Dielectric characterization of hydrothermally PREPARED (Cu,Sb)-doped $BaTi_{1-x}Zr_xO_3$

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Powders of copper-doped $BaTi_{1-x}Zr_xO_3$ have been synthesized using the hydrothermal process. The starting materials were powders of BaO and TiO_2, $ZrO_2.xH_2O$ gel, and an aqueous solution of Cu^{2+} / Sb^{5+}. The obtained powders were cold compacted and sintered at 1280°C. Impedance spectroscopy measurements have been performed on these ceramics and the results were analyzed using the empiric Cole-Cole model. A procedure to evaluate the electric properties of the grain boundary and bulk grain has been developed based on electric polarization model of double layered dielectrics.

I. Introduction:

Recently, there has been an increased interest in ferroelectric materials because of their growing use in electronic, electrooptic, optical and microwave devices[1,2]. The study of pure and doped perovskite-type $BaTi_{1-x}Zr_xO_3$ is of great interest, since this material possesses interesting properties which makes it potentially useful for these applications. It is known that the curie point of $BaTi_{1-x}Zr_xO_3$ can be adjusted by varying the Ti:Zr ratio[3,4]. As a result, various properties of this material can be tailored for specific applications and operating temperatures.

In this paper, we present structural and dielectric characterization of hydrothermally prepared Cu and Sb-doped $BaTi_{1-x}Zr_xO_3$ (x=0 (BTO) and x=0.2 (BZT)). We also present an attempt of evaluation of the individual electrical properties of bulk grains and grain boundaries using the frequency dependence of the dielectric permittivity.

II. Experimental procedure:

A solution of $Ba(OH)_2$ is prepared by dissolving barium oxide (BaO, 99.9 %) in distilled water. On the other hand, Zirconium nitrate $Zr(NO_3)_2$, $7H_2O$ was dissolved in water and ammonium hydroxide (NH_4OH) was subsequently added to form a ZrO_2,yH_2O precipitate. Finally, a mixture ($Ba(OH)_2$, TiO_2, ZrO_2,yH_2O, Cu^{2+} or Sb^{5+} aqueous solution) was introduced in an autoclave in the presence of sodium hydroxide (NaOH) and heated to 140°C and maintained at this temperature for 14 hours. The obtained product is filtered, washed to eliminate Na^+ ions and dried at 100°C.

The dried powders were cold-pressed (0.6 Tons/cm^2) into pellets of diameter 13 mm and thickness 0.5 mm, they were subsequently calcined at 1280°C for 3 hours. The X-ray diffraction (XRD) studies were performed in a station equipped with a Siemens M386-X-A3 goniometer using the CuKa radiation. The dielectric permittivity was measured as a function of temperature at 1kHz, and as a function of frequency for various temperatures above the Curie point, for frequencies ranging from 40 to 100Hz, using a Keithley 33230 LCZ meter controlled by a computer. The pellets used for this purpose were coated by silver paint which is subsequently dried in air. All the measurements were performed in a vacuum chamber evacuated with a mechanical pump down to a pressure of 10 Pa.

III. Results and discussion:

Figure 1 present typical XRD diagrams of calcined 1% Cu/Sb-doped BTO and BZT powders. These spectra showed room-temperature stabilization of the cubic phase (also named pseudo-cubic phase). This stabilization is associated to small grain size of the powders obtained using this method (0.2µm for BTO [5]).

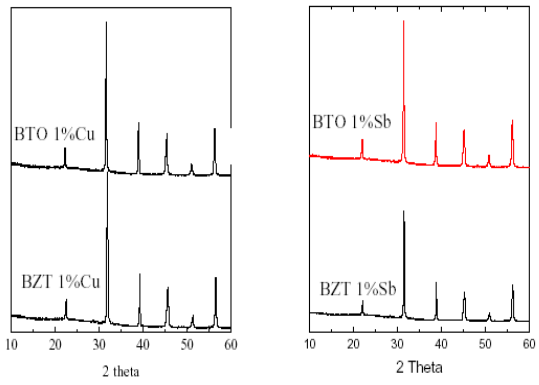

Figure 1: XRD patterns of 1280°C treated 1% Cu and Sb-doped BTO and BZT

The temperature dependence of the dielectric constant of 1% Cu and Sb-doped BTO and BZT is presented in figure 2. In both cases, the effective dielectric constants are small compared with those of solid state reaction prepared BTO ceramics.

