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Synthesis of Lead free Ceramics and their Dielectrical and Piezoelectrical Properties

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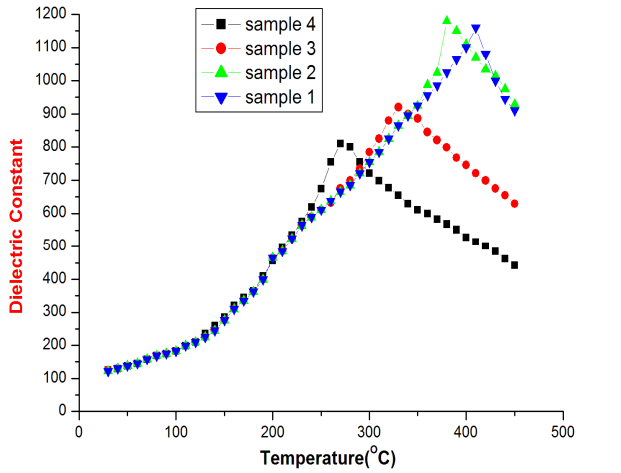
ABSTRACT

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 proprieties 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 Tc=410°C and it also found that increase of rare earth ions decreased the transition temperature.

Graphical Abstract



Temperature Vs Dielectric constant of undoped and doped $NaKNbO_3$ ceramics

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% NaNbO3 i.e, $Na_{0.5}$ $K_{0.5}NbO_3$ maximum piezoelectric coefficients of d_{33} = 80pc/N and Kp = 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 Mattias and Rameika [5] have studied the dielectric properties of $KNbO_3$ and $NaNbO_3$ Crystals. Dungan et.al [6] studied the ferroelectric properties of $NaNbO_3$.The piezoelectric properties of $NaSrNbO_3$ have been studied by Tannery [7]. The main objective of this work is to study the effect of rare earth ion Pr^{3+} on dielectric and piezoelectric proprieties of $Na_{0.5}$ $K_{0.5}NbO_3$ceramics with the stoichiometric formula Na_xK_{X-3Y} $Re^{3+}NbO_3$ 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_2CO_3, Pr_2O_3 and Nb_2O_5 with 99.9% purity. Very careful handling of K_2CO_3 is essential to avoid the moisture absorption. The starting materials were dried at 200^0C 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 $NakNbO_3$ ceramics

S.No	Composition	Represented as
01	$Na_{0.5}$ $K_{0.5}$ NbO_3	Sample-1
02	$Na_{0.50}$ $K_{0.35}$ $Pr_{0.05}$ NbO_3	Sample-2
03	$Na_{0.50}$ $K_{0.20}$ $Pr_{0.10}$ NbO_3	Sample-3
04	$Na_{0.50}$ $K_{0.05}$ $Pr_{0.15}$ NbO_3	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 950^0C 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. $inch^{-1}$. The disks were placed on a platinum foil and sintered in air at 1050^0C 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 700^0C 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.

$$Є = cd/Є_o A \qquad - (1)$$

Where c is the capacitance of the sample, d is the thickness of the sample, A is the surface area of the sample, $Є_o$ is the free space permittivity ($8.85x\ 10^{-12}$ 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^{-1}. 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 figures1 to 5 for Pr^{3+} substituted (Na K) 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 (Tc). 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) NbO_3 shows a sharp transition temperature Tc is 410^0C which is in good agreement with the reported value [13]. It is found that with the increase of rare earth Pr3+ 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 $NaKNbO_3$ 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 La^{3+}. Also it is found that as the dopant content increases, the dielectric constant at transition temperature ϵ_{Tc} decreases as shown in table 2. The values of Dielectric constant at room temperature ϵ_{RT} , dielectric constant at ferro-para phase transition ϵ_{Tc} and the phase transition temperature Tc and the dielectric loss are presented in table 2.

