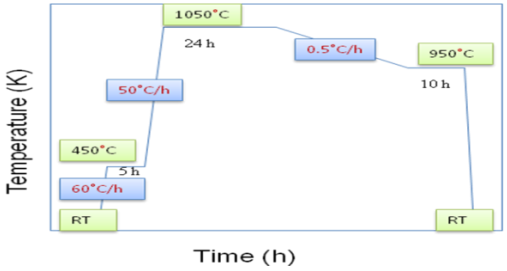
I. Introduction

KNN single crystals are expected to exhibit improved dielectric properties than KNN ceramics. Recently, $(K_{0.5}Na_{0.5})NbO_3$ single crystal growth by the solid state reaction method using $KTaO_3$ seed crystal was reported [1]. However, electrical properties have not been studied. It was also reported that the $0.95(K0.5Na0.5)NbO_3$–$0.05LiNbO_3$ single crystals grown by Bridgman method possess rounded hysteresis loop which implies that there is large leakage current induced by the defects. Until now, reports on the temperature dependence of dielectric properties in KNN single crystal are rare to find [2]. Crystallographically engineered single crystals of $KNbO_3$ have been found to possess good dielectric properties [3]. Single crystals of $(K_{(1-x)}Na_x)NbO_3$ have been grown by the flux method using NaF and KF as fluxes [4,5]. Difficulties were experienced in growing crystals with high potassium ratios. Single crystals with a composition of $(K_{0.5}Na_{0.5})$ NbO_3 were grown using the KF/NaF flux [5]. In the present study, small amount of boron oxide are added in KF/NaF flux and good quality single crystals are grown with a composition of $(K_{0.5}Na_{0.5})NbO_3$ which have better dielectric properties.

The optimum dielectric response in this system is reported [6] for the composition $K_{0.5}Na_{0.5}NbO_3$, which corresponds to the morphotropic phase boundary, reported by Tennery and Hang [7]. Lead free single crystals have shown better electromechanical properties than their polycrystalline equivalents [8]. The aim of the present work is to grow high quality KNN single crystals having better dielectric properties. For this purpose a modified flux method was used by adding a second component, i.e. B_2O_3. The domain structure, microstructure and dielectric response of KNN single crystals were investigated and the compositional homogeneity in the KNN single crystals has also been studied.

II. Experiment

Raw materials of high-purity (99.9%) powders of Na_2CO_3, K_2CO_3 and Nb_2O_5 were weighed to obtain the composition according to the formula of $(Na_{0.5}K_{0.5})$ NbO_3. The weighed powder was mixed thoroughly using temperature solution method using KF flux with a small amount of boron oxide. The KNN calcined powders were mixed in KF–NaF eutectic composition. The weight ratio of the calcined powders, KF, NaF and B_2O_3 was 5: 2: 1:0.5. The weighed powders were mixed and grinded for 4 h using mortar. Then, the mixture was taken into a Pt-crucible and heat treated using several temperature cycles. The optimum temperature cycle for the growth of larger KNN single crystals is given in the figure (1). After holding at 1050 ℃ for 24h, for proper homogenisation, the temperature was reduced to 950 ℃ at the rate of .5 ℃/hr and then to room temperature at a faster rate. The as-grown crystals were washed with double distilled water and dilute nitric acid repeatedly to remove the flux. The photographs of the crystals are shown in the figure(2). In the flux method, a degree of supersaturation was changed by the cooling rate during crystal growth or by changing the amount of flux composition. The obtained KNN crystals were white in colour. The morphology of the single crystals was studied confirmed using scanning electron microscopy and atomic force microscopy.



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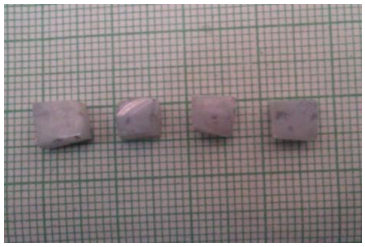


Fig. 1, 2. Temperature cycle for KNN single crystals photographs of obtained Pure KNN single crystals.

