



## Synthesis of Lead free Ceramics and their Dielectrical and Piezoelectrical Properties

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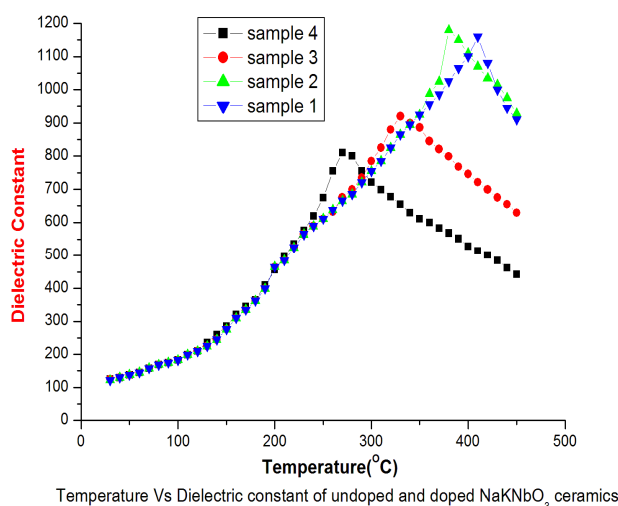
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### ABSTRACT

Sodium Potassium niobate ( $Na_{0.5}K_{0.5}NbO_3$ ) ceramics with Perovskite structure are widely used for piezoelectric applications. The low dielectric constants and improved piezoelectric activity make these materials desirable for transducer applications. These materials are synthesized by solid state reaction technique. The main objective of this work is to study the effect of rare earth ion  $Pr^{3+}$  on dielectric and piezoelectric properties of  $Na_{0.5}K_{0.5}NbO_3$  ceramics with the formula  $Na_xK_{x-3Y}Re^{3+}NbO_3$  with  $X=0.05$  and  $Y=0, 0.05, 0.10$  and  $0.15$ . It reports that sample-1 showing a sharp transition temperature at  $T_c=410^\circ C$  and it also found that increase of rare earth ions decreased the transition temperature.

### Graphical Abstract



**Keywords:** Solid state method, Sintering, Dielectric and Piezoelectric studies.

## INTRODUCTION

The phenomenon of ferroelectricity in Rochelle salt from the measurement of its dielectric properties observed and reported [1,2]. The dielectric and piezoelectric properties Potassium sodium niobate were reported [3]. It was found that the piezoelectric properties of these KNN near MPB at 50mole% NaNbO<sub>3</sub> i.e, Na<sub>0.5</sub> K<sub>0.5</sub>NbO<sub>3</sub> maximum piezoelectric coefficients of  $d_{33} = 80\text{pc/N}$  and  $K_p = 0.36$ . Therefore, intensive research effect has been focused on the KNN near MPB. The niobates of Sodium and Potassium to be ferroelectric has reported by Matthias [4] and also Matthias and Rameika [5] have studied the dielectric properties of KNbO<sub>3</sub> and NaNbO<sub>3</sub> Crystals. Dungan et.al [6] studied the ferroelectric properties of NaNbO<sub>3</sub>.The piezoelectric properties of NaSrNbO<sub>3</sub> have been studied by Tannery [7]. The main objective of this work is to study the effect of rare earth ion Pr<sup>3+</sup> on dielectric and piezoelectric properties of Na<sub>0.5</sub> K<sub>0.5</sub>NbO<sub>3</sub>ceramics with the stoichiometric formula Na<sub>x</sub>K<sub>x-3y</sub> Re<sup>3+</sup>NbO<sub>3</sub> with X=0.05 and Y=0, 0.05, 0.10 and 0.15.

## MATERIALS AND METHODS

The raw materials are synthesized by solid state reaction technique [8] and the ceramic compositions under investigation were analytical reagent (AR) grade Na<sub>2</sub>CO<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> with 99.9% purity. Very careful handling of K<sub>2</sub>CO<sub>3</sub> is essential to avoid the moisture absorption. The starting materials were dried at 200°C for one hour to remove absorbed moisture. Suitable proportions of the starting materials in accordance with the solid state reaction of the following table 1.

