Growth and characterization of undoped and Mn doped lead-free piezoelectric NBT–KBT single crystals

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ABSTRACT

Lead-free piezoelectric single crystals of undoped and 1 wt% Mn doped 0.80 Na0.8Bi0.2TiO3–0.20 K0.8Bi0.2TiO3 (NKBT) was grown using self-flux. Powder X-ray diffraction analysis revealed that the grown crystals belong to tetragonal system at room temperature. The lattice strain was calculated from Williamson Hall relation for undoped and Mn doped NKBT crystals. A significant change is observed in dielectric behavior of Mn doped NKBT when compared to undoped sample. The diffuseness increased substantially on Mn doped NKBT which masked the ferroelectric to antiferroelectric transition in the dielectric constant plot. The AC impedance study revealed that the conduction is governed by the singly ionized oxygen vacancy. Further, the decrease in the conductivity on Mn doping suggests that Mn replaces the Bi vacancy, which reduces the oxygen vacancy.

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1. Introduction

Piezoelectric materials are the key components of ultrasonic sensors, transducers and actuators. The growth of piezoelectric single crystals is an important issue in this context, as single crystals offer much higher piezoelectric and electromechanical properties over polycrystalline ceramics [1–4]. The field of piezoelectric applications is dominated by the lead based materials. However, environmental hazard is a major concern with the lead based materials as lead is a toxic material [5]. In view of this, materials with low lead content or free from lead, for example, lead-free soldering material, are preferred from the view-point of environmental impact. Similarly, a demand for lead free piezoelectric crystals has increased as well. A lot of research in the quest of a suitable lead free piezoelectric material is being carried out. Much of the research have been focused on (Bi0.5Na0.5)TiO3 (BNT)-based oxides [6–8], bismuth layered structure oxides [9], BaTiO3 based solid solutions [10,11] and tungsten bronze-type oxides [12,13]. In recent years NBT based material has attracted considerable attention because of its potential application as a lead-free piezoelectric candidate. To improve its piezoelectric properties, many investigations have been widely carried out on NBT–BT, NBT–KBT ceramics and single crystals [6,14]. The high coercive field of NBT causes difficulty in the process of poling of the sample. However, when solid solution of NBT is formed with tetragonal potassium bismuth titanate (K0.8Bi0.2TiO3; space group symmetry P4mm), the coercive field is lowered [15]. Further, like PZT system [16], the complex system of NBT and KBT [Bi0.5(K,Na1−x)0.5TiO3] shows a reasonably good piezoelectric property near its morphotropic phase boundary (MPB; 0.16 < x < 0.2), in comparison to the other lead free piezoelectrics [17–19]. Also, it has been reported for ceramic and thin films that introduction of a small amount of dopants, such as MnO2, in NKBT influences the ferroelectric and electrical properties [20,21]. However, a little investigation has been carried out on doped NKBT-based single crystals so far. In the present work, lead-free single crystals of undoped NKBT (0.80NBT–0.20KBT) and 1 wt% Mn-doped NKBT were grown by self flux. Powder XRD measurements are carried out on both the undoped and Mn-doped samples. Further, the effect of Mn doping on the dielectric and ac conductivity behavior of NKBT is discussed.

2. Crystal growth

Conventional high temperature flux method was employed to grow undoped and Mn doped NKBT single crystals from the raw powders of Bi2O3 (99.9%), TiO2 (99.5%), Na2CO3 (99.95%), K2CO3 (99%) and Mn2O3(98%). Bi2O3, Na2CO3 and K2CO3 were used as flux. The oxide and carbonate powders were weighed according to the
stoichiometric ratio. The raw powders were thoroughly mixed and
put into a platinum crucible. Calcination was done at 850 °C for 48 h
for the solid state reaction. The reacted 0.80NBT–0.20KBT powder
was mixed with 1 wt% MnO₂ for doping and 25 wt% of excess
Na₂CO₃, K₂CO₃ and Bi₂O₃ that acts as the self-flux in the subsequent
growth experiment. The dopant and self flux added polycrystalline
materials were heated to 1150 °C at a heating rate of 100 °C/h. For
homogenization, the temperature is maintained for 24 h. For
subsequent growth of crystals slow cooling was employed from
1150 to 900 °C at a rate of 2 °C/h, which is then cooled to 700 °C at a
rate of 5 °C/h and, finally, from 700 °C to room temperature at a rate
of 100 °C/h. The grown undoped and Mn doped NKBT crystals are
shown in Fig. 1.

3. Characterization techniques

To confirm the crystalline nature and phase formation, powder
X-ray diffraction was carried out on undoped and Mn doped NKBT
crystal using Rigaku make diffractometer. The diffraction data was
recorded using CuKα in the 2θ range of 20–70° at 0.02° step. For
various electrical measurements, plates were prepared from the
grown undoped and Mn doped NKBT crystals and electroded with
high temperature curing silver paste. Dielectric and conductivity
studies were carried out using the HP4194A impedance analyzer.

