Ba$_{1-x}$Ca$_x$TiO$_3$ AND THE DIELECTRIC PROPERTIES

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Abstract. *Ba$_{1-x}$Ca$_x$TiO$_3$ material samples with x changing from zero to 1 were fabricated by the solid state reaction method at a temperature of 1200 ℃ in the ambient atmosphere. Crystalline structure of the material samples was recorded and identified by X-ray diffraction and Raman scattering. Analyzing the X-ray patterns found that Ba can be completely substituted by Ca with the concentration lower than 11 at%. The frequency dependence of the impedance (C) and AC conductance (G) of all the samples were recorded in a frequency range lower than 10 MHz by using an impedance analyzer HP 4192A. It was found that in the low frequency range lower than 1 MHz the dielectric constant and its loss decrease as Ca substituted for Ba. Besides an abnormal in the frequency dependence of the dielectric constant was observed for all samples in the higher frequency range up to 10 MHz.*

I. INTRODUCTION

The ferroelectric material perovskite BaTiO$_3$ have attracted much attentions of the worldwide scientists and technologies [6, 8, 9] because it is one of the lead-free pezoelectric materials that has huge applications in the electronic industry, such as: ultrasonic sensors, ultrasound machines, vibrating membrane, generators, converters...Recently Xiaobin Ren [1] reported a new experimental result dealing with a new compound BaZr$_{1-z}$Ti$_z$O3-xBa$_{1-y}$Ca$_y$TiO$_3$ (BZT-xBCT) that its piezoelectric parameter d$_{33}$ is significantly improved, reached to 620 pC/N with x of 50 at%, higher than the maximal values 580 pC/N of the PZT-5H that was reported until now. After the report of Ren many investigations focused on this topic were carried out by other authors [2-5, 7, 11-13]. As was known the feroelectric properties of the pezoelectric are strongly changed and improved around the point of the material phase competitions that is induced by the substitution of an appropriated constituent. In case of BZT-xBCT the substitution of Ca for Ba in BaTiO$_3$ affects directly on piezoelectric property of the material that is consequently related with its phase structure. To understand the relation between material structure and its pezoelectric properties we have

done a systematical research on the substitution effect of Ba by Ca. In this paper we present the infuence of Ca substitution effect on crystalline structure, micro morphological structure, dielectric properties, and piezoelectric of the $BaTiO_3$.

II. EXPERIMENTAL DETAILS

$Ba_{1-x}Ca_xTiO_3$ (BCTx) material samples (with x= 0%; 10%; 12%; 14%; 16%; 18%; 20% and 30%) were fabricated by the solid state reaction method. The starting $BaCO_3$, $CaCO_3$ and TiO_2 powder with purity of 3N were weighed to get the atomic ratio of Ba:Ca:Ti = 1-x:x:1. These powders were mixed and grinded in a mortar, after that the powder was pressed in pellet samples with diameter of 1 cm and thickness of 1 mm. The samples were calcinated at 1100 ˚C for 5 hours in the ambient atmosphere and after that they were grinded, pressed in pellet and heated again at 1300˚C for 6 hours.

X-Ray diffraction patterns of all the samples were recorded at room temperature by using a diffractometer D5000-SIEMENS equipped with $Cu_{K\alpha}$(λ= 1,5406Å) radiation. Raman scattering spectra were recorded by a Micro- Raman JOBIN YVON Labram 2 with resolution of about 1.3 cm^{-1}. The 632.8 nm laser beam of He-Ne laser was used as the exciting light. Frequency dependence of the dielectric constant of the material samples was measured by using an impedance analyzer HP-4192A.

III. RESULTS AND DISCUSSION

The first interest of our research is searching the substitution of Ca for Ba on structure of $Ba_{1-x}Ca_xTiO_3$ by means of X-ray diffraction and Raman scattering. Fig. 1 presents X-ray patterns of all the prepared samples. It shows that all the samples exhibit tetragonal structure of BTO as reported in [14]. It is clearly seen that the samples doped with Ca of concentration lower than 14 at% (x = 0.14) are high pure, identified to the single tetragonal phase. There are no another secondary phases. However, when the doped Ca concentration is higher than 16 at% (x ≥ 0.16), in the X-ray patterns of these samples appear new diffractive peaks, marked with * symbol in the patterns. These diffraction peaks may belong to a new unknown material phase formed when Ca concentration exceeded 14 at%. Intensity of these peaks slightly increases in dependence of the doped Ca concentration.

