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Structural Characterization and Dielectric Properties of Gd Doped SrBi$_2$Ta$_2$O$_9$

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ABSTRACT

An analysis of the effect of Gd impurities on the structural and dielectric properties was performed in the Sr$_{1-x}$Gd$_x$Bi$_2$Ta$_2$O$_9$ and Sr$_{1-x}$Gd$_x$V$_y$Bi$_2$Ta$_2$O$_9$ ceramics systems for different compositions. Rietveld analysis was performed in all cases. The temperature dependence of the dielectric constant ($\varepsilon/\varepsilon_o$) was useful to describe the nature of phase transition in both systems. A non Curie-Weiss behavior above the transition temperature is observed. It is found that in both, Sr$_{1-x}$Gd$_x$Bi$_2$Ta$_2$O$_9$ and Sr$_{1-x}$Gd$_x$V$_y$Bi$_2$Ta$_2$O$_9$ systems, the diffuseness coefficient γ values are around 2 indicative of diffuse behavior. The analysis is complemented with a study of the dielectric constant as a function of frequency and the results are explained in terms of the high disorder associated to the random location of the Gd ions in the samples.

Keywords: SBT ceramics; Gadolinium doped SrBi$_2$Ta$_2$O$_9$; ferroelectric phase transition

INTRODUCTION

SrBi$_2$Ta$_2$O$_9$ (SBT) is a ferroelectric material that is attracting much interest as an unleaded alternative for PZT in ferroelectric non-volatile memory devices (*FeRAM*). SBT presents very good fatigue endurance and lower switching voltages [1, 2]. SBT is an Aurivillius type oxide, consisting of perovskite layers (SrTa$_2$O$_7$)$^{2-}$ sandwiched between (Bi$_2$O$_2$)$^{2+}$ layers [3, 4]. It has been demonstrated by Noguchi *et al*. that rare earth (RE) cations of La, Ce, Pr, Nd and Sm as well as Bi are substituted at the *A* site with Sr vacancies modifying substantially the SBT properties. It has been also reported that such doping induces a

larger remnant polarization (*Pr*) as compared with pure SBT in spite of having a smaller spontaneous polarization [5–7]. Recently, it has been reported that Pr-doped SBT ceramics exhibit a large remnant polarization and low coercitive field [8–11]. The purpose of this work is to study the effects of doping on the SBT layered perovskite with a gradually increasing amount of gadolinium as well as the introduction of vacancies in $Sr_{1-x}Gd_xV_yBi_2Ta_2O_9$(SBT-Gd-V) compound. The nature of the phase transition is analyzed by means of the Uchino model performing a detailed study as a function of composition.

EXPERIMENTAL PROCEDURE

The $Sr_{1-x}Gd_xBi_2Ta_2O_9$ and $Sr_{1-x}Gd_xV_yBi_2Ta_2O_9$systems, with x = 0, 0.05, 0.08, 0.10, 0.15, were prepared in ceramic form by solid-state reaction. Powders of $SrCO_3$, Bi_2O_3, Ta_2O_5 and Gd_2O_3 were mixed in stoichiometric proportions by ball milling. The resulting powders were calcined at 900°C for 3 hours, pressed into 1 cm diameter discs and sintered at 1250°C for 3 h under a Bi_2O_3 controlled atmosphere.

　　Phase identification in the samples was carried out with a BRUKER XP X-ray diffractometer using Cu-Kα radiation and Ni filter. Intensities were measured in steps of 0.02° for 6 seconds in the 5° to 120° 2θ range at room temperature. The crystallographic phases were identified by comparison with the X-ray patterns of the JCPDS database. Crystallographic parameters were obtained using the QUANTO program [12].

　　Silver electric contacts were deposited on 10 mm diameter, 1 mm thick disk samples for capacitance and dielectric measurements performed with an LCR bridge (HP-4284A) from room temperature to 500°C.

RESULTS AND DISCUSSION

X-ray diffraction patterns of SBT-Gd and SBT-Gd-V show that the samples are essentially single phase of the $A2_1am$ space group (Fig. 1). No second phases were detected in any of the samples. Rietveld refinement results confirm that the SBT-Gd is a solid solution with Gd atoms on the Sr site. Detailed results of the structural refinement are listed in the Table 1. For x = 0, the lattice parameters a = 5.5195(3), b = 5.5170(4) and c = 25.052(2) Å are in good agreement with the reported data for SBT [11, 13].

