

Effect of Processing on Synthesis and Dielectric Properties of Lead free $(\text{Bi}_{0.98}\text{R}_{0.02})_{0.5}\text{Na}_{0.5}\text{TiO}_3$ Ceramics

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Abstract. In the present work, an effort has been made to synthesize $(\text{Bi}_{1-x}\text{R}_x)_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BRNT) system with compositions $x = 0$ & 0.02 , where $R = \text{La}, \text{Nd}$ and Gd by Semi-Wet Technique. Processing of the composition with $x = 0$ has been optimized by two precursor solution one by citric acid and other by ethylene glycol. The XRD patterns of these samples, prepared by ethylene glycol precursor solution, have shown pure phase of perovskite structure with a rhombohedral symmetry. The studies on structure, phase transitions and dielectric properties for all the samples have been carried out over the temperature range from RT to 450°C at 100 kHz frequency. It has been observed that two phase transitions (i) ferroelectric to anti-ferroelectric and (ii) anti ferroelectric to paraelectric occur in all the samples. All samples exhibit a modified Curie-Weiss law above T_c . A linear fitting of the modified Curie-Weiss law to the experimental data shows diffuse type transition. The dielectric properties of BNT ceramics have been found to be improved with the substitution of rare earth elements.

1. Introduction

Lead oxide based ceramics with perovskite structure have been the subject of attraction for high performance sensors, actuators, transducers and other applications. In recent years many fields have expressed the need for actuating and sensing devices which can be used at higher temperatures ($> 400^\circ\text{C}$) such as automotive, aerospace, and related industrial applications. Lead, in most of the cases, constitutes more than 60 % of the composition of these piezoelectric devices. Lead, which is volatile and known to be highly toxic, is released to the atmosphere during sintering, caused serious environmental and health problems [1]. This has led to replace lead (Pb) in the field of piezoelectric ceramics. A lot of research has been carried out on lead free piezoceramic products in the last fifty years.

Pure BNT, discovered by Smolensky et al. in 1961, is a ferroelectric having Bi^{3+} and Na^+ complex ions on the A-site of ABO_3 type perovskite structure with a rhombohedral symmetry. Because of a large remanent polarization ($P_r = 38 \mu\text{C}/\text{cm}^2$) at room temperature, BNT ceramic is considered as one of the promising candidates for lead free piezoelectric ceramics [2]. However, the poling of pure BNT ceramic is very difficult due to its high coercive field ($E_c = 7.3 \text{ kV}/\text{mm}$). The pure BNT ceramic usually exhibits weak piezoelectric properties. To improve the electrical and piezoelectric properties of the material, a number of BNT based solid solutions and a number of processing methods have been studied extensively [3-4].

In the present work, a new lead free $(\text{Bi}_{1-x}\text{R}_x)_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ceramic system where $R = \text{Nd}, \text{Gd}$ and La have been investigated by the partial substitution of R^{3+} for Bi^{3+} on A-sites in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ using ethylene glycol precursor by novel semi wet technique and its structural, phase transitions, dielectric properties and ferroelectric properties have been studied. To the best of my knowledge, the BRNT system has been synthesized and studied first time using semi wet technique in BNT System. This technique has been applied to make other systems to study their electrical properties [5].



2. Experimental

A novel Semi-wet technique was used to prepare pure BNT and $(\text{Bi}_{1-x}\text{R}_x)_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BRNT) system with compositions $x = 0.02$, where $R = \text{Nd, La and Gd}$, using analytical-grade metal oxides or nitrate powders of sigma Aldrich as raw materials such as Bi_2O_3 (99%), NaNO_3 (99%), Nd_2O_3 (99.9%), La_2O_3 (99.9%), Gd_2O_3 (99.9%), TiO_2 (99.9%) citric acid and ethylene glycol. In this process, appropriate amount of nitrates solutions of A-site cations and ethylene glycol/ citric acid were added with continuous stirring at appropriate temperature. An aqueous ammonia solution was added drop wise to adjust the pH of the solution (6-8) in the citric acid solution. Both the precursor solution was dehydrated by putting on heater at 80°C for 3 hrs to form a viscous gel which was placed in an oven at 150°C for overnight to combust the gel into ash powder. Here precursor solutions are expected to distribute the cations atomically homogeneously throughout the polymeric structure forming a polymeric complex. The ash, highly fine, homogeneous and highly reactive was mixed with appropriate amounts of TiO_2 powder thoroughly in ethanol using mortar pestle for 2 hrs followed by solid state route.