4. Results and discussion

Powder XRD pattern of the undoped and Mn doped NKBT
crystals are shown in Fig. 2. The obtained crystals possess
perovskite phase which is evident from the pattern. No significant
difference in the XRD pattern was observed for Mn doped sample.
The powder X-ray diffraction profiles (1 1 1) and (2 0 0) of pseudo-
cubic reflection is analyzed. Single intensity profile is observed in
(1 1 1) reflection whereas (2 0 0) reflection comprises of two distinct
peaks. This confirms that the global symmetry of the grown crystal
is tetragonal. The calculated lattice parameters are a = b = 3.895(0) Å,
c = 3.908(7) Å and lattice volume is 59.300(2) Å³ which is in good
agreement with the earlier reported value [22] for pure NKBT. The
calculated lattice parameter for Mn doped NKBT are a = b = 3.877
(8) Å, c = 3.855(3) Å and lattice volume is 56.516(7) Å³.

Fig. 3 illustrates the strain developed in the crystalline lattice of
undoped and Mn doped NKBT crystals (inset) as calculated by the
Williamson–Hall relation: \(\beta \cos \theta = \kappa \lambda / \tan \theta + \eta \sin \theta\), where \(\beta\) is the full
width at half maximum in radians, \(\theta\) is the Bragg diffraction angle
of the peak, \(\kappa\) is the Scherrer constant, \(\lambda\) is the wavelength of the X-
rays and \(r\) is the crystallite size. The value of \(\eta\) is calculated from the
slope of \(\beta \cos \theta \sin \theta\) vs \(\sin \theta\) plot. It is found to be 1.7 × 10⁻² for pure NKBT
and -1.14 × 10⁻³ for Mn doped NKBT crystals. For pure NKBT
crystals, the positive slope indicates that the strain is tensile
whereas in Mn doped NKBT the slope is negative which indicates
that the strain is compressive strain. After Mn doping, most of the
Mn ions were likely to enter into Bi-site due to the smaller size of
Mn³⁺ [\(R(Mn³⁺) = 81\) pm (low spin) and \(97\) pm (high spin)] and Mn⁺
[\(R(Mn⁺) = 72\) pm (low spin) and \(78.5\) pm (high spin)] when
compared to Bi⁵⁺ [\(R(Bi^{5+}) = 117\) pm]. Therefore Mn sits in Bi vacant

![Fig. 1. As-grown undoped and Mn doped NKBT crystals.](image1)

![Fig. 2. Powder X-ray diffraction pattern of undoped and Mn doped NKBT crystals.](image2)

![Fig. 3. W–H plot for undoped and Mn doped NKBT crystals (inset).](image3)
sites and reduces the vacancies. Hence the strain is reduced in Mn doped NKBT crystals when compared to undoped NKBT crystals.

The temperature and frequency dependent dielectric constant and loss [100] oriented undoped and Mn doped NKBT crystals for are shown in Figs. 4 and 5. The measurements were carried out at twenty different frequencies varied from 100 Hz to 1 MHz but the dielectric constant and dielectric loss data corresponding to 30, 50, 150 and 600 kHz are presented here for the sake of clarity. For undoped NKBT (shown in Fig. 4), there are two anomalies in the temperature dependent dielectric plot. The first anomaly ($T_d$) is at about 165 °C which corresponds to a change from ferroelectric phase to an anti-ferroelectric phase [6–8,17]. The maxima exhibits a clear dependency on frequency, i.e., $T_d$ gradually shifted toward higher temperature with the increase in frequency. The second dielectric peak ($T_m$) at ~323 °C corresponds to a change from the antiferroelectric phase to a paraelectric phase which is almost independent of frequency.

The dielectric behavior for the Mn-doped sample exhibits characteristic differences in comparison to the undoped sample, as shown in Fig. 5. It is evident that on Mn-doping, the dielectric permittivity has been increased and the loss has reduced. The maximum dielectric constant at 30 kHz for undoped NKBT is ~3080 and Mn doped NKBT crystal is ~3371. It has been reported that defect dipole $MnV_o$ ($Mn$ in Ti site and $V_o$ refers to the oxygen vacancy) are created in ferroelectric materials such as PZT when Mn is doped [23]. These defect dipoles can align due to the comparatively high mobility of the oxygen vacancy, to produce an internal bias field, consequently decreasing the relative permittivity and loss tangent [24]. However, for NKBT, dielectric constant increased on Mn doping signifying that the defect dipoles are possibly not created in NKBT. A similar behavior is also reported for NBT [25].