　　It was observed that, as *x* is increased the *a* and *b* lattice parameters decrease but *c* remains essentially constant and, as a consequence, the unit cell volume linearly decreases. To explain this fact, the different ionic radii of Sr^{+2} (1.44 Å with twelve coordination) and Gd^{+3} (1.02 Å with eight coordination) are taken into account as main factors for the unit cell volume reduction. The orthorhombic distortion expressed by the *b/a* ratio remains constant. These
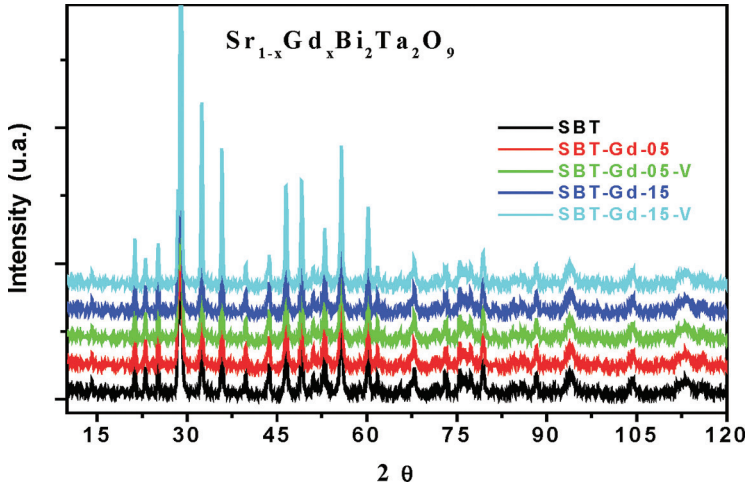
Figure 1. X-Ray diffraction patterns for the $Sr_{1-x}Gd_xBi_2Ti_2O_6$ ($0 < x < 0.15$) samples with and without vacancies at room temperature.

values confirm the occupation of the small Gd ion of the Sr site, affecting mainly the *ab*-plane in the structure.

DIELECTRIC BEHAVIOR

Figure 2 shows the dependence of the dielectric constant with temperature, measured at 1 kHz for the SBT-Gd and SBT-Gd-V systems. It was observed that the transition temperature and permittivity values depend strongly of Gd

Table 1
Space group: $A2_1am$. Atomic positions: Bi: 8b (x, y, z); Sr: 4a (0, y, 0); Ta: 8b (x, y, z); O(1): 4a (x, y, 0); O(2): 8b (*x*, y, *z*), O(3): 8b (x, y, *z*), O(4): 8b (*x*, y, z) and O(5): 8b (x, y, z)

X =	0.0	0.05	0.08	0.1	0.15
a (Å)	5.5195 (3)	5.5076 (2)	5.5102 (2)	5.5092 (4)	5.4965 (4)
b (Å)	5.5170 (4)	5.5133 (3)	5.5034 (3)	5.5010 (2)	5.5041 (2)
c (Å)	25.052 (2)	25.036 (3)	25.028 (3)	25.024 (4)	25.018 (4)
b/a	0.9995	1.0010	0.9988	0.9985	0.9986
V (Å^3)	762.86	760.22	758.96	758.40	756.89
R_p (%)	6.4	9.9	9.9	12.2	13.5
R_{wp} (%)	10.8	15.1	14.9	19.3	22.2
R_{exp} (%)	3.8	7.7	7.8	7.6	7.7
χ^2 (%)	2.8	1.9	1.9	2.6	2.8
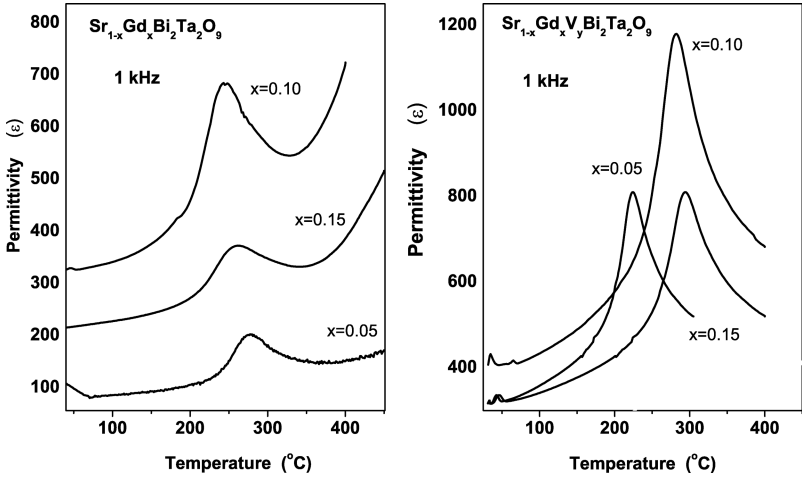
Figure 2. Permittivity curves as function of temperature for $Sr_{1-x}Gd_xBi_2Ta_2O_9$ and $Sr_{1-x}Gd_xV_yBi_2Ta_2O_9$ samples, measured at the fixed frequency of 1 kHz.