The X-ray diffraction patterns of the samples show that the diffraction peaks slightly shifted to the larger angle 2θ in dependence of Ca concentration. It may be related with the ion size Ca^{2+} that is smaller than the ion size of Ba^{2+}. It is supposed that the difference of ion diameter of Ca and Ba induces crystalline lattice deformation when Ca substituted for Ba in BTO. This crystal deformation increased and enlarged as Ca substituted concentration increased and consequently to form a new structure that has been observed when Ca concentration is larger than 16 at%.

In aim to confirm our above discussion we took Raman scattering measurement for the BCT samples. Raman spectra of the samples have been shown in Fig. 2. All the Raman peaks were observed at wavenumbers of 726, 526, 304, 256 and 186 cm^{-1}, identified to the vibration modes of BTO tetragonal phase. It is clearly seen that all the vibration modes slightly shifted to the higher wavenumber when the concentration of Ca increased. This obtained result probably is related with the decrease of the equivalent mass of the Ba-O-Ca bonds and unit cell volume of the material when Ca ion substituted for Ba in BTO. Furthermore we can see the increase
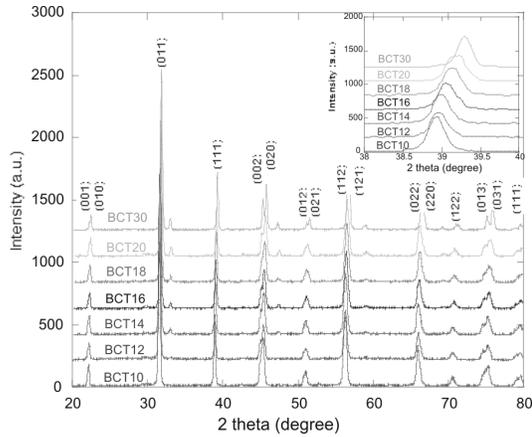
Fig. 1. The X- ray diffractive schema of the material samples BCT.
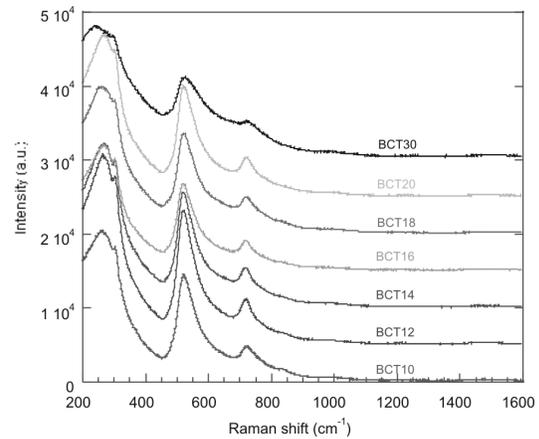
Fig. 2. The Raman scattering spectrum is at a room temperature of the material samples BCT.
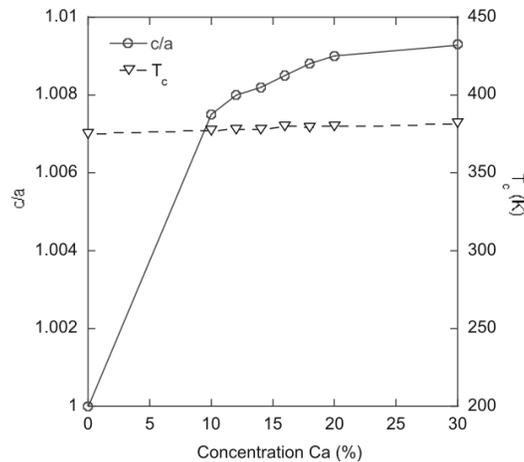
Fig. 3. The c/a ratio and T_c versus Ca concentratioin substituted for Ba in the BCT