III. Result and Discussion

A. X-Ray Diffraction Studies:

Figure (3) represents the room temperature powder X-ray diffraction pattern of the $(K_{0.5}Na_{0.5})$ NbO_3 single crystal. This pattern shows that the obtained crystals belong to perovskite phase. The structure of $(K_{0.5}Na_{0.5})$ NbO_3 powder belongs to orthorhombic symmetry, with lattice parameters a = 3.950Å, b = 3.946Å and c = 3.448Å respectively. The orthorhombic phase is generally characterized by (110)/(001) peak splitting around 23 °and (220)/(002) peak splitting around 45 °.

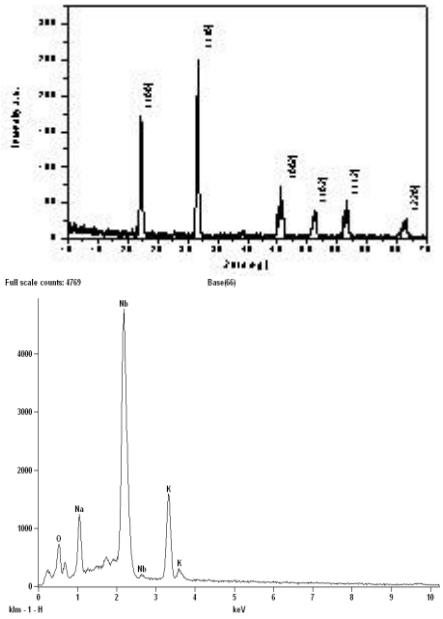
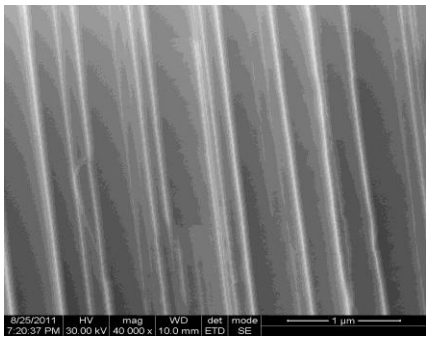


Fig. 3, 4. XRD patterns of KNN single crystals EDS pattern from the $(K0.5Na0.5)NbO_3$ single-crystal

B. SEM-EDS and AFM Studies:

In order to determine the composition of the KNN single crystal, Energy Dispersive Spectral analysis (EDS) has been done. The mean atomic percentages of K, Na and Nb in the KNN crystals were close to the ratios taken during growth. According to EDS analysis, K, Na, and Nb are evenly distributed throughout the KNN single crystals and quite similar for both crystals cut in parallel and perpendicular directions. This is due to thin-layered growth patterns as shown in Fig. (5). Tabular layers of 80–240 μm in width and approximately 2.5 μm in thickness were observed parallel and perpendicular to the growth direction. Generally, the configuration of crystals depends on the degree of supersaturation. Domain pattern of $(K0.5Na0.5)$ NbO_3 single crystals were studied by AFM. The laminar domain structure and spindle like domain structure of KNN single crystals are observed. The domain width of laminar layers is found to be in the range of 5 μm to 20 μm. The surface morphology of the crystals observed through SEM was similar to that observed by AFM except some changes in the cross-sectional view. The fine microstructure on the crystal surface was observed using AFM and the image is shown in Fig(6). This feature is useful in making facet interfaces in ultrasonic transducers. The orthorhombic structure leads to more complicated patterns of domain distribution than those of tetragonal structures[11]. The variation in domain size in ferroelectric materials is a result of equilibrium condition between the energy of the domain walls and the energy of electric and elastic fields created by the spontaneous polarization and strain. Due to the existence of simple lamellar twin structure, the crystal contains a higher elastic energy. Banded twin structures were also observed. The morphology and surface micro-structure of KNN single crystal were studied using AFM and the surface roughness was found to be about 6.96nm.