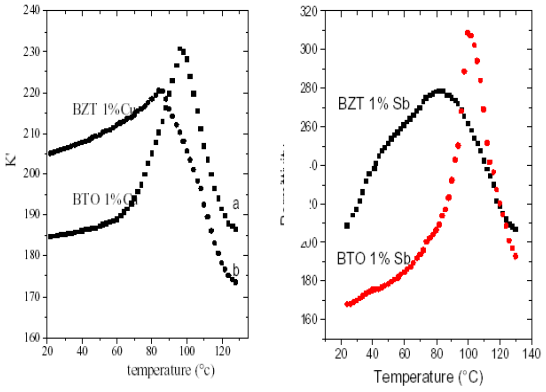

Figure 2: Temperature dependence of permittivity of Cu and Sb-doped BTO and BZT.

On the other hand, these curves denotes a ferroelectric behavior, namely, the ferroelectric to paraelectric (tetragonal to cubic) which occurs around 94°C for Cu and Sb-doped BTO and around 84°C for Cu and Sb-doped BZT.

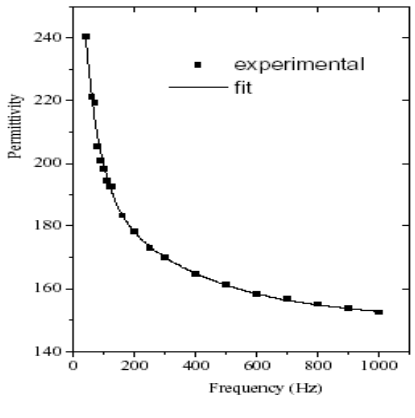

Figure 3: Typical curve of frequency dependence of permittivity

The presence of the tetragonal phase can be explained by the presence of an eventual quadraticity gradient in the grains[9].

The measurements of frequency dependence of the dielectric constant have been performed in the samples for temperatures higher than the transition temperature. Figure 3 shows a typical frequency dependence of the dielectric constant of 1%Cu-doped BTO at 140°C. In this Figure, the dots stand for measured data. It was not possible to fit the data with the monodispersive Debye formula:

$$K=K_{\infty}+\frac{K_s-K_{\infty}}{1+j\omega\tau}$$

where $K_{¥}$ and K_s, are high and low frequency permittivities, t is the relaxation time. This is expected since The Debye's idealized treatment applies only to certain dilute solutions of large molecules in non-polar solvents. In the following we will discuss the fits using the polydispersive cole-cole formula:

$$K=K_{\infty}+\frac{K_s-K_{\infty}}{1+(j\omega\tau)}$$

(line curve in the figure 3) where a is the Cole-Cole parameter. The fitting computations were undertaken on the measured complex impedance data to obtain individual values of $K_{¥}$, K_s, t and a .

It is assumed that the sample can be ideally represented by a double layer dielectric, representing bulk grain and grain boundaries. Based on this model, $K_{¥}$, K_s, and t can be expressed as[10]:

$$K_s=\frac{(d_1K_1\ {}_2^2+d_2K_2\ {}_1^2)(d_1+d_2)}{(d_1\ {}_2+d_2\ {}_1)^2}$$

$$K_{\infty}=\frac{K_2K_1(d_1+d_2)}{d_1K_2+d_2K_1}\ ,\ =\frac{d_1K_2+d_2K_1}{d_1\ {}_2+d_2\ {}_1}K_0$$

Where d_i, s_i and K_i (i=1,2) are thickness , dc conductivity and permittivity respectively of each layer. Subscripts 1 and 2 represent bulk grain and grain boundary, respectively. The mean grain size d_1 is much larger than the thickness d_2 of the highly resistive grain boundary layer: $d_1>>d_2$. The relation $d_1s_2 >> d_2s_1$ holds also due to the highly resistive character of the grain boundary layers. In these conditions, equations 1, 2 and 3 can be reduced to :

$$1=(\frac{K_0}{})\frac{K_s^2}{K_s-K_{\infty}}\ ,\qquad K_2=\frac{d_2}{d_1}K_s$$

and

$$K_1=\frac{K_sK_{\infty}}{K_s-K_{\infty}}\ .$$

Values of s_1, K_1 and $(d_2/d_1).K_2$ can then be deduced from those of $K_{¥}$, K_s, and t.