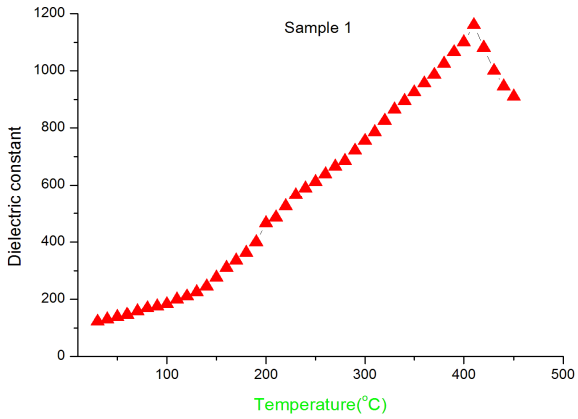


Figure 1. Variation of temperature with dielectric constant for Sample 1

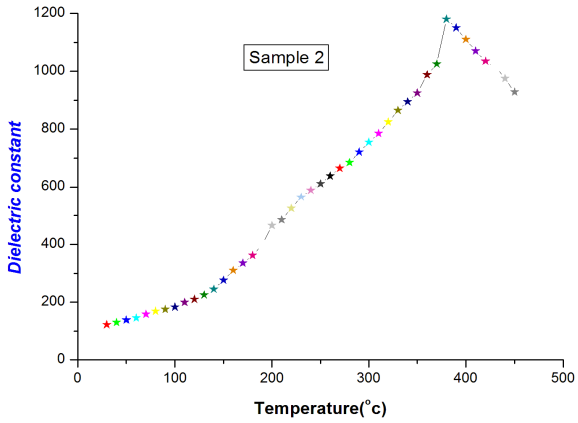


Figure 2. Variation of temperature with dielectric constant for Sample 2

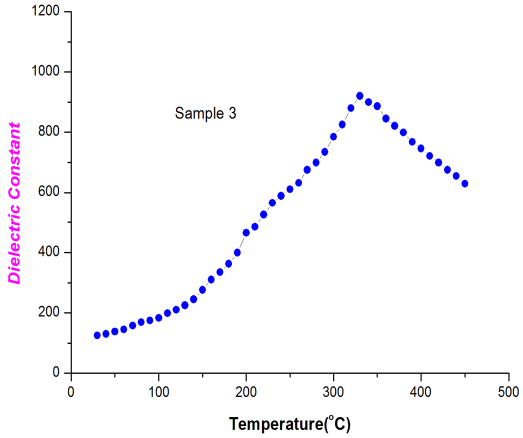


Figure 3. Variation of temperature with dielectric constant for Sample 3

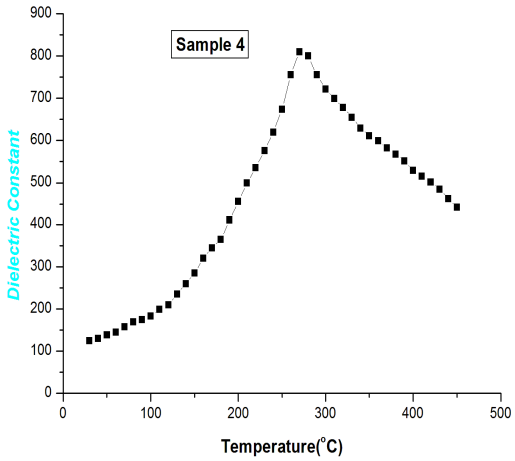


Figure 4. Variation of temperature with dielectric constant for Sample 4.

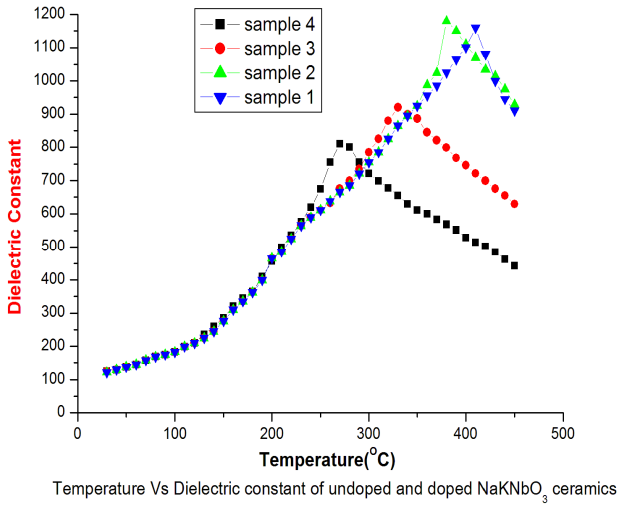


Figure 5: Temperature vs Dielectric constant of undoped and doped $NaKNbO_3$ ceramics

