

Synthesis, Characterization and Dielectric Properties of $K_{1-x}Na_xNbO_3$

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Abstract The samples of $K_{1-x}Na_xNbO_3$ ($x=0.4, 0.2, 0$) ceramics (PSN) have been prepared by the conventional solid-state reaction method and sintering process. The prepared samples have been characterized by XRD. All the prepared samples show orthorhombic structure at room temperature. Dielectric and Electrical properties of PSN system have been investigated in the temperature range $45^{\circ}C-245^{\circ}C$, and at 1MHz frequency. It is observed that dielectric constant, loss tangent and electrical conductivity increases with increasing temperature. Near the transition temperature dielectric constant, loss tangent and electrical conductivity of these samples show anomalous behaviour with temperature.

Keywords Transition Temperature, Dielectric Constant, Loss Tangent, Electrical Conductivity

1. Introduction

ABO_3 Perovskite type materials are of considerable technological importance, particularly with respect to their physical properties such as ferro, pyro- and piezo-electricity, dielectric susceptibility, linear & non linear electro-optic properties etc. The change in physical properties is particularly large when the external conditions, such as temperature, pressure, electric-field, composition 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 ABO_3 perovskite structure $K_{1-x}Na_xNbO_3$ for some of the compositions has 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 ceramic ($K_{1-x}Na_xNbO_3$) with perovskite structures are widely used for transducer applications with broad ranges of technologically important dielectric, piezoelectric, ferroelectric and electro-optic properties. The structure of PSN system at room temperature is 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 ($\epsilon_1 = 155, \epsilon_2 = 44, \text{ and } \epsilon_3 = 980$) with extremely high electro-optic coefficients ($r_{42}=380\text{pm/V}$, $r_{33}=64\text{pm/V}$). This

makes $KNbO_3$ vary attractive for opto-electronic devices, including high-speed electro-optic switches, modulators, and frequency doublers [4-7]. Dielectric measurements on this material were first reported by Matthias and Remeika [8] and then by Shirane et. al. [9] and observed well defined ferroelectric hysteresis loops from room temperature to $400^{\circ}C$, 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. [10]. Cross [11] has predicted, theoretically, the phase-diagram of $KNbO_3$ - $NaNbO_3$ mixture from phenomenological arguments. The mixing of $NaNbO_3$ in $KNbO_3$ ceramics play an important role on the ferroelectric Curie temperature, dielectric constant, grain size as well as the planer mechanical coupling coefficient (k_p) value [12-13], 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 investigation to investigate this system with a varying composition and temperature range. In this paper, we report the results of investigation on dielectric constant, tangent loss and electrical conductivity of the ceramic system $K_{1-x}Na_xNbO_3$ ($x=0.4, 0.2 \text{ \& } 0$) prepared by solid state reaction method and sintering process, in the temperature range $45^{\circ}C-245^{\circ}C$, and at 1 M Hz frequency.

2. Preparation

The starting material was dried at $200^{\circ}C$ for one hour to remove absorbed moisture. Different compositions of $K_{1-x}Na_xNbO_3$ for ($x=0.4, 0.2 \text{ \& } 0$) 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 $950^{\circ}C$ for 2h, for carbonate removal.

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After cooling, in dry air, the calcined mixtures were weighed to ensure complete carbonate removal.

The pre-sintered mixture was ground and pressed into pellets of 10mm 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.

3. Characterization

X-ray powder studies were performed at room temperature with a SEIFERT 3000P X-ray diffractometer using filtered Cu K α_1 radiation of 1.540598 Å 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 ceramic samples exhibit the orthorhombic symmetry. The sub cell parameters were obtained using the auto-X computer software and were compatible with those obtained earlier for ceramics [10,12-17]. The results are summarized in following table-

Table A. Lattice parameters of $K_{1-x}Na_xNbO_3$ for different compositions at room temperature

composition	Lattice parameters °A		
	a	b	c
KNbO ₃	4.027	4.057	3.958
K _{0.8} Na _{0.2} NbO ₃	4.002	4.040	3.946
K _{0.6} Na _{0.4} NbO ₃	3.998	4.011	3.919

4. Measurements

The variation of dielectric constant, loss tangent and electrical conductivity at 1MHz frequency, in the temperature range 45°C-245°C have been studied and plotted in Fig. 1, 2 & 3 respectively. These measurements were performed on HP Impedance Analyzer and FLUKE RCL meter, PM 6306.

5. Result and Discussions

We have measured dielectric constant, loss tangent of K_{0.6}Na_{0.4}NbO₃, K_{0.8}Na_{0.2}NbO₃ and KNbO₃ ceramic pellets using HP Impedance Analyzer and Fluke RCL meter PM 6304, at the temperatures from 45°C to 245°C. The temperature dependence of dielectric constant, loss tangent and conductivity at 1MHz have been shown in Figs 1, 2 & 3, and tables-1,2 & 3, respectively.

From these figures (Fig.1-3) and tables (Tables 1-3), 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. It is 225°C for KNbO₃, 215°C for K_{0.8}Na_{0.2}NbO₃ and 205°C for K_{0.6}Na_{0.4}NbO₃, which shows that transition temperature from orthorhombic to tetragonal shifts towards lower temperature as we increases the quantity of anti-ferroelectric

material sodium niobate in the mixed system of $K_{1-x}Na_xNbO_3$, which is in agreement with previous observations[1,18]. Lattice parameters of $K_{1-x}Na_xNbO_3$ for different compositions at room temperature have been shown in table-A, which shows a decrease in lattice parameters as we add antiferroelectric material NaNbO₃ in mixed system of $K_{1-x}Na_xNbO_3$ ceramic.