The variation of the bulk grain dc-conductivity with temperature (Figure 4) is found to fit an arrhenius law $s_1 = s_0.\exp(-E/kT)$, where s_0 is the high temperature conductivity and E is the activation energy.

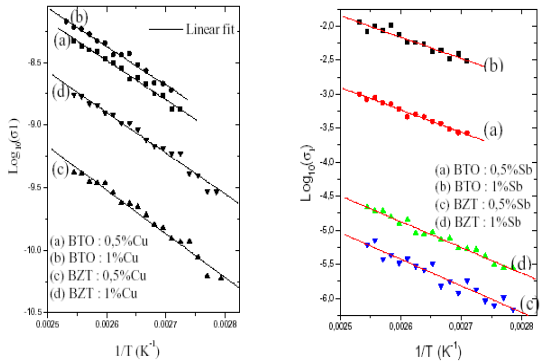

Figure 4: Temperature dependence of the calculated dc conductivity of the bulk grain of Cu and Sb-doped BTO and BZT.

The obtained activation energies are shown in table 1. A slight variation of the activation energy with Cu doping is observed in the case of BTO, while, in the case of BZT, this variation is very pronounced.

	Samples	E (eV)
TO	1%Cu	0.55
	0.5%Cu	0.53
ZT	1%Cu	0.57
	0.5%Cu	0.62
TO	1%Sb	0.62
	0.5%Sb	0.65
ZT	1% Sb	0.75
	0.5% Sb	0.77

Table 1: Activation energies of the calculated dc conductivities of the bulk grain.

Figure 5 show the temperature dependence of $(d_2/d_1).K_2$. Only a slight variation of this argument., with an average value of 246 for Cu-doped BTO and 238 for doped BZT. The corresponding values K_2 are rather weak since the factor (d_2/d_1) is very small ($d_2/d_1 << 1$). The low value of K_2 can explain the low values of the effective dielectric constant of the samples.

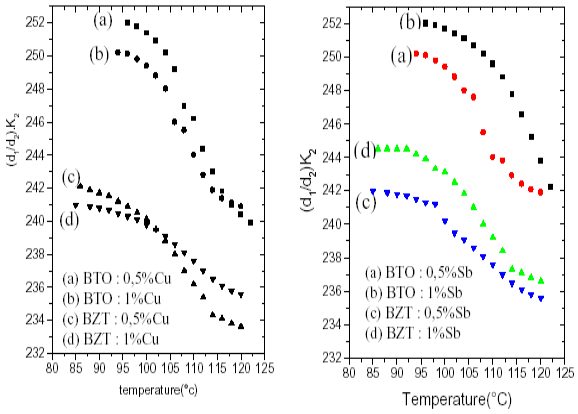

Figure 5: Temperature dependence of the calculated $(d_1/d_2).K_2$ of Cu and Sb-doped BTO and BZT.

Figures 6 represent the calculated dielectric constant of the bulk grain. The curves show a diffuse character of the transition. This is more pronounced in BZT than in BTO and is well marked for 1% doped than for 0,5% doped samples.

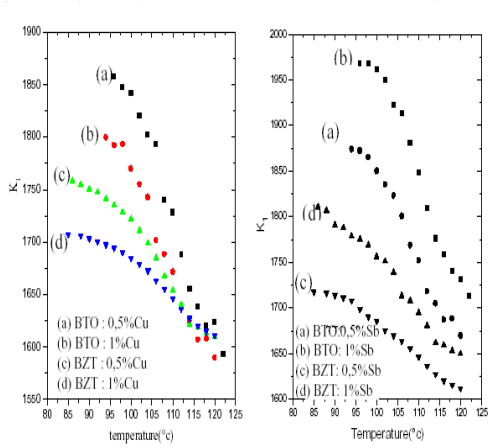

Figure 6: Temperature dependence of the calculated dielectric constant of the bulk grain of Cu and Sb-doped BTO and BZT.

This result can be attributed to spatial fluctuations in the concentrations of the substituted ions leading to the coexistence of regions of different curie temperature [11]. The diffuse nature of the transition may also be attributed to the quadraticity gradient which leads to a distribution of transition temperatures.

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