Influence of Pr dopant on the dielectric properties and Curie temperatures of $\text{Ba}_{1-3x}\text{Pr}_{2x}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$ ($0.01 \leq x \leq 0.05$) ceramics

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Abstract Three perovskite-structured ceramic phases $\text{Ba}_{1-3x}\text{Pr}_{2x}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$ (BPTS- x) with $x = 0.01, 0.03$, and 0.05 have been synthesized by solid-state reaction method. Obtained BPTS- x ceramics were investigated by X-ray diffraction and dielectric properties measurements. Analysis of all the ceramic samples using X-ray diffraction method at room temperature and its Rietveld refinement inferred rhombohedral structure with the space group $R\bar{3}c$. The temperature variation of real permittivity gives evidence of the ferroelectric phase transition and of the relaxation behavior. With increasing Pr concentration, the degree of diffuse phase transition was enhanced, and a linear reduction in the transition temperature was produced. The conductivity spectra have been investigated by the Jonscher universal power law ($\sigma(\omega) = \sigma_{dc} + A\omega^s$) and attributed to hopping conduction mechanism.

1 Introduction

According to their behavior, the ferroelectric materials with perovskite-like structure may be divided into different

classes depending on whether they are classical or relaxor ferroelectrics [1]. Relaxor ferroelectrics are characterized by their broad dielectric transition, known as diffuse phase transition with frequency dispersion [2, 3]. Many investigations have been devoted to the study of the relaxation parameters in order to achieve their use in satisfactory capacitors and actuators [4]. However, most typical relaxors are lead-based perovskite compounds, which are environmentally unfriendly because of the toxicity of lead [5, 6]. Up now, current research is oriented to environment friendly applications using lead-free-materials [7–9]. Ceramics based on barium titanate (BaTiO_3) are frequently used to manufacture multilayer ceramic capacitor and thermistors owing to their high dielectric constant [10]. Homovalent or heterovalent substitutions of barium or titanium ions were shown to give rise to various behaviors and properties [11, 12]. In addition, the aim for application was to prepare lead-free ceramics with such properties close to room temperature. In fact, up to now, lead free relaxor presented value of T_m often widely lower than room temperature [13].

The aim of the present work is to obtain a relaxor with T_m near the room temperature by adding Pr^{3+} at the Ba^{2+} site and Sn^{4+} at the Ti^{4+} site simultaneously. The details of relaxor and ferroelectric properties of the $\text{Ba}_{1-3x}\text{Pr}_{2x}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$ (BPTS- x) ceramics were investigated.

2 Experimental procedure

In analogy to our previous work [14], the conventional solid-state reaction technique was used for the synthesis of BPTS- x . The starting materials were reagent BaCO_3 , Pr_6O_{11} , TiO_2 , and SnO_2 taken in stoichiometric ratio. The surface of the sintered specimens were analyzed through

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Table 1 Some physical compounds of $\text{Ba}_{1-3x}\text{Pr}_{2x}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$

	$x = 0.01$	$x = 0.03$	$x = 0.05$
a (Å)	5.65 (2)	5.61 (4)	5.58 (1)
c (Å)	13.83 (5)	13.79 (2)	13.72 (3)
V (Å ³)	382.45 (3)	375.67 (2)	369.56 (1)
R_p (%)	3.6	3.7	4.2
R_{wp} (%)	4.1	4.3	4.6
χ^2	3.3	2.8	2.7
d_{theo} (g/cm ³)	4.09	4.31	4.31
d_{exp} (g/cm ³)	3.59	4.01	4.11
C	0.87	0.93	0.95
Tolerance factor	0.924	0.915	0.905
r_A (Å)	1.203	1.177	1.154
Crystallite size (D) ^a (nm)	110.45	109.60	105.79
D_{MEB} (nm)	326	307	295

$$^a D = \frac{0.9\lambda}{\beta \cos \theta}$$

Table 2 The parameters C , T_{dev} , T_m , ε'_m , T_0 , and ΔT_m for $\text{Ba}_{1-3x}\text{Pr}_{2x}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$ at 1 kHz

Composition	$x = 0.01$	$x = 0.03$	$x = 0.05$
$C \times 10^4$ (K)	4.0	3.9	2.58
T_{dev} (K)	218	201	175
T_0 (K)	209	188	168
T_m (K)	201	187	170
$\Delta T_m = T_{\text{dev}} - T_m$ (K)	17	14	5
ε'_m	1220.78	932.53	804.21

scanning electron micrograph (SEM) using a Philips XL30 Scanning Electron Microscope. Room temperature powder X-ray diffraction patterns were recorded on Siemens D-5000 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54059$ Å) in the angle $20^\circ \leq 2\theta \leq 120^\circ$ with 18 s counting time for each step of 0.016° in order to determine the structure for all prepared ceramic composition. For the dielectric characterization, the sintered disc (of 1-mm thickness and 8-mm diameter) was polished, electroded with fine silver paint, and then connected to the LCR meter.