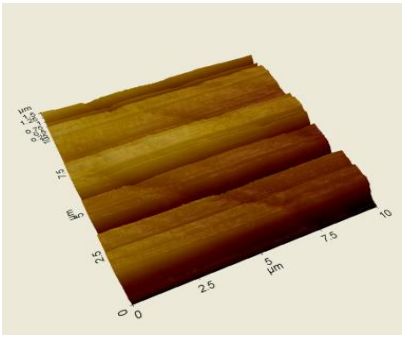


Fig. 5, 6. Microstructure of KNN crystal grown by Flux method. Domain structure of KNN single-crystal

C. Dielectric Studies

Dielectric measurements were made from room temperature to 500 ℃ for the grown KNN single crystals. Fig.(7) shows the temperature dependence of the dielectric permittivity at frequencies of 1kHz, 10kHz and 100kHz. Two dielectric permittivity peaks are observed at temperatures of about 210 ℃ and 429 ℃. The peaks arise due to phase transitions from orthorhombic → tetragonal and tetragonal → cubic respectively. Fig.(8) shows the variation of dielectric loss with temperature for $(K_{0.5}Na_{0.5})NbO_3$ single crystal at frequencies of 1kHz, 10kHz and 100kHz.. According to $KNbO_3$-$NaNbO_3$ (KN-NN) phase diagram[12,13], the phase transition sequence is orthorhombic → tetragonal→ cubic (O → T → C) with increasing temperature for K/Na ratio around 0.50:0.50 in KN-NN system. Therefore KNN single crystals are normal ferroelectrics with first-order phase transition. The dielectric

loss falls remarkably with increasing frequency from 1 kHz to 100 kHz. The higher dielectric loss observed in $(K_{0.5}Na_{0.5})NbO_3$ single crystal at lower frequencies implies that the movement of defects increases with increasing frequency. The significant rise of dielectric loss above 225 ℃ may be due to the ionic conduction at higher temperature range.

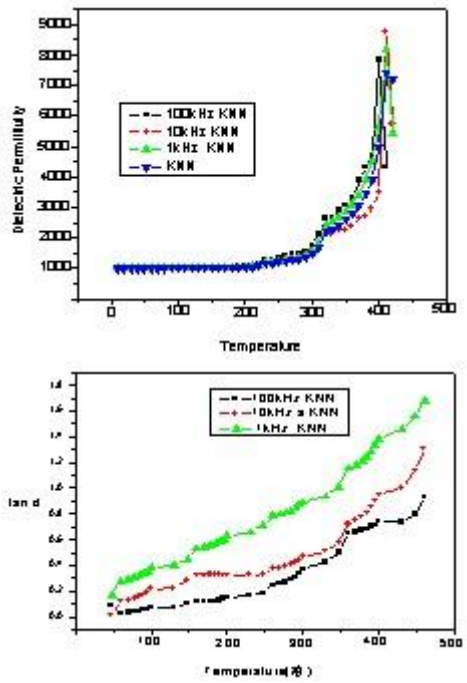


Fig. 7, 8. The temperature dependence of dielectric permittivity and dielectric loss of KNN single crystal.

Two phase transitions from the orthorhombic to the tetragonal phase at 190 ℃ and from the tetragonal to cubic phase at 390 ℃ were observed by Kizaki *et al*[9]. The same has been reported by D.Lin et al as 205 ℃ and 393 ℃ respectively [10]. The differences in the reported phase transition temperatures of KNN single crystal prepared was due to the composition fluctuations in the crystals due to flux growth. Also the dielectric permittivity ε_r values for KNN single crystals are found to be slightly lower compared to the reported values. No significant difference was observed in the loss factor tan δ.