Pure BNT and BRNT powders were calcined at 750°C and $850\text{-}900^\circ\text{C}$ for 2 hrs respectively. These calcined powders were again grounded and mixed thoroughly with a polyvinyl alcohol (PVA) binder solution and then pressed into the form of disk with 12 mm diameter and 1.5 mm thickness. The sintering of all these samples was carried out at $1150\text{-}1200^\circ\text{C}$. The crystalline structure of the sintered samples was examined using XRD analysis with $\text{Cu-K}\alpha$ radiations (DX-1000). The dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of BRNT ceramics at 100 kHz were measured as a function of temperature using LCR meter (Hioki 3522). P – E loop tracer (Marine india), was used to measure the polarization hysteresis at 50 Hz.

3. Result and Discussion

In the present work, preparation of pure $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ was optimized using two chemical precursors by citric acid and ethylene glycol. These samples are abbreviated as BNT-CA and BNT-EG [Figure 1 (a, b)]. It is observed from the XRD patterns that the sample prepared by ethylene glycol precursor solution, has shown better phase formation whereas BNT-CA has formed partially along with the presence of other phase identified as $\text{Bi}_2\text{Ti}_2\text{O}_7$ [6]. The experimental density observed in BNT-EG sample was 5.69 gm/cm^3 which is 95 % of theoretical density. Therefore, a typical composition with $x = 0.02$ in the $(\text{Bi}_{1-x}\text{R}_x)_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BRNT) system, where $R = \text{La, Nd and Gd}$ were prepared by semi wet technique using ethylene glycol precursor.

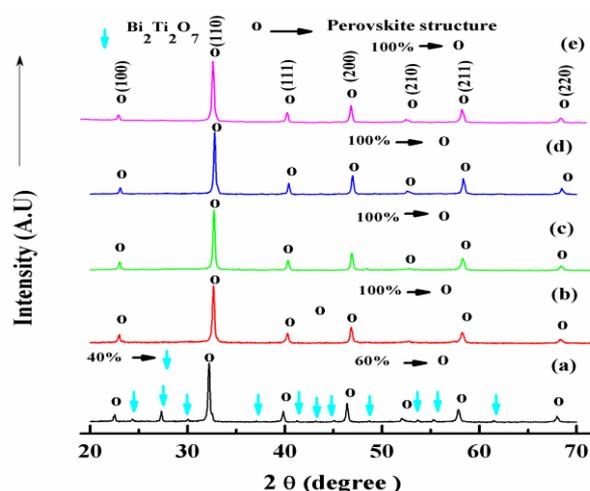


Figure 1. XRD patterns of BRNT ceramics (a) BNT-CA, (b) BNT-EG, (c) R = La, (c) R = Nd and (c) R =Gd

Figure 1(c-e) shows the XRD patterns of BRNT ceramics. All the samples exhibit single phase formation with a rhombohedral structure. The substitution of La^{3+} , Nd^{3+} , and Gd^{3+} in BNT has significantly influenced the dielectric behaviour [Figure 2]. The highest value of ϵ_r (~ 1120) and lowest value of $\tan \delta$ (~ 0.040) are obtained with the addition of Gd in the BNT system at room temperature. The electrical parameters of BRNT ceramics at 100 kHz are tabulated in Table 1. Two dielectric anomalies are clearly shown in all the samples at temperature T_1 and T_2 , termed as ' T_d ' and ' T_m ' respectively, which corresponds to dielectric transitions from ferroelectric (FE) to anti-ferroelectric (AFE) and anti-ferroelectric (AFE) to paraelectric (PE) respectively. In case of La doping, both phase transitions T_d and T_m shifts towards high temperature. This may be due to the partial replacement of A-site cation with larger ionic radius and larger amount, decreases the relative displacement of B-site cation with respect to the oxygen octahedral cage, hence, this increases transition temperature. Moreover, it has been observed that T_d shifts towards low temperature while T_m continuously increased with Nd and Gd for $x = 0.02$ in BRNT ceramics. The detailed explanation was given somewhere else [7-8].