3 Results and discussion

3.1 Structural analysis

The phase identification of polycrystalline $\text{Ba}_{1-3x}^{2+}\text{Pr}_{2x}^{3+}\text{Ti}_{0.95}^{4+}\text{Sn}_{0.05}^{4+}\text{O}_3^{2-}$ ($x = 0.01, 0.03$, and 0.05) pellets was performed by X-ray diffraction with $\text{Cu K}\alpha$ radiation. The X-ray diffraction pattern for a typical $x = 0.01$ sample is shown in Fig. 1. The diffraction results indicate that all the samples

are in single phase without any impurity and the samples have a rhombohedral lattice structure with space group $R\bar{3}c$ in which Ba/Pr atoms are at $6a(0, 0, 1/4)$ positions, Ti/Sn at $6b(0, 0, 1/2)$, and O at $18e(x, 0, 1/4)$ position. The structural parameters are obtained by refining the experimental data by Rietveld FULLPROF program (version 1.9c-May 2001-LLB-JRC) [15] and are listed in Table 1 along with the respective residuals viz. R_{wp} (weighted pattern), R_p (pattern), and R_{exp} (expected pattern) and goodness of fit χ^2 . The lattice parameters and the unit cell volume V obtained decrease nearly monotonically with increasing Pr-concentration because of the increase of smaller cation Pr^{3+} for Ba^{2+} .

Notice that the stability of the $\text{Ba}_{1-3x}\text{Pr}_{2x}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$ compounds having perovskite-type structure can be discussed in term of the tolerance factor value defined by Goldschmidt as $t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}$ [16], where r_A , r_B , and r_O are ionic radii of A, B, and oxygen, respectively, in the perovskite ABO_3 structure.

The distorted perovskite-type structure is stable over the range $0.75 \leq t \leq 1.06$. Based on Shannon's ionic radii [17], $r_{\text{Ba}}^{2+} = 1.216$ Å, $r_{\text{Pr}}^{3+} = 1.178$ Å, $r_{\text{Ti}}^{4+} = 0.605$ Å, $r_{\text{Sn}}^{4+} = 0.69$ Å, and $r_{\text{O}}^{2-} = 1.32$ Å. The calculated t values (see Table 1) were included in the distorted perovskite stability range.

The SEM micrograph shows homogenous microstructure and uniform grain size distribution with average particle size. In addition, we can clearly observe that the grain size is different in all the samples and estimated to be mostly within 295–326 nm (see Table 1).

The particle sizes obtained by SEM are much larger than those calculated by X-ray diffraction (Table 1), which indicates that each particle observed by SEM basically consists of several crystalline grains. The experimental density is determined from the weight and geometrical dimensions of the cylindrical pellets and then compared to theoretical density determined from X-ray measurements. The compactness is thus calculated as the ratio $C = d_{\text{exp}}/d_{\text{theor}}$. Table 1 shows the values of d_{exp} , d_{theor} , and C .

3.2 Dielectric properties

Temperature dependence of dielectric constant for BPTS- x ceramics measured at 1 kHz are shown in Fig. 2. The dielectric constant show a typical behavior of a ferroelectric material: it increases with temperature rise to its maximum value (ε'_m) at the Curie temperature T_C (or at the maximum temperature T_m). For $x = 0.01, 0.03$, and 0.05 , the values of T_C and ε'_m are listed in Table 2.

It is observed that the compounds undergo a transition phase from ferroelectric to paraelectric for all the samples. As the x value increases from 0.01 to 0.05, ε_{max} decreases, and T_C shifts to lower temperature, resulting from

Fig. 1 Rietveld plots for $\text{Ba}_{0.97}\text{Pr}_{0.02}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$ compounds synthesized by solid-state reaction; I_{obs} (solid), I_{cal} (circles), Bragg positions (bars), and $I_{\text{obs}} - I_{\text{cal}}$ (solid, lower)

Fig. 2 Dielectric constant spectra of the entire system ceramics

the replacement of the Ba^{2+} site by Pr^{3+} . However, a similar observation has been made by Hongwei Chen [18] for $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$.