content but in a different way in each system. For SBT-Gd samples, a well defined dielectric peak is observed in consistency with the monophasic character of the system. With the increase of Gd content up to $x = 0.10$ the permittivity increases as well. It is proposed that small amounts of Gd in the structure enhances the local polarization field due to the structural distortion affecting the polarization of the whole system and lowering the transition temperature by a few degrees. The lattice modes are affected by the presence of an ion with a different polarizability, resulting in a system with a lower critical temperature. However, for Gd content higher than $x = 0.10$ there is a lowering of the dielectric properties. This fact suggests that Gd contents higher than $x = 0.1$, lower the permittivity values, increase the transition temperature and broaden the phase transition due to a higher cationic disorder introduced by Gd resulting in the decrease of the long range ferroelectric order.

For SBT-Gd-V there are similarities and differences. In terms of differences, we found that transition temperature shifting is influenced by the introduction of vacancies in the Sr-site in a stronger way than in SBT-Gd samples (Fig. 2). The transition temperature for $x = 0.05$ is 225°C, lower than the same composition in the SBT-Gd system and with higher permittivity values. The presence of vacancies could lead to a higher capacity for displacement of the ferroactive ion and a better incorporation of Gd in the structure forming a matrix of higher polarizability. Although a better incorporation of Gd is presumed supported by the higher permittivity values and sharper curves compared with SBT-Gd samples, some complex dipolar interactions may be present to account for the shifting of T_c toward the SBT transition temperature when the Gd content is increased. Regarding similarities, the permittivity values increased up to
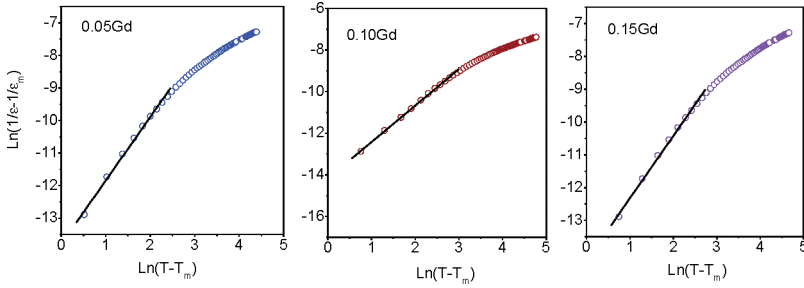
Figure 3. $\text{Ln}(1/\varepsilon - 1/\varepsilon_m)$ as function of $\text{Ln}(T - T_m)$ for $Sr_{1-x}Gd_xV_yBi_2Ta_2O_9$ ceramics. The solid lines represent the least square fit to the plot $\text{Ln}(1/\varepsilon - 1/\varepsilon_m)$ vs $\text{Ln}(T - T_{\varepsilon m})$.

x = 0.10. These results show this composition to be the limit to enhance the permittivity value regardless if the system includes vacancies or not.

To state the type of ferroelectric-paraelectric transition we use the modified Curie-Weiss law [14, 15] to describe the diffuseness of the phase transition:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_{\varepsilon_m})^\gamma}{C_1} \tag{1}$$

where γ y C_1 are assumed to be constant, and $1 < \gamma < 2$. Far from the transition temperature, a Curie-Weiss behavior of the dielectric permittivity with
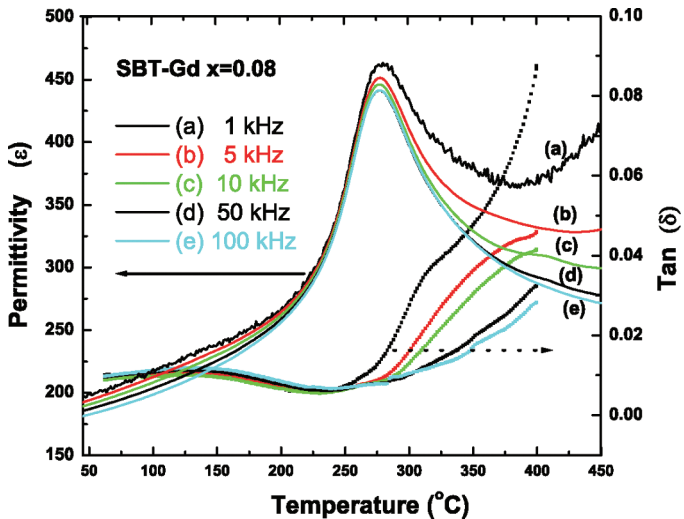

