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Dielectric and electrical properties of $K_{1-x}Na_xNbO_3$ system

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Dielectric and electrical properties of $K_{1-x}Na_xNbO_3$ (*x*=0, 0.2, 0.4) ceramics have been investigated in the temperature range 35-250°C at different frequencies in the range 0.1-1 MHz. The samples have been prepared by the conventional solid-state reaction method and sintering process. It is observed that dielectric constant, loss tangent and electrical conductivity increase with increasing temperature. Near the transition temperature, dielectric constant, loss tangent and electrical conductivity of these samples show anomalous behaviour. All the prepared samples show orthorhombic structure at room temperature.

Keywords: Transition temperature, Dielectric constant, Loss tangent, Electrical conductivity

1 Introduction

The class of materials known, as perovskite is of considerable technological importance, particularly with respect to their physical properties such as pyro- and piezo-electricity, dielectric susceptibility, linear and non-linear electro-optic etc. Many of these properties vary enormously from one perovskite to another. The change in physical properties is particularly large when the external conditions, such as temperature, pressure, electric-field etc. are altered. Such effects occur in connection with the simultaneous presence of phase transition in the system, where the atomic structure of the perovskite changes either discontinuously or continuously into another form. The dielectric properties of perovskite structure $K_{1-x}Na_xNbO_3$ for some of the compositions have been extensively studied at high temperature[1] and it shows a number of ferroelectric phases with high spontaneous polarization. The solid solution of ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$ exhibits good piezoelectric properties[2,3]. Potassium sodium niobate ceramics ($K_{1-x}Na_xNbO_3$) with perovskite structures are widely used for transducer applications with broad ranges of technologically important dielectric, piezoelectric, ferroelectric and electro-optic properties. The structure at room temperature, which, basically of the orthorhombic type. $K_{1-x}Na_xNbO_3$ (*x*=0) is a particularly promising ferroelectric with its combination of relatively low dielectric constant (ε1=155, ε2=44 and ε3=980) with extremely high electro-optic coefficients (r_{42}=380 pm/V, r_{33}=64 pm/V). This makes $KNbO_3$ very attractive for opto-electronic devices, including high-speed electro-optic switches, modulators and frequency doublers[4-7]. Because of the interest in this material for high frequency, electro-optical devices, investigation and analysis of dielectric properties have been studied on $KNbO_3$ pellets as well as mixed ceramics[8-11]. Dielectric measurements on this material were first reported by Matthias and Remeika[12] and then by Shirane *et al.*[13] and observed well defined ferroelectric hysteresis loops from room temperature to 400°C, for compositions from about 10 to 100% (mol) of K in $K_{1-x}Na_xNbO_3$. Dielectric properties were reported by Narayan Murty *et al*[14]. Cross[15] has predicted theoretically, the phase-diagram of $KNbO_3$-$NaNbO_3$ mixture from phenomenological arguments. The mixing of $NaNbO_3$ in $KNbO_3$ ceramics plays an important role on the ferroelectric curie temperature, dielectric constant, grain size as well as the planer mechanical coupling coefficient (k_p) value[16-17] because $NaNbO_3$ is anti-ferroelectric at room temperature, when mixed with small amount of $KNbO_3$, becomes ferroelectric, which creates interest in the present study. Hence, this system has been investigated by varying composition and temperature range. In this paper, the results of investigation on dielectric constant, tangent loss and electrical conductivity of the ceramic system $K_{1-x}Na_xNbO_3$ (*x*=0, 0.2 and 0.4) prepared by solid state reaction method and sintering process with temperature range 35-250°C in the frequency range 0.1-1 MHz has been reported.

2 Experimental Details

The raw materials used for preparing the compositions from this system are sodium carbonate, potassium carbonate and niobium pentaoxide. The two carbonates were both reagent-grade products of the Qualigens Fine Chemicals and the niobium pentaoxide was 99.9% purity from Fluka Chemie AG CH-9471 Buchs. The starting material was dried at 200°C for one hour to remove absorbed moisture. Different compositions of $K_{1-x}Na_xNbO_3$ (PSN) for (x=0, 0.2 and 0.4) were prepared by weighing the sodium carbonate, potassium carbonate and niobium penta-oxide (starting materials) in proper stoichiometric proportions. The mixture was calcined in the platinum crucible in air at 950°C for 2 h for removal of carbonate. After cooling it in dry air, the calcined mixtures were weighed to ensure complete carbonate removal.

The pre-sintered mixture was ground and pressed into pellets of 10 mm diameter. All the pellets were placed on a platinum crucible and sintered in air at 1050°C for 26 h. The sintered pellets were electroded using air-drying silver paste for dielectric measurements.