In most ferroelectrics, the relationship between temperature and dielectric constant above the Curie temperature can be expressed fairly accurately with simple equation called the Curie–Weiss law [19, 20]:

$$\frac{1}{\varepsilon'} = \frac{T - T_0}{C}, \quad (1)$$

where T_0 is the Curie–Weiss temperature, and C is the Curie–Weiss constant. The inverse dielectric constant ($1/\varepsilon'$) as a function of temperature at 1 kHz for all ceramic samples is plotted in Fig. 3. The experimental data were fitted by Eq. (1) using a fitting program, and the fitting results for

C and T_0 are summarized in Table 2. For the classical ferroelectrics, the order of the ferroelectric–paraelectric phase transition can be determined from the value of T_0 . In case $T_0 \neq T_m$, the phase transition is of the first order. If $T_0 = T_m$, this transition is of second-order type [21]. In our study, it was apparent from Fig. 3 that the values of $T_0 = T_m$ for all the samples, which indicates the typical second-order ferroelectric phase transition.

Deviation from the Curie–Weiss law can be defined by ΔT_m as follows [19, 22]:

$$\Delta T_m = T_{\text{dev}} - T_m, \quad (2)$$

where T_{dev} denotes the temperature above which the dielectric constant follows the Curie–Weiss law.

T_{dev} and ΔT_m are also listed in Table 2. The difference in T_m , ΔT_m , is commonly used to measure the extent of frequency dispersion and thereby the degree of relaxor behavior [23, 24]. As listed in Table 2, the values of T_{dev} , T_m , and ΔT_m decrease gradually with the augment of Pr-doping level, which indicates that paraseodyme can decrease the diffuseness of the phase transition of BTS ceramics.

In order to further characterize the dielectric dispersion and diffuseness of the phase transition, a modified empirical expression proposed by Uchino and Nomura [25] was employed in the present work:

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \frac{(T - T_m)^\gamma}{C'}, \quad (3)$$

where C' and γ are assumed to be constant. The value γ evolves from $\gamma = 1$ for Curie–Weiss behavior to $\gamma = 2$ for

Fig. 3 The plot of inverse dielectric constant as a function of temperature at 1 kHz for BPTS- x ($x = 0.01, 0.03$, and 0.05) ceramics

ideal relaxor ferroelectric behavior. Based on the temperature plots of ϵ' at 1 kHz, the graphs of $\log(1/\epsilon' - 1/\epsilon'_m)$ versus $\log(T - T_m)$ for the $\text{Ba}_{1-3x}\text{Pr}_{2x}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$ ceramics were plotted, giving the results shown in Fig. 4. A linear relationship is observed for Pr-doped BTS ceramics. By least-squared fitting the experimental data to the equation, the γ was determined. As the praseodymium content increases from 0.01 to 0.05, the diffuseness constant γ de-

Fig. 4 Plots of $\log(1/\epsilon' - 1/\epsilon'_m)$ vs $\log(T - T_m)$ for ceramic BPTS- x ($x = 0.01, 0.03$, and 0.05) at 1 kHz (symbol: experimental data; solid line: fitting to Eq. (3))

creases from 1.70 to 1.15. It is evident that the diffuseness of the phase transition of Pr-doped BTS ceramics decreases with the increase of Pr content. This is because the ferroelectric ceramics with small grain sizes exhibit more remarkable diffuse phase transition [26].

As is seen from a number of recently reported relaxors [27, 28], the slope of ϵ' at $T > T_m$ can be scaled with the empirical Lorentz-type relation:

$$\frac{\epsilon_A}{\epsilon'} = 1 + \frac{(T - T_A)^2}{2\delta^2}, \quad (4)$$

where δ is a measure of the degree of diffuseness of the permittivity peak, T_A ($< T_m$) and ϵ_A ($> \epsilon_m$) are the fitting parameters defining the temperature and magnitude of the Lorentz peak. This equation gives a more agreeable description of the experimental data than the previously used relation $\frac{\epsilon_m}{\epsilon'} - 1 = \frac{(T - T_m)^\gamma}{2\delta^2}$ [29]. It describes the static conventional relaxor susceptibility, which provides the dominant contribution to the permittivity peak at temperatures above the temperature of the dielectric maximum. All the samples show good agreements to this formula above T_m . A curve fitted by Lorentz-type relation for $\text{Ba}_{1-3x}\text{Pr}_{2x}\text{Ti}_{0.95}\text{Sn}_{0.05}\text{O}_3$ ceramic is shown in Fig. 5. The values of δ decrease with increasing Pr content, i.e., from $\delta = 53.70$ for $x = 0.01$ to $\delta = 42.21$ for $x = 0.05$. This indicates that the degree of relaxor behavior decreases with increasing Pr content, which is consistent with the above-mentioned observation and previous results [30, 31] on other systems.