Figure 4. Permittivity vs. Temperature for the x = 0.08 sample at different frequencies.

temperature is observed with strongly broadened curves in all cases, however, a non Curie-Weiss behavior above the transition temperature is observed. The limiting values $\gamma = 1$ and $\gamma = 2$ reduce the expression to the Curie-Weiss law valid for the case of a normal ferroelectric and to the quadratic dependence valid for an ideal ferroelectric relaxor, respectively. For $Sr_{1-x}Gd_xV_yBi_2Ta_2O_9$ samples, values of $\gamma =$ 1.94, 1.75 and 1.94 for polycrystals with x $=$ 0.05, 0.10 and 0.15 respectively, were obtained from the slope of the $Ln(1/\varepsilon\text{-}1/\varepsilon_m)$ vs $Ln(T\text{-}T_{\varepsilon m})$ curve using a least square fit in the T $>$ Tε_m region where the Curie-Weiss law does not hold, as shown in Fig. 3. The values of γ for the studied system are slightly smaller than those for relaxor materials ($\gamma = 2$) indicating the diffusive character of the transition.

The persistence of the polar behavior beyond T_c is explained by the presence of small ferroelectric nuclei embedded in the paraelectric matrix that results after the nominal transition temperature has been surpassed.

The temperature dependence of the dielectric constant ($\varepsilon/\varepsilon_o$) for the SBT-Gd-V with x $=$ 0.08 at different frequencies is shown in Fig. 4. As frequency is increased, ε_m decreases slightly and a slight shifting of the dielectric peak toward higher temperatures is observed. It corroborates the diffuse character of the system.

In Fig. 5 is also observed that the transition temperature (Tm) does not decrease with Gd content. The linear behavior of Tm with Gd concentration leads to the conclusion that gadolinium is incorporated in the perovskite structure of the SBT system, forming monophasic solid solutions in accordance with the XRD observations.
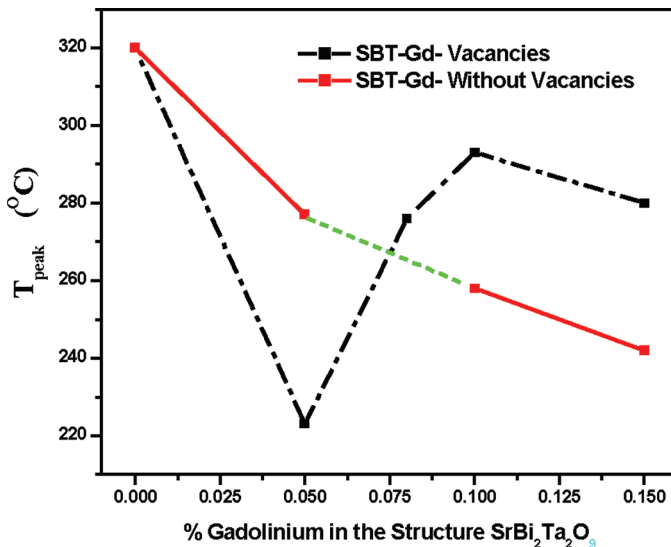
Figure 5. Curie Temperature variation with Gd composition in SBT-Gd and SBT-Gd-V systems.

CONCLUSIONS

The electrical properties of the monophasic SBT-Gd system with different concentration of Gd-ion and vacancies were studied. X-ray diffraction patterns show that all the samples are a single phase. Rietveld analysis show that the Gd-ion substitutes the Sr-ion in the main structure ($A2_1am$ space group)**.** The permittivity curves show broad phase transitions, typical of ferroelectrics with diffuse phase transition in both systems being more pronounced in SBT-Gd samples. This fact was confirmed by the non Curie-Weiss behavior above the transition temperature and the slight dispersion with frequency in SBT-Gd-V compound. Additionally, it was found that the magnitude of the permittivity is increased by adding vacancies in the Sr site (SBT-Gd-V). The presence of vacancies could lead to a larger displacement of the ferroactive ion and to a better incorporation of Gd into the structure forming a matrix of higher polarizability. The obtained results show that the x = 0.1 composition is the limit to enhance the permittivity properties regardless of whether or not if the system includes vacancies.

ACKNOWLEDGMENTS

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