**Table 1.** Compositions of doped and undoped NaKNbO<sub>3</sub> ceramics

S.No	Composition	Represented as
01	Na <sub>0.5</sub> K <sub>0.5</sub> NbO <sub>3</sub>	Sample-1
02	Na <sub>0.50</sub> K <sub>0.35</sub> Pr <sub>0.05</sub> NbO <sub>3</sub>	Sample-2
03	Na <sub>0.50</sub> K <sub>0.20</sub> Pr <sub>0.10</sub> NbO <sub>3</sub>	Sample-3
04	Na <sub>0.50</sub> K <sub>0.05</sub> Pr <sub>0.15</sub> NbO <sub>3</sub>	Sample-4

The compositions are dry ground into fine power for three hours and then mixed thoroughly in presence of alcohol to improve the homogeneity and ball milled for 24 h and dried. The mixture was calcined in a platinum crucible in air at 950°C for one hour. After cooling in dry air the calcined mixture were weighed to ensure completed carbonate removal. The pre sintered mixture was ground and pressed into disks by applying a pressure about 5-10 tons sq. inch<sup>-1</sup>. The disks were placed on a platinum foil and sintered in air at 1050°C for 15 h. Careful control of firing conditions was essential to produce required ceramic properties. The sintered disks were polished and electrode with air drying silver paste and fired at 700°C for 2 h. The studies on the prepared materials have been performed Hewlett Packard LF impedance analyser model 4192A through an intermediary accessory model 16095A. Then the capacitance measurements were taken at 1 KHz frequency from room temperature to 450°C. Then the dielectric constant is calculated by using the relation.

$$\epsilon = cd/\epsilon_0 A \quad - (1)$$

Where c is the capacitance of the sample, d is the thickness of the sample, A is the surface area of the sample,  $\epsilon_0$  is the free space permittivity ( $8.85 \times 10^{-12}$  F/m). In the present work, the ceramic specimens were polled by the method of Belding and McLaren [9]. The poling procedure involves heating of the sample in highly viscous silicon oil to temperatures between 100-110°C and then applying a d.c field of about 20-30 KV cm<sup>-1</sup>. Piezoelectric and dielectric measurements were carried out on poled specimens after 24 h poling, in accordance with the procedure by the IRE standards [10]. Piezoelectric coupling coefficients of ferroelectric ceramics are measured by the resonance-anti

resonance technique [11]. The piezoelectric charge coefficient,  $d_{33}$  is measured directly using channel products Berlincourt  $d_{33}$  meter at 100Hz. The electromechanical coupling factors [12] are material constants for crystals, and for ceramics they depend on degree of poling.