3.3 Frequency dependent conductivity studies

It well known that conductivity in ferroelectrics appreciably affects the properties in the sense that there will be a competition between the growth of the ferroelectric phase and the

Fig. 5 Dielectric constants of BPTS- x ($x = 0.01, 0.03$, and 0.05) as a function of temperature at 1 kHz

free charge carriers. Conductivity studies help to illustrate the effects of conductivity not only on the domain structure and its motion, but also on the nature of charge carriers.

Variation of ac conductivity with frequency can be understood from Fig. 6.

The conductivity plots of BPTS- x possess the following characteristics:

- Plateau region at lower frequencies corresponds to σ_{dc} .
- Dispersion at high frequencies. The frequency at which the dispersion takes place is known as hopping frequency [32].
- With respect to the increase in Pr content in the compound, ac conductivity was found to be increasing.

The ac conductivity behavior obeys the Jonscher's power law governed by the relation [33]

$$\sigma = \sigma_{dc} + A\omega^s,$$

where σ_{dc} is the dc conductivity in a particular range of temperature, A is a temperature-dependent parameter, and s is the temperature-dependent exponent in the range of $0 \leq s \leq 1$. The exponent s represents the degree of interaction between mobile with the lattices around them, and the prefactor exponent A determines the strength of polarizability [34]. The detailed analysis of σ_{ac} of BPTS- x suggests that the universal power law is obeyed. It is confirmed by the typical fit of the above equation to the experimental data (inset in Fig. 6).

The value of parameter s calculated from the slope σ vs $\log(f)$ curves is found to be less than unity and decreases with increase in temperature. The trend of change in s with temperature is shown in Fig. 7. The temperature dependency of s of disordered systems has been explained by two physical processes such as correlated barrier hopping (CBH) [35] and quantum mechanical tunneling (QMT) like electron tunneling (ET) [36], small polaron tunneling (SPT) [35], and large polaron tunneling (LPT) [37]. From the trend of change in s with temperature, it is presumed that the correlated barrier hopping is suitable. According to this model, the conduction occurs via polaron hopping process where two polarons simultaneously hop over the potential barrier between two charged defect states and the barrier height is correlated with the inter-site separation via a Coulombic interaction. Therefore, the conduction in the system could be considered due to the short-range translational type hopping of charge carriers [38–40]. This indicates that the conduction process is thermally activated. The exponent s for this model is given by

$$s = 1 - \frac{6k_B T}{[W_m + k_B T \ln(\omega\tau_0)]}. \quad (5)$$

The first approximation of this equation gives the simple expression for s as [41]

$$1 - s = \frac{6k_B T}{W_m}, \quad (6)$$

where W_m is the binding energy, which is defined as the energy required to remove an electron completely from one site to another site. The characteristic decrease in slope with the rise in temperature is due to the decrease in binding en-

Fig. 6 Variation of conductivity (σ) of BPTS- x ($x = 0.01, 0.03$, and 0.05) with frequency at room temperature. The *inset* shows the nonlinear fitting of conductivity (σ)

Fig. 7 Variation of index s and binding energy (W_m) with temperature for BPTS- x . The *inset* shows the variation of binding energy hopping ($R_{\min}$) with temperature at 1 kHz

ergy [42] as illustrated in Fig. 7. Using the values of the binding energy minimum hopping distance $R_{\min}$ is calculated [43]:

$$R_{\min} = \frac{2e^2}{\pi \epsilon_0 \epsilon W_m}, \quad (7)$$

where e is the electronic charge, ϵ_0 is the permittivity of free space, and ϵ is the dielectric constant.

The inset in Fig. 7 shows the variation of $R_{\min}$ with temperature at 1 kHz. A similar order of decrease in $R_{\min}$ was also reported by K. Prasad et al. for the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{ZrO}_3$ system [44].

4 Conclusion

Pr-substituted $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ ceramics were synthesized via the solid-state reaction method. Perovskite single-phase BPTS- x compounds for $0.01 \leq x \leq 0.05$ were obtained. The Rietveld refinement shows that the composition has a rhombohedral perovskite structure with space group $R\bar{3}c$. Dielectric study of the composition shows typical characteristics of relaxor ferroelectrics, with broad and dispersive permittivity maxima, based on empirical parameters (ΔT_m , δ , and γ). The ac conductivity was found to obey the universal power law. The pair approximation type correlated barrier

hopping (CBH) model accurately describes the mechanism of charge transport in BPTS- x system. Such compositions could be excellent materials both for highly stable ferroelectric memory and for high-temperature piezoelectric applications.

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