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 Qm and frequency constant Np values are increases with the increase of dopant concentration. The mechanical quality factor Qm is one of the most important factors for an ultrasonic transducer. Low Qm 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 $NaKNbO_3$ ceramics

S.No	Compositions	Kp	Q_m	K_{31}	d_{33} pC/N	Np (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

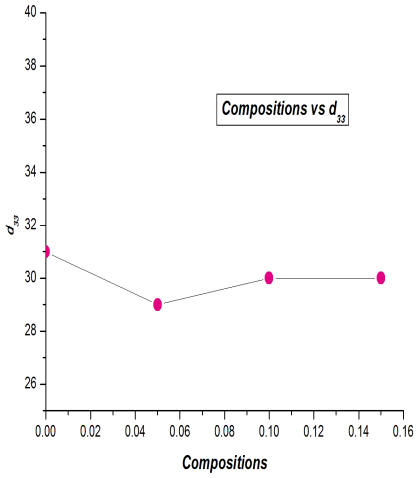


Figure 6(a). Variation of d_{33} with concentration of Pr^{3+}

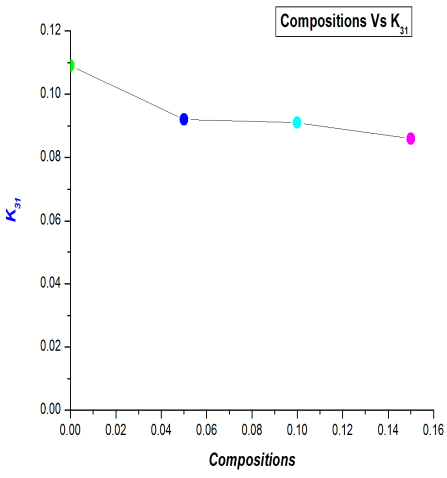


Figure 6(b). Variation of k_{31} with concentration of Pr^{3+}

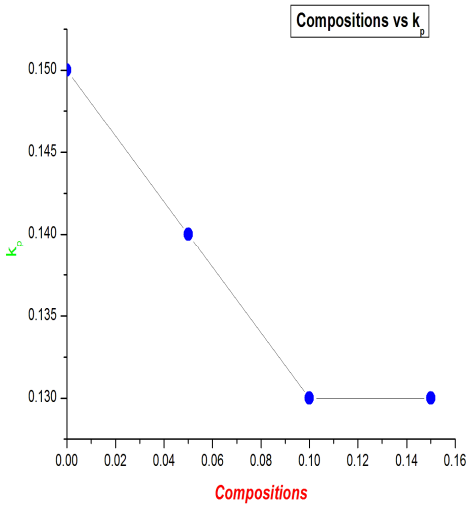


Figure 6(c). Variation of k_p with concentration of Pr^{3+}

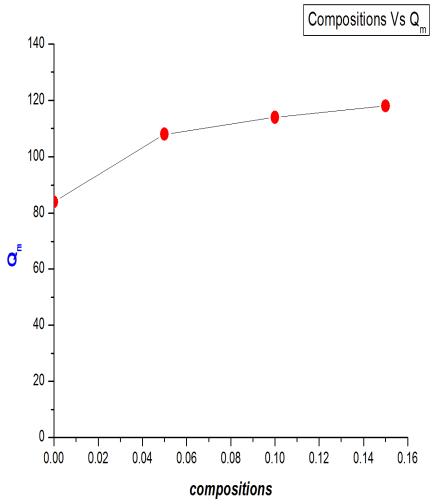


Figure 6(d). Variation of Q_m with concentration of Pr^{3+}

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 Pr^{3+} dopant concentration. The piezoelectric constant values are presented in table 3. The variation of d_{33} with concentration of Pr^{3+} is shown in the figure 6(a). The variation of k_{31} with concentration of Pr^{3+} is shown in the figure 6(b). The variation of kp with concentration of Pr^{3+} is shown in the figure 6(c). The variation of Q_m with concentration of Pr^{3+} is shown in the figure 6(d).