X-ray powder studies were performed at room temperature with a SEIFERT 3000P. X-ray diffractometer using filtered Cu Kα1 radiation of 1.540598Å wavelength in which Ni is used as filter. The instrument is well calibrated with silicon standard samples and the lines obtained are matching with the standard lines. At room temperature, all PSN ceramics show the orthorhombic symmetry. The sub-cell parameters were obtained using the auto-X computer software and compatible with those obtained earlier for ceramics[14,16-21]. The results are presented in Table 1.

The variations of dielectric constant, loss tangent and electrical conductivity at frequency 0.1 MHz and 1 MHz in the temperature range 35-250°C are shown in Figs 2-7, respectively. These measurements were performed on RCL meter model FLUKE PM 6306.

3 Results and Discussion

We have measured dielectric constant, loss tangent of $K_{0.6}Na_{0.4}NbO_3$, $K_{0.8}Na_{0.2}NbO_3$ and $KNbO_3$ ceramic pellets using HP Impedance Analyzer and LCR meter PM 6304 have been measured in the temperature range 35-250°C. The effect of mixing of Na in $KNbO_3$, i.e, $K_{1-x}Na_xNbO_3$ on the lattice parameters is shown in Fig. 1. All the lattice parameters, i.e., *a*, *b*

Table 1 — Lattice parameters of $K_{1-x}Na_xNbO_3$ for composition at room temperature

Composition	Lattice parameter (Å)		
	a	b	c
$KNbO_3$	4.027	4.057	3.958
$K_{0.8}Na_{0.2}NbO_3$	4.002	4.04	3.946
$K_{0.6}Na_{0.4}NbO_3$	3.998	4.011	3.919

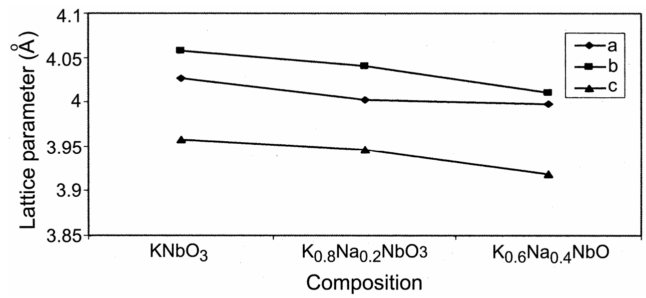

Fig. 1 — Composition dependence of lattice parameters

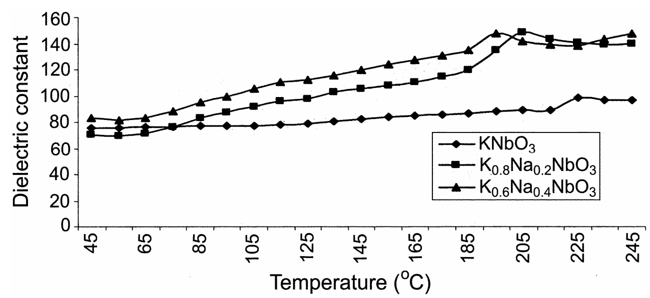

Fig. 2 — Variation of dielectric constant with temperature for $K_{1-x}Na_xNbO_3$ at 1 MHz

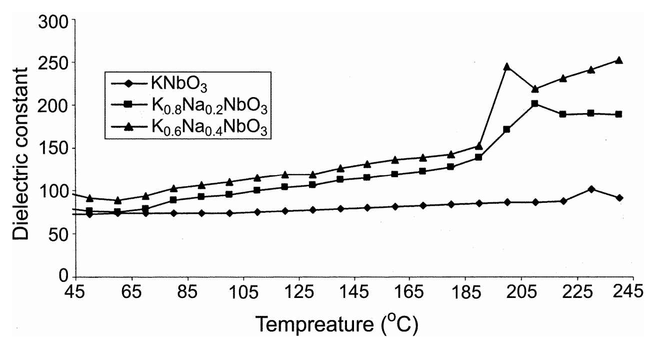

Fig. 3 — Variation of dielectric constant with temperature for $K_{1-x}Na_xNbO_3$ system at 100 kHz

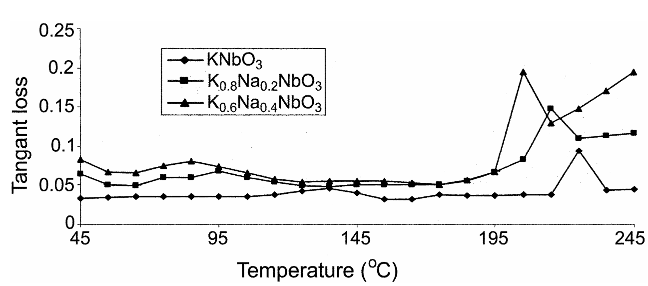

Fig. 4 — Variation of tangent loss with temperature for $K_{1-x}Na_xNbO_3$ system at 1 MHz