Also, the $T_d$ peak disappears in the temperature dependent dielectric constant plot for Mn doped NKBT. However, a careful observation reveals that the anomaly is still persisted in the dielectric loss part. But it is noteworthy that it had substantially diminished. Further, the value of $T_m$ shifted toward lower temperature on Mn doping: 318 °C for Mn:NKBT in comparison to 323 °C from undoped sample at 30 kHz. Also, the $T_m$ shows frequency dependence. The variation in the temperature of the dielectric maxima shifted with frequency in the order of 2 °C (inset of Fig. 5). This signifies a mild relaxor like behavior in Mn doped NKBT. A similar observation has been reported for ceramic sample as well [26]. Mn acts as dilation center and generates a random field in the system which consequently destroys the long range order in NKBT and leads to the relaxor-like behavior as observed.
Further, to get an insight of the diffused phase transition, the dielectric data was fitted with the modified Curie–Weiss equation. It is well known that for classical ferroelectrics, the dielectric permittivity follows Curie–Weiss law: 
\[ \varepsilon = \varepsilon_0 (T - \theta) \]
where the Curie–Weiss constant, \( \theta \) is the Curie–Weiss temperature and \( \varepsilon_0 \) is the dielectric permittivity at temperature \( T \). However, for diffused phase transition (DPT) the equation is [27,28]:
\[ \frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{2\varepsilon_m \delta} \]
where \( \varepsilon_m \) is the maximum value of the dielectric constant occurred at temperature \( T_m \), \( \delta \) is the diffuseness of the dielectric dispersion and \( \gamma \) is the critical exponent. The plot for pure and Mn doped NKBT crystals are shown in Fig. 6. For undoped and Mn doped NKBT crystals, the values of \( \gamma \) were found to be 1.52 and 1.90 and the values of \( \delta \) are 63 and 103, respectively. It implies that the diffusiveness has increased substantially on doping with 1 wt% of Mn. The phase transition at \( T_d \) is masked in the diffused dielectric anomaly for Mn:NKBT. But the transition is still evident in the dielectric loss plot.

In Mn doped NKBT crystals, the conductivity can be mainly attributed to the oxygen vacancies, Bi vacancies and impurity defect (Mn). Different conduction mechanisms in materials correspond to different temperature ranges. The dominant defect structure with lower activation energy controls the conductivity. In perovskite, generally, Mn\(^{3+} \) or Mn\(^{2+} \) ions replaces the Ti site, which consequently increases the conductivity [29]. However, there are reports of Mn replacing the Bi ions also [30]. To study the effect of Mn in NKBT the AC conductivity of the undoped and doped samples were measured and \( \ln \sigma \) versus the inverted temperature (1000/T) was plotted (Fig. 7). The plot was fitted with the Arrhenius relation:
\[ \sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right) \]
where \( E_a \) is the activation energy, \( \sigma_0 \) is the pre-exponential factor, \( k \) is the Boltzmann constant and \( T \) is the temperature in Kelvin. The slope of the graph enables the determination of the activation energy \( E_a \). The activation energy for undoped NKBT is 0.42 eV and Mn doped NKBT is 0.23 eV in the range of 400–500 K. The order of activation energy is that of conduction of singly ionized oxygen vacancy which is 0.2–0.5 eV for perovskites [31,32]. The activation energy corresponding to the doubly ionized oxygen vacancy is 0.6–1.2 eV. Further, the conductivity was found to decrease on Mn doping which signifies that the concentration of oxygen vacancy has decreased. This suggests that Mn rather replaces the Bi ion in the A site. As Bi is volatile, during the growth of NKBT crystal, Bi vacancies are created which introduce the oxygen vacancies for charge balance. However, when Mn is doped, as it sits in the Bi vacant sites it reduces the concentration of oxygen vacancy and consequently reduces the conductivity. The observation is consistent with the dielectric measurement where the loss is reduced on Mn doping.

5. Conclusions

Lead-free piezoelectric single crystals of undoped and 1 wt% Mn doped 0.80 \( \text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - 0.20 \text{K}_0.5\text{Bi}_{0.5}\text{TiO}_3 \) were grown by spontaneous nucleation technique using self-flux. The grown crystals belong to the tetragonal system. The lattice strain is decreased in Mn doped NKBT crystals. The diffuseness in the dielectric anomaly increased substantially on Mn doping which masked the ferroelectric to antiferroelectric transition. The AC impedance study revealed that the activation energy is \( \sim 0.2–0.4 \) eV which suggests that the conduction is governed by the singly ionized oxygen vacancies. Further, the decrease in the conductivity on Mn doping signifies that Mn ions replace the Bi vacancies resulting into a decrease in the concentration of oxygen vacancy.

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References