D. Raman Studies

Raman spectroscopy can be used to accurately determine the tetragonality ratio of the perovskite structure. Moreover the displacement of the active ferroelectric ion in lead-free KNN-modified single crystal can also be determined from Raman spectra. The observed vibrations are shown in Fig(9). The vibration can be resolved into external modes related to cations and internal modes related to coordination polyhedra. The full Raman spectra of KNN consist of stretching and bending modes of NbO_6 octahedra. υ_1, υ_2, and υ_3 are stretching modes and υ_4, υ_5, and υ_6 are bending modes. There was a spectral change observed in the spectra less than 275 cm^{-1} and the modes around 525, 575, and 815 cm^{-1} exhibited similar behaviors to that of pure $KNbO_3$. There are no soft modes observed, as occurs for a large number of mixed ferroelectrics. The band at 808 cm^{-1} arises from the short Nb=O stretching mode (υ_1+υ_5). The band at 555 cm^{-1} represents a doubly-degenerate symmetric O-Nb-O stretching vibration (υ_1). The band at about 261 cm^{-1} arises from the stretching vibration of the Nb-O bonds (υ_5). The above modes are characteristic of the NbO_6 octahedron, providing evidence for the formation of the perovskite phase. Three optical modes related to υ_1, υ_2 and υ_3 vibrations of the NbO_6 octahedra lie in the range 500–700 cm^{-1}.

The internal vibrations are due to the octahedral NbO_6 molecular group. The vibration modes of the NbO_6 octahedron can be decomposed into two bond stretching vibrations of $A_1g(\upsilon_1)$ and $Eg(\upsilon 2)$. The υ_1 vibration is related to symmetric A_1g type mode, which represents the Nb-O bonds vibration, υ_2 means doubly degenerated Eg vibrations of the O-Nb-O bonds and υ_3 is triply degenerated T_{1u} vibration of the Nb-O bonds. The υ_1, υ_2, υ_3 vibrations are stretching modes of the NbO_6 octahedral group. The other three normal bending vibrational modes are triply degenerated ν_4 with T_{1u} symmetry of the O-Nb-O bonds; triply degenerated ν_5 with T_{2g} symmetry of the O-Nb-O bonds; and triply degenerated υ_6 with T_{2u} symmetry of the O-Nb-O bonds. Recently, Raman analyses on KNN-based systems indicate that vibrations of NbO_6 octahedron are sensitive to the occurrence of phase transitions.

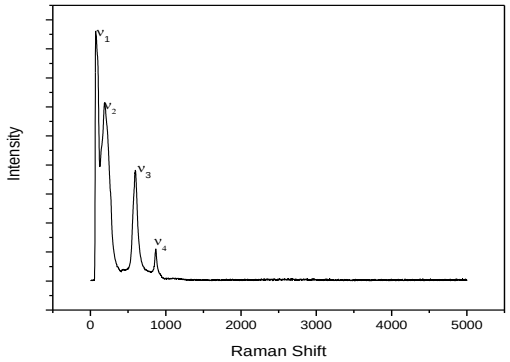


Fig. 9. Raman spectrum of KNN single crystal

IV. Conclusion

KNN single crystals were grown by high temperature solution method using KF flux modified with boron oxide. The addition of small amount of B_2O_3 allows growing crystals at slightly lower temperature. XRD pattern confirmed the crystallinity of the grown crystals and the absence of any secondary phases. Crystal size was observed to be dependent on the amount of boron oxide used and the cooling rate during growth. Two phase transition temperatures for transitions from orthorhombic to tetragonal and tetragonal to cubic are found to be at 210 ℃ and 429 ℃ respectively for KNN single crystal and the dielectric loss falls remarkably with increasing frequency from 1 kHz to 100 kHz according to the dielectric measurements. Thin layered growth of the laminar domain structure and spindle like domain structure with surface roughness of about 6.96nm are observed in KNN single crystals.

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