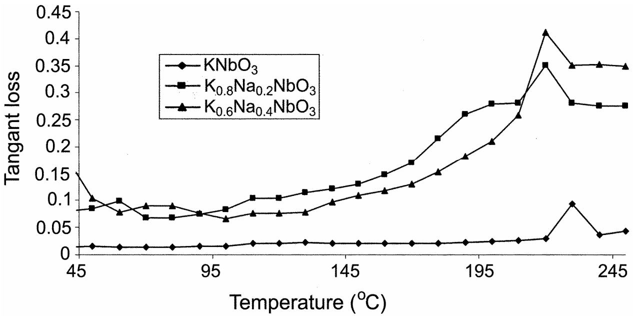

Fig. 5 — Variation of tangent loss with temperature for $K_{1-x}Na_xNbO_3$ at 100 kHz

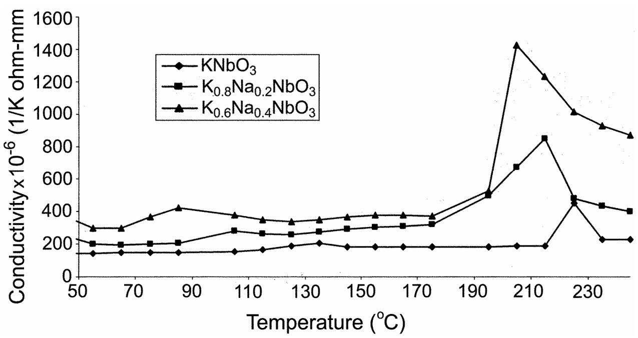

Fig. 6 — Variation of electrical conductivity with temperature for $K_{1-x}Na_xNbO_3$ system at 1 MHz

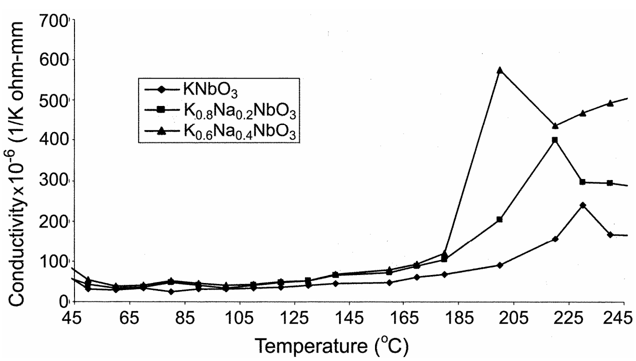

Fig. 7 — Variation of conductivity with temperature for $K_{1-x}Na_xNbO_3$ system at 100 kHz

and *c* show similar nature of variation. The values of the lattice parameters have been found to be increasing by increasing the % of Na in $K_xNa_{1-x}NbO_3$ up to approximately 2% of Na, thereafter, they are decreasing, thereby, showing a compositional transition with anomaly at 2%, which may be due to the difference in size of atom of K and Na. The temperature dependence of dielectric constant, loss tangent and conductivity at 1 MHz and 100 kHz is shown in Figs 2-7, respectively. Hence, it is observed that the mixed system of $K_{1-x}Na_xNbO_3$ has a transition from orthorhombic to tetragonal at about 220°C(Figs 2-7). It is 225°C for $KNbO_3$, 215°C for $K_{0.8}Na_{0.2}NbO_3$ and 205°C for $K_{0.6}Na_{0.4}NbO_3$, which show that transition temperature from orthorhombic to tetragonal shifts towards lower temperature as the quantity of anti -ferroelctric material sodium niobate in the mixed system is increased, which is in agreement with previous observations[1,22].

4 Conclusions

The results show that the mixing of Na is effective in promoting the densification of the ceramics and can be well sintered and exhibit a dense, pure perovskite structure which is due to the presence of oxygen vacancies. For most KNN-based solid solutions, the piezoelectric properties are enhanced[23] but with a reduced T_c. Therefore, by 2% mixing of Na, the transition temperature is 215°C whereas by 4% mixing of Na, transition temperature reduces to 205°C, which shows that transition temperature from orthorhombic to tetragonal shifts towards lower temperature as we increase the quantity of anti-ferroelectric material $NaNbO_3$ in the mixed system.

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