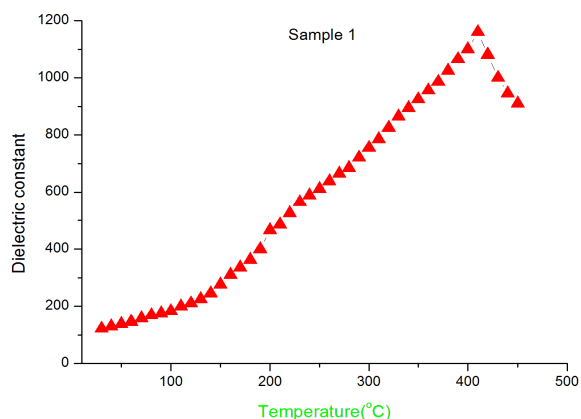
## RESULTS AND DISCUSSION

**Dielectric Studies:** The experimental results of dielectric constant as a function of temperature at 1 KHz are shown in figures 1 to 5 for  $\text{Pr}^{3+}$  substituted (Na K)  $\text{NbO}_3$  ceramics. From these temperature dependence of dielectric constant curves, it is clear that dielectric constant increases with the increase of temperature to certain temperature and further dielectric constant decreases even if the temperature increases and this phase transition temperature which also known as Curie temperature ( $T_c$ ). The values of ferroelectric – para electric phase transition temperature are presented in table 1. It is clear from the figure 1 that the pure (Na K)  $\text{NbO}_3$  shows a sharp transition temperature  $T_c$  is  $410^\circ\text{C}$  which is in good agreement with the reported value [13]. It is found that with the increase of rare earth  $\text{Pr}^{3+}$  dopant, the transition temperature decreased which can be seen figures 2, 3 and 4. Further as shown in figure 5 the dielectric peaks have become much broader compared to undoped ceramics. Such an observation also reported by Guo et.al, [14].

**Table 2.** Dielectric data of doped and undoped  $\text{NaKNbO}_3$  ceramics

S.No	Composition	Transition Temperature $T_c$ (°C)	Dielectric Constant at RT	Dielectric constant at $T_c$	Density gm/cc	Dielectric Loss
01	Sample-1	410	254	1160	4.60	0.081
02	Sample-2	380	207	1180	4.59	0.99
03	Sample-3	330	180	920	4.60	0.072
04	Sample-4	270	146	810	4.57	0.045

Similar type of peak broadening with the increase of rare earth trivalent dopant and the decrease in peak dielectric constant with the increase of dopant content is reported [15] in the rare earth  $\text{La}^{3+}$ . Also it is found that as the dopant content increases, the dielectric constant at transition temperature  $\epsilon_{T_c}$  decreases as shown in table 2. The values of Dielectric constant at room temperature  $\epsilon_{RT}$ , dielectric constant at ferro – para phase transition  $\epsilon_{T_c}$  and the phase transition temperature  $T_c$  and the dielectric loss are presented in table 2.



**Figure 1.** Variation of temperature with dielectric constant for Sample 1

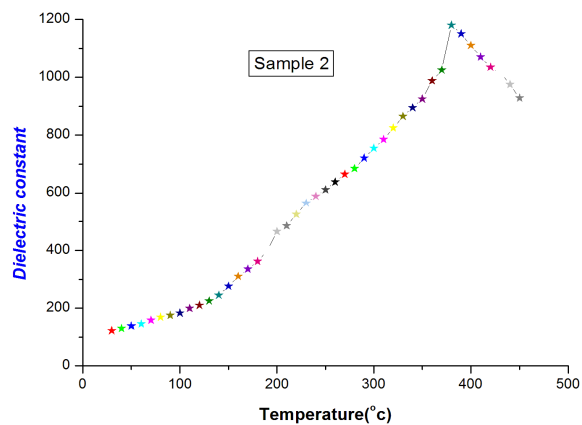


Figure 2. Variation of temperature with dielectric constant for Sample 2

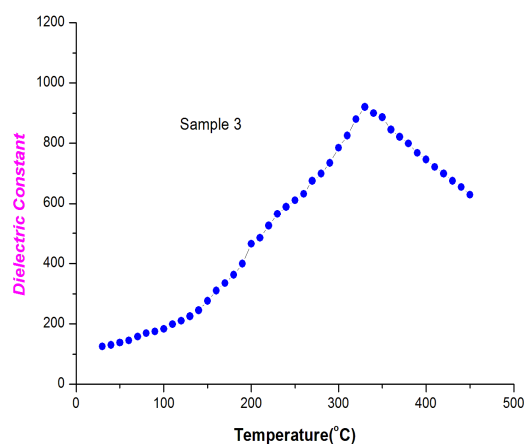


Figure 3. Variation of temperature with dielectric constant for Sample 3

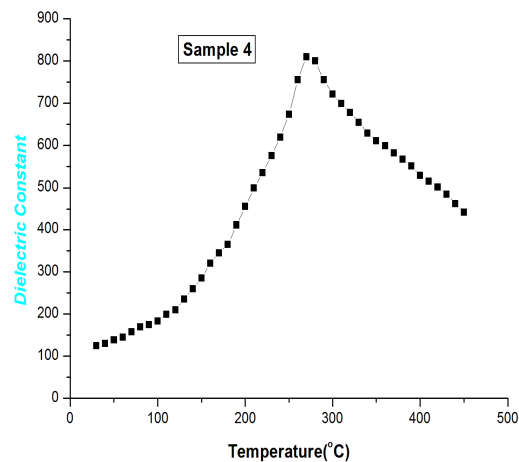


Figure 4. Variation of temperature with dielectric constant for Sample 4.