of Raman line half-width in dependence of Ca concentration. It is supposed to be related with an increasing the crystalline lattice deformation that was concluded from the X-ray diffraction result. The relation between structure and ferroelectric properties of the material samples is the second interest of our research. In the next paragraph we have devoted our attention to qualify this relation by means of measurement of dielectric constants in dependence of frequency and temperature for all the samples. At first we search the dependence of dielectric constant of the samples on Ca doped concentration. As shown in Fig. 3 the para-ferroelectric phase transition temperature slightly increases in dependence of Ca doped concentration. This observed result may be related with an increase of the orthorhombic property of the dielectric system, which is expressed by an increase of c/a ratio as presented in Fig. 3. One of the most important questions is that how is relaxation behavior of this dielectric system? In demand of to analyze and to explain the

relaxation process of the dielectric system in dependence of Ca substituted concentration we have done measurement the frequency dependence of dielectric constant. Our measurement obtained results are presented in Fig. 4.
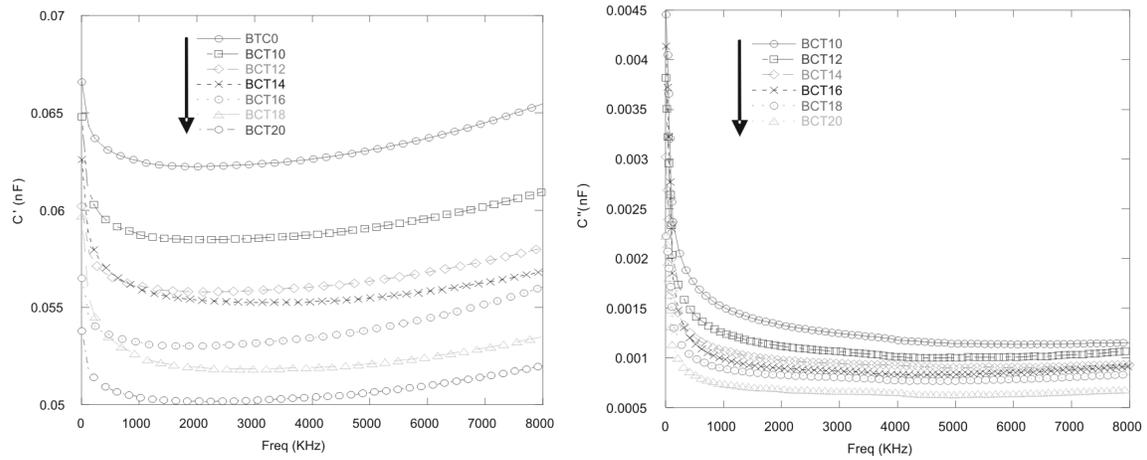
Fig. 4. Frequency dependence of the impedance of the material samples (BCT)
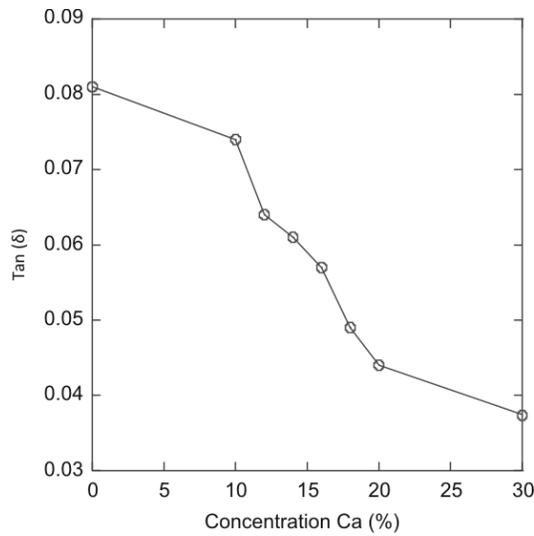
Fig. 5. The dielectric loss versus Ca concentration substituted for Ba in the BCT