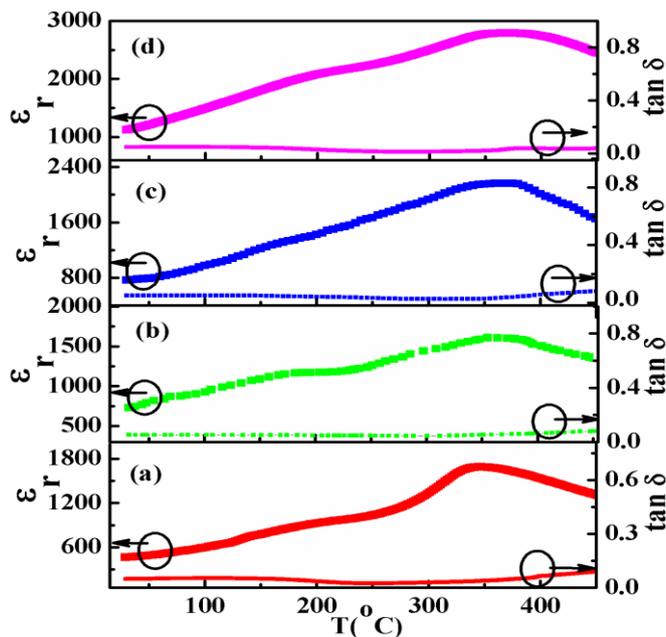


Figure 2. Temperature dependence of ϵ_r and $\tan \delta$ of BRNT ceramics at 100 kHz (a) BNT-EG, (b) R = La, (c) R = Nd and (d) R = Gd.

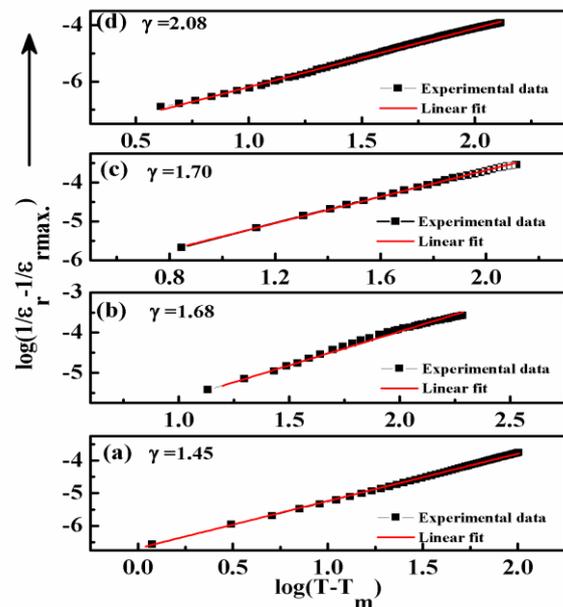


Figure 3. The $\log(1/\epsilon_r - 1/\epsilon_{rmax})$ versus $\log(T - T_m)$ of BRNT ceramics at 100 kHz (a) BNT-EG, (b) R = La, (c) R = Nd and (d) R = Gd.

The diffuseness in the phase transition can be described by the equation in relaxor ferroelectrics [9], where ϵ_{rmax} is the maximum value of dielectric constant at T_m , γ is the degree of diffuseness and C is the Curie like coefficient. γ can have a value ranging from 1 for normal ferroelectric to 2 for an ideal relaxor ferroelectric. A linear relationship is observed in all the samples above T_m . It has been observed that γ of all ceramic samples is < 2 , which attributes that the phase transition is diffused type [Figure 3].

Table 1. The electrical properties of all samples in BRNT ceramics.

$(\text{Bi}_{1-x}\text{R}_x)_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ($x = 0.02$)	ϵ_r	Tan δ	T_d ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	γ	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
R = 0	461	0.04	179	350	1.45	13.11	33.20
R = La	730	0.05	200	355	1.68	17.31	30.11
R = Nd	765	0.05	145	370	1.70	31.64	25.63
R = Gd	1120	0.04	160	370	2.08	27.39	26.03

4. Conclusion

In summary, ethylene glycol prepared BNT and BRNT samples have shown better crystallization and pure phase formation. The structural, phase transition and electrical properties of all the samples have been investigated. A linear fitting of the modified Curie- Weiss law to experimental data shows that all the samples have diffuse type phase transition. The highest value of dielectric constant ($\epsilon_r \sim 1120$) and low value of dielectric loss (Tan $\delta \sim 0.04$) is obtained for Gd doped sample at room temperature.

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