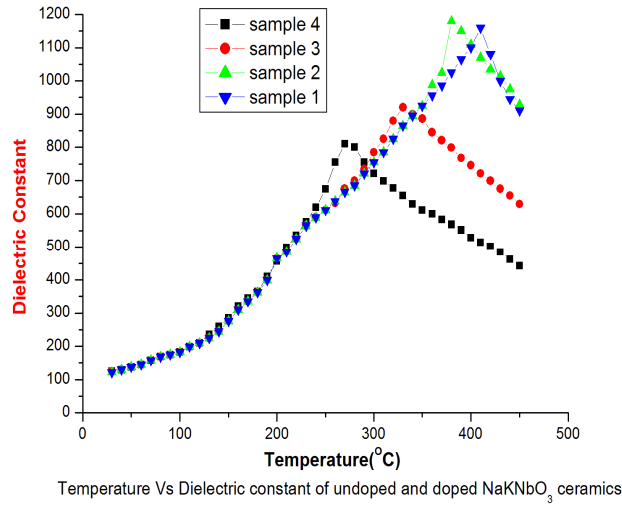


Figure 5: Temperature vs Dielectric constant of undoped and doped NaKNbO<sub>3</sub> ceramics

**Piezoelectric Studies:** The piezoelectric coupling coefficient values are presented in table 3. The planar coupling coefficient  $k_p$  is found to be 15% for unmodified compositions. Further the decrease in  $k_p$  values observed with the increase of  $Pr^{3+}$  dopant. However, the mechanical quality factor  $Q_m$  and frequency constant  $N_p$  values are increases with the increase of dopant concentration. The mechanical quality factor  $Q_m$  is one of the most important factors for an ultrasonic transducer. Low  $Q_m$  piezoelectric ceramic is suitable for wide band Ultrasonic transducer. The transverse coupling factor  $k_{31}$  is quite low for these ceramics. For unmodified Sodium Potassium Niobate, it is about 0.109 and it is further decreases with the increase of  $Pr^{3+}$  dopant.

Table 3. Piezoelectric data of doped and undoped NaKNbO<sub>3</sub> ceramics

S.No	Compositions	$K_p$	$Q_m$	$K_{31}$	$d_{33}$ pC/N	$N_p$ (Hz-m)
01	Sample-1	0.15	84	0.109	31	2681
02	Sample-2	0.14	108	0.092	29	2711
03	Sample-3	0.13	114	0.091	30	2844
04	Sample-4	0.13	118	0.086	30	2891