Fig. 4 presents the frequency dependence of the real and imaginary parts of capacitance of all the samples. Using data of the real and imaginary part of the capacitance presented in Fig. 4 we have estimated the dielectric loss ($\tan\delta = \varepsilon'/\varepsilon''$) for all the samples in dependence of frequency. The obtained result is presented in Fig. 5. It shows that the dielectric loss of all the samples is small and decreases as Ca doped concentration increased. This obtained result promises hopeful

applications of the dielectric material. In addition we see that the frequency dependence on the dielectric constant rapidly decreases in the low frequency range and then increases gradually in the frequency range higher than 2.5 MHz. This increase of the dielectric constant is an abnormal result. Probably it is related with a dielectric resonance effect with a wide distribution. It is essential to qualify and to analyze this abnormal result in detail. For the frequency range lower than 2.5 MHz the dielectric constant decreases as Ca doped concentration increased as shown in Fig. 6.
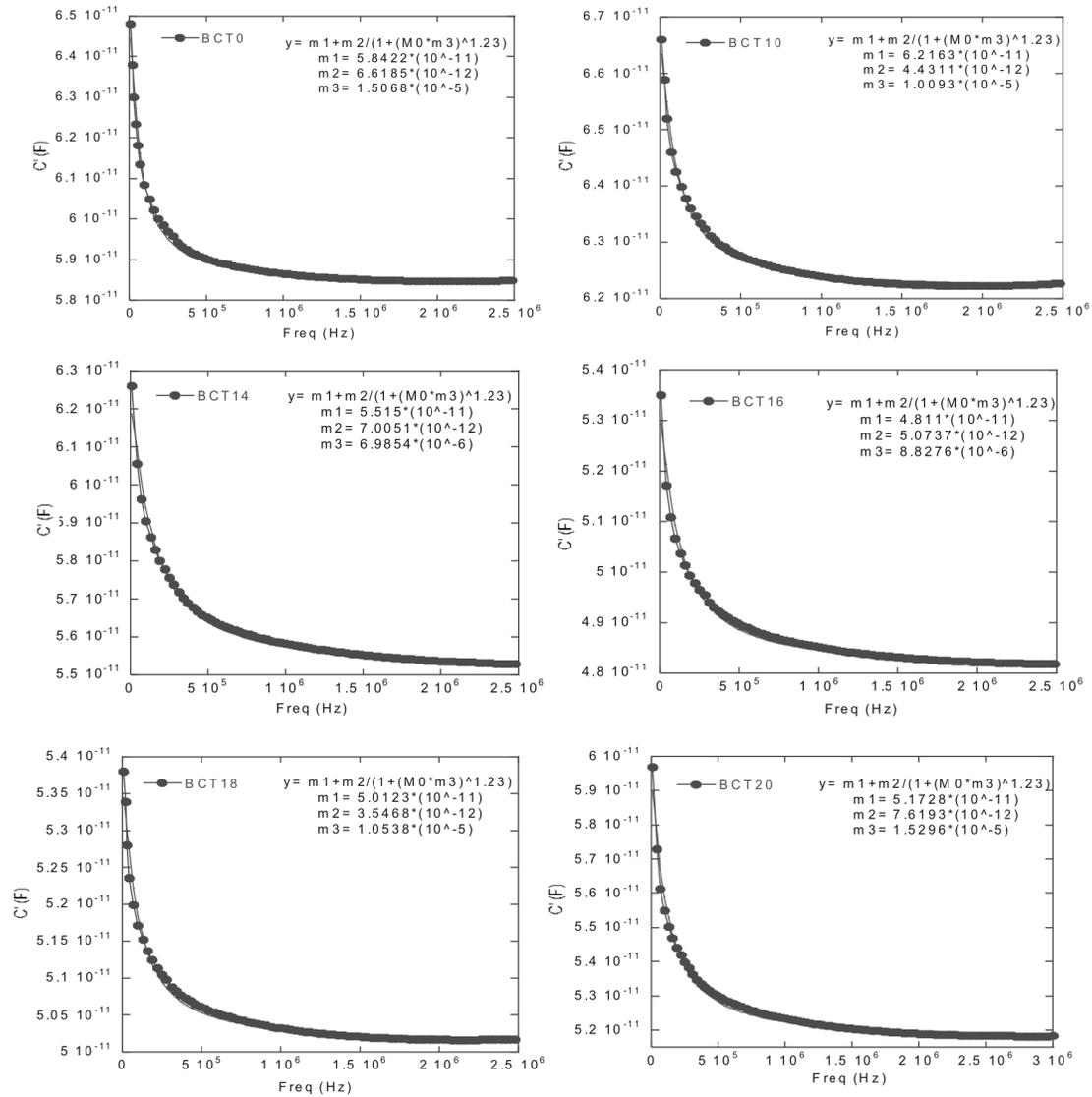
Fig. 6. Frequency dependence of the real dielectric permittivity of the material samples (closed circle – experimental data, lines – fitting results)