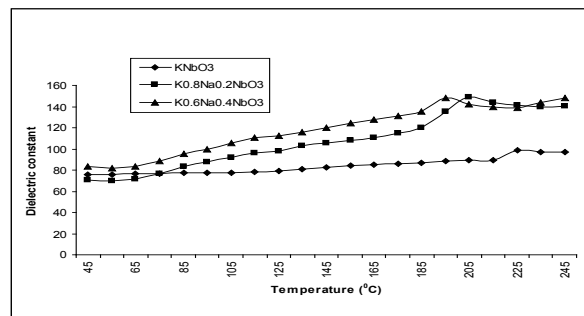


Figure 1. Variation of dielectric constant with temperature for $K_{1-x}Na_xNbO_3$ at 1 MHz

Table 1. Variation of dielectric constant with temperature for $K_{1-x}Na_xNbO_3$, at 1 MHz frequency

Temperature °C	KNbO ₃	K _{0.8} Na _{0.2} NbO ₃	K _{0.6} Na _{0.4} NbO ₃
45	76.17	70.57	83.680
55	76.17	69.88	81.910
65	76.52	71.41	83.270
75	76.88	76.81	88.670
85	77.22	83.57	95.320
95	77.39	87.35	99.690
105	77.71	92.11	105.20
115	78.58	96.23	110.40
125	79.18	97.81	112.06
135	81.10	102.61	115.49
145	82.74	105.50	120.27
155	83.95	107.75	124.01
165	85.14	110.37	127.45
175	86.13	115.11	130.77
185	87.35	120.25	134.93
195	88.54	135.34	148.03
205	89.39	149.11	141.86
215	89.73	144.07	139.39
225	98.58	141.05	138.67
235	97.17	139.48	143.46
245	96.60	140.48	147.98

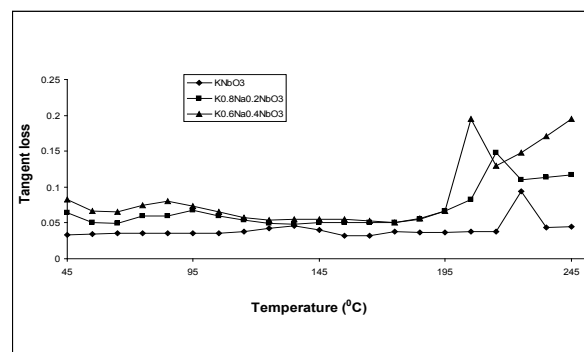
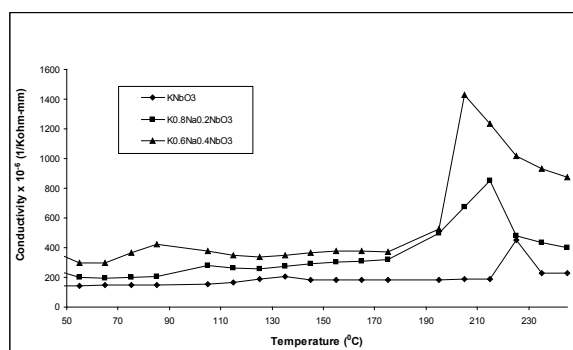


Figure 2. Variation of tangent loss with temperature for $K_{1-x}Na_xNbO_3$ system at 1 MHz

Table 2. Variation of loss tangent for $K_{1-x}Na_xNbO_3$, with temperature, at 1 MHz frequency

Temperature $^{\circ}C$	$KNbO_3$	$K_{0.8}Na_{0.2}NbO_3$	$K_{0.6}Na_{0.4}NbO_3$
45	0.033	0.064	0.082
55	0.034	0.051	0.066
65	0.035	0.049	0.065
75	0.035	0.060	0.074
85	0.035	0.068	0.080
95	0.035	0.060	0.073
105	0.036	0.054	0.065
115	0.038	0.049	0.057
125	0.043	0.047	0.054
135	0.046	0.048	0.055
145	0.040	0.050	0.055
155	0.032	0.050	0.055
165	0.032	0.050	0.053
175	0.038	0.050	0.051
185	0.037	0.055	0.056
195	0.037	0.066	0.067
205	0.038	0.082	0.086
215	0.038	0.102	0.130
225	0.040	0.110	0.148
235	0.044	0.114	0.171
245	0.045	0.117	0.195

**Figure 3.** Variation of electrical conductivity with temperature for $K_{1-x}Na_xNbO_3$ system at 1 MHz**Table 4.** Variation of electrical conductivity of $K_{1-x}Na_xNbO_3$ with temperature, at 1 MHz frequency

Temperature $^{\circ}C$	$KNbO_3$ ($\times 10^{-6}$)	$K_{0.8}Na_{0.2}NbO_3$ ($\times 10^{-6}$)	$K_{0.6}Na_{0.4}NbO_3$ ($\times 10^{-6}$)
45	141	250	372
55	145	198	299
65	147	195	298
75	150	255	364
85	151	265	422
95	152	290	405
105	155	278	380
115	164	264	349
125	188	257	340
135	205	276	350
145	184	290	366
155	182	301	380
165	181	310	378
175	181	322	369
185	181	365	417
195	183	498	528
205	187	677	707

6. Conclusions

Our results shows 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 and this is attributed to the fact of the presence of oxygen vacancies. For most KNN-based solid solutions, the piezoelectric properties are enhanced but with a reduced T_c [19]. Therefore as 20% mixing of Na, transition temperature is $215^{\circ}C$ whereas 40% mixing of Na, transition temperature reduces to $205^{\circ}C$, 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, $K_{1-x}Na_xNbO_3$.

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