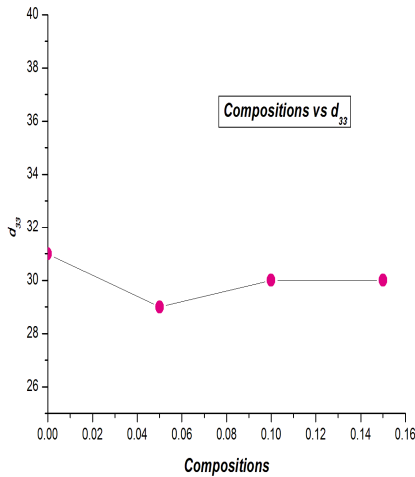


Figure 6(a). Variation of  $d_{33}$  with concentration of  $Pr^{3+}$

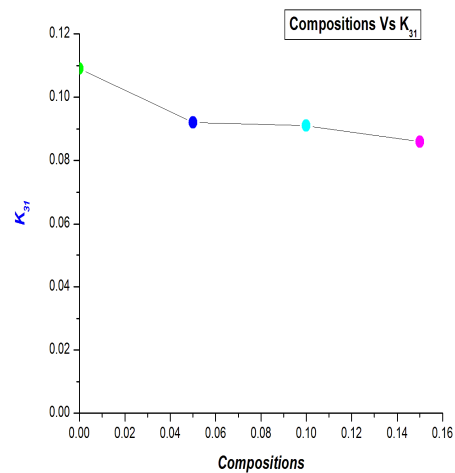


Figure 6(b). Variation of  $k_{31}$  with concentration of  $Pr^{3+}$

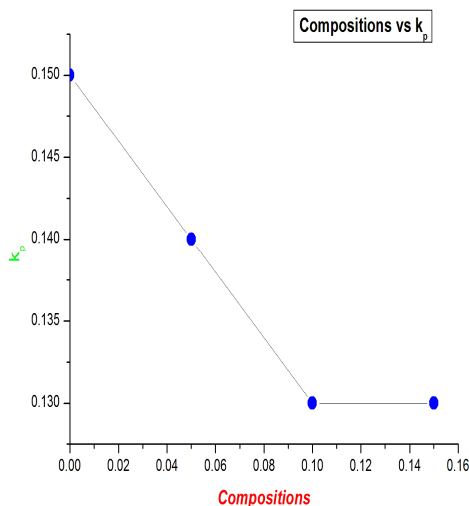


Figure 6(c). Variation of  $k_p$  with concentration of  $\text{Pr}^{3+}$

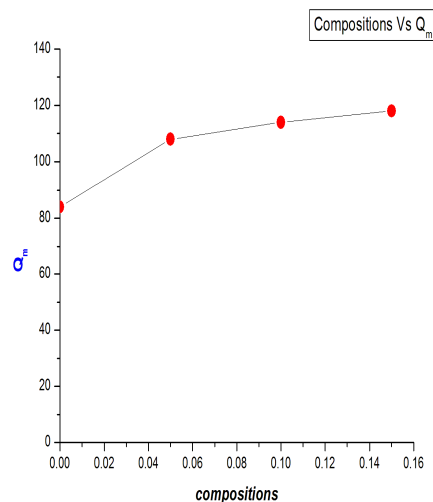


Figure 6(d). Variation of  $Q_m$  with concentration of  $\text{Pr}^{3+}$

The piezoelectric constant values for pure composition are in good agreement with the reported values [16,17]. The piezoelectric strain coefficient  $d_{33}$  is obtained 32 for unmodified pure composition. Further it is found that there is no much change with the  $\text{Pr}^{3+}$  dopant concentration. The piezoelectric constant values are presented in table 3. The variation of  $d_{33}$  with concentration of  $\text{Pr}^{3+}$  is shown in the figure 6(a). The variation of  $k_{31}$  with concentration of  $\text{Pr}^{3+}$  is shown in the figure 6(b). The variation of  $k_p$  with concentration of  $\text{Pr}^{3+}$  is shown in the figure 6(c). The variation of  $Q_m$  with concentration of  $\text{Pr}^{3+}$  is shown in the figure 6(d).

## APPLICATION

The results of new ceramics have low  $Q_m$  piezoelectric ceramic is suitable for wide band Ultrasonic transducer and the transverse coupling factor  $k_{31}$  is quite low for these ceramics

## CONCLUSIONS

It reports that sample-1 showing a sharp transition temperature at  $T_c=410^\circ\text{C}$  and it also found that increase of rare earth ions decreased the transition temperature. Low  $Q_m$  piezoelectric ceramic is suitable for wide band Ultrasonic transducer. The transverse coupling factor  $k_{31}$  is quite low for these ceramics. For unmodified sodium potassium niobate, it is about 0.109 and it is further decreases with the increase of  $\text{Pr}^{3+}$  dopant.

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