In order to analyze dielectric relaxation process for all the samples we use an empirical Debye formula as presented below:

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/[1 + (j\omega\tau)^{1-\beta}] \tag{1}$$

where ε^* is the complex dielectric permittivity, ε_s and ε_∞ are the static and high frequency dielectric permittivity, respectively, τ is the relaxation time and $1 > \beta \geq 0$ is an empirical parameter concerning with the distribution function of the relaxation time, which was accepted first time by K.S. Cole and R.H. Cole [5].
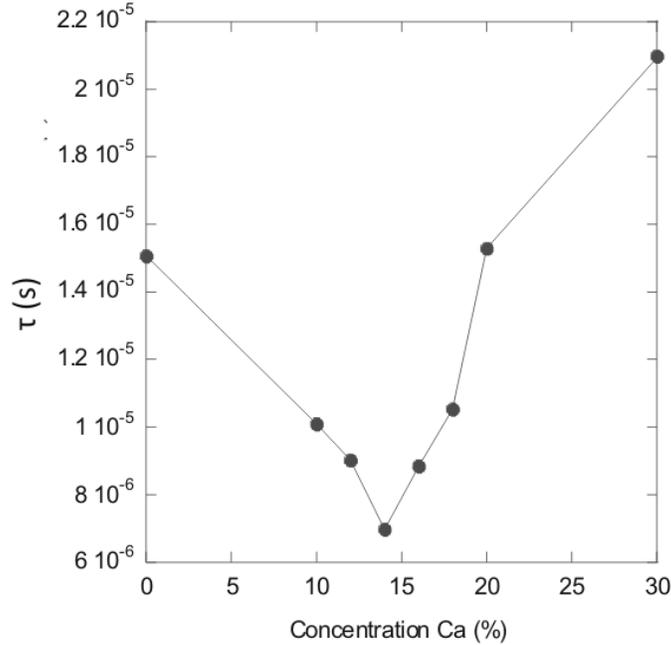
Fig. 7. The relaxation time versus Ca concentration substituted for Ba in the BCT

Fig. 6 exhibits a good fit for the real part of dielectric permittivity in dependence of frequency from 0 Hz to 2.5 MHz by using the equation (1). From the fitting parameters we have estimated relaxation time values for all the sample material. The dependence of the estimated relaxation time on Ca doped concentration can be seen in Fig. 7. It is clearly seen that the dielectric relaxation time decrease to a minimal value of $1.5 \ 10^{-6}$ s as Ca doped concentration increases to 14 at%. After that it increases in dependence of the Ca concentration. The decrease of the dielectric relaxation time as the Ca doped concentration increased up to 14 at% may be concerned with that the ion radius of Ca^{2+} ion is smaller than that of Ba^{2+} ion. However this explanation induces a question that why the recorded value of dielectric relaxation time at the critical Ca concentration of 14 at% is minimal? Turning back to X-ray diffraction we have known that the substitution of Ca for Ba induces crystalline lattice deformation in structure of BTO and this deformation process enlarged when Ca doped concentration increased to a critical concentration so that induced a change in structure. This crystalline deformation reasonably is a main reason to create a morphology phase competition and to pin the dielectric dipole state so that to prolong the dielectric

relaxation process as well as to improve piezoelectric property of material. This obtained result is an experimental evidence to believe that the material is a promising candidate for manufacturing the lead-free piezoelectric material having high piezoelectric constant.

ACKNOWLEDGEMENTS

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