APPLICATION

The results of new ceramics have low Qm 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 Tc=410^{o}C and it also found that increase of rare earth ions decreased the transition temperature. Low Qm 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.

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REFERENCES

[1]. J. Valasek, Piezo-electric and allied phenomena in Rochelle salt, *Physical review*, **1920,** 15, 537.
[2]. J. Valasek, Piezo-electric and allied phenomena in Rochelle salt, *Physical review*, **1921,** 17(4), 475.

[3]. L. Egerton, D. M. Dillon, Piezoelectric and dielectric properties of ceramics in the system potassium-sodium niobate, *Journal of the American Ceramic Society*, **1959,** 42(9), 438-442.
[4]. B.T. Matthias, *Phys. Rev.*, **1949,** 75, 771.
[5]. B. T. Matthias, J. P. Remeika, Dielectric properties of sodium and potassium niobate, *Physical Review*, **1951.** 82(5), 727.
[6]. R. H. Dungan, R. D. Golding, Metastable ferroelectric sodium niobate, *Journal of the American Ceramic Society*, **1964,** 47(2), 73-76.
[7]. V. J. TENNERY, Dielectric Properties and Phase Transitions of Ferroelectric Sodium-Strontium Niobates, *Journal of the American Ceramic Society*, **1966,** 49(7), 376-379.
[8]. Raghavendra, Vemuri, B. Suryanarayana, K. Chandra moui, P. V. Achary, A ferroelectric Study on the effect of Lead Barium Niobate (PBN) ceramics, *International Journal of Innovative Research in Science, Engineering and Technology (IJIRSET)*, **2017,** 6(2), 2817-2821.
[9]. J. H. Belding, M. G. McLaren, Behavior of Modified Lead Zirconate-Lead Titanate Piezoelectric Ceramics Under High Electric Fields, *American ceramic society bulletin*, **1970**, 49(12), 1025.
[10]. I. IRE, Standards on Piezoelectric Crystals, Measurement of piezoelectric ceramics, *Proc. IRE*, **1961,** 49, 1161.
[11]. I. IRE, Standards on piezoelectric crystals: determination of the elastic, piezoelectric, and dielectric constants, Proc. *IRE*, **1958,** 46, 764-778.
[12]. Berlincourt, Don, "Variation of electroelastic constants of polycrystalline Lead titanate zirconate with thoroughness of poling." *The Journal of the Acoustical Society of America*, **1964,** 36 (3), 515-520.
[13]. G. Shirane, R. Newnham, R. Pepinsky, Dielectric Properties and Phase Transitions of $NaNbO_3$ and (Na, K) NbO_3, *Physical Review*, **1954,** 96(3), 581.
[14]. Y. Guo, K. I. Kakimoto, H. Ohsato, Structure and electrical properties of lead-free $(Na_{0.5}K_{0.5})$ NbO_3-$BaTiO_3$ ceramics, *Japanese journal of applied physics*, **2004,** 43 (9S), 6662.
[15]. S. Narayana Murty, K. Umakantham, A. Bhanumathi, Ferroelectric behaviour of lanthanum doped (NaK) NbO3 ceramics, *Ferroelectrics*, **1988,** 82, 141-147.
[16]. L. Egerton, D. M. Dillon, Piezoelectric and dielectric properties of ceramics in the system potassium-sodium niobate, *Journal of the American Ceramic Society*, **1959,** 42(9), 438-442.
[17]. B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric ceramics. *Academic press, (London, New York)* **1971,** 923.