

Effect of Pr_6O_{11} Substitution on Structural and Dielectric Properties of BaZrTiO_5 Ceramic Materials

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Abstract — In the present work, we studied the effect of the substitution of BaO by Pr_6O_{11} , on the structure, dielectric and electrical properties of BaTiZrO_5 ceramics. Samples of general formula $(99.2-x) \text{BaO} \cdot x\text{Pr}_6\text{O}_{11} \cdot 0.5\text{TiO}_2 \cdot 0.3\text{ZrO}_2$ ($x = 0.1, 0.2, 0.5$ and 0.6) named $\text{P}_1, \text{P}_2, \text{P}_3$ and P_4 respectively were prepared by conventional ceramic method. The structure of the prepared samples was studied using X-ray diffraction, water absorption % and SEM. Addition of Pr_6O_{11} minimized the presence of closed pores and thus led to improved densification. The crystallize size of the prepared samples was calculated and found in the range 22-26 nm. The effect of the substitution by Pr_6O_{11} on breakdown field, dielectric constant, ac resistivity was investigated. Finally, it was found that, the substitution BaO by Pr_6O_{11} improves the physical properties of BaTiZrO_5 ceramics by increasing their break down field, ac resistivity and dielectric constant that makes these ceramics useful in the technological applications.

Keywords: *BaTiZrO₅ ceramics; water absorption; breakdown field SEM; dielectric constant; ac resistivity.*

I. INTRODUCTION

BaTiO_3 ceramics is a ferroelectric material with a high dielectric constant and high insulation resistance. Therefore, it used in electric ceramic capacitors, thermistors, piezoelectric transducers and a variety of electro-optic devices [1, 2]. Barium titanate (BaTiO_3) a perovskite structure, has been widely investigated because of its dielectric and ferroelectric properties [3, 4]. Ceramics materials based on $\text{BaTiO}_3\text{-R}_2\text{O}_3$ system (R = rare earth, mostly Zr, Pr, La and Nd) are used for preparation passive electronic components. BaTiO_3 slightly doped with rare earth oxides is semi-conductor and is used for manufacture of switching, heating and regulating devices. The increasing of amounts of rare earths oxides with BaTiO_3 exhibits high electrical resistivity and is used in manufacturing high stable capacitors [5].

The electric properties of $\text{BaTiO}_3\text{-R}_2\text{O}_3$ depend on the chemical composition, crystal structure, and grain size. To produce semiconductive ceramics, a small amount of rare metal oxide such as $\text{ZrO}_2, \text{Pr}_2\text{O}_3$ was added [6, 7]. ZrO_2 plays a critical role in maintaining the electrical properties of BaTiO_3 ceramics. It was found that, the sintering temperature of BaZrTiO_3 is always (1350 -1400°C), when $\text{ZrO}_2, \text{ZnO}, \text{CuO}$ and SiO_2 are added, the sintering temperature decrease by 100-300°C and dielectric constant rising [8-10]. The (Ca, Zr) co-doped BaTiO_3 ceramics was earlier used in capacitor composition [11-13].

Praseodymium oxide is a rare earth metal oxide that has not been used for microelectronic applications so far. Based on thermo dynamical considerations it should be stable against silicon. Praseodymium oxide (PrO_x) has different oxygen compositions, with x ranging from 1.5 to 2 due to the multiple oxidation states (+3 and +4) of Pr. Variations in oxygen vacancy ordering lead to different phases including two cubic phases for PrO_2 and manganese oxide(Mn_2O_3) structure for Pr_2O_3 . In addition, praseodymium oxide exhibits negligible hysteresis and excellent reliability characteristics. The partial replacement of Ti^{4+} by Sn^{4+} produces the $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$, solid solution that shows diffuse phase-transition behavior and Curie temperature (T_C) decreases with the Sn^{4+} incorporation [14-16]. Recently, the effect of rare earth metal ions on the structural and electrical properties of BaTiO_3 has been studied by many authors [17-19]. In the present work the effect of the substitution by a small amount of rare earth metal oxide such as Pr_6O_{11} on the structure, electrical and dielectric properties of BaZrTiO_5 ceramics is investigated.

II. EXPERIMENTAL

Samples of general formula $(99.2-x) \text{BaO} \cdot x\text{Pr}_6\text{O}_{11} \cdot 0.5\text{TiO}_2 \cdot 0.3\text{ZrO}_2$ ($x = 0.1, 0.2, 0.5$ and 0.6) named $\text{P}_1, \text{P}_2, \text{P}_3$ and P_4 respectively were prepared by conventional ceramic method using high-purity oxide powders BaO, $\text{ZrO}_2, \text{TiO}_2$ and Pr_6O_{11} . After ball-milling for 3 h, the mixture of raw materials was calcined at 600°C for two hours. The obtained powders were re-milled for one hour. The fine powder pressed

into pellets (12 mm in diameter and 6 mm in thickness) by uniaxial pressing (ca. 70 MPa) using polyethylene glycol as binder. The pellets were sintered in the temperature range from 800 to 1000°C for 1/2 hour in air to get dense samples. Sintered pellets were polished for physical, microstructure and dielectric properties measurements. The density of the samples was measured by the Archimedes method with water as the liquid medium. The microstructure of samples were characterized by X-ray diffraction (XRD, Rigaku D/max-A X-ray diffractometer) using $\text{CuK}\alpha$ radiation. Microstructures of fracture surfaces were observed by a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS). Dielectric properties as a function of frequency and temperature of the sintered disks was measured using an automatic measurement system with an A PM 6304 programmable automatic LCR bridge.

III. RESULTS AND DISCUSSION

Figure 1 shows the water absorption% as a function of firing temperature. All investigated mixes showed a decrease in water absorption as temperature of firing increases. Physical properties results showed that, better densification is observed in discs fired at 1000 °C for 1/2 h, after that deformation started. All mixes showed low values of water absorption. Based on these results, 1000°C temperature was chosen the suitable maturing temperature.

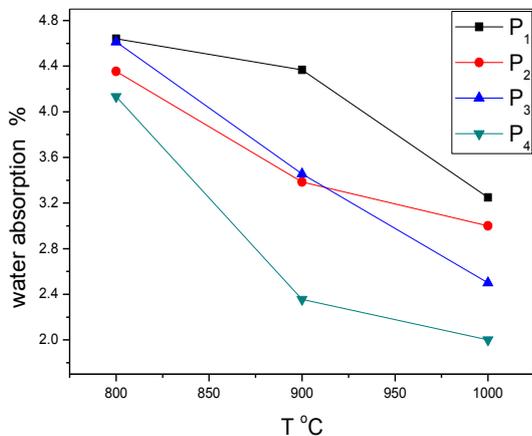


Fig. 1 Water absorption % of the prepared samples as a function of firing temperature

The density of BaZrTiPrO_8 ceramic samples doped with various amounts of Pr_6O_{11} is shown in Fig.2. It is also clear that, as firing temperature increases the density of the prepared samples increases. Maximum density was realized at temperature of 1000 °C, and above 1000 °C sintering temperature, the density of all examined samples decreased. This decrease can be attributed to the increase in intergranular porosity as a result of discontinuous grain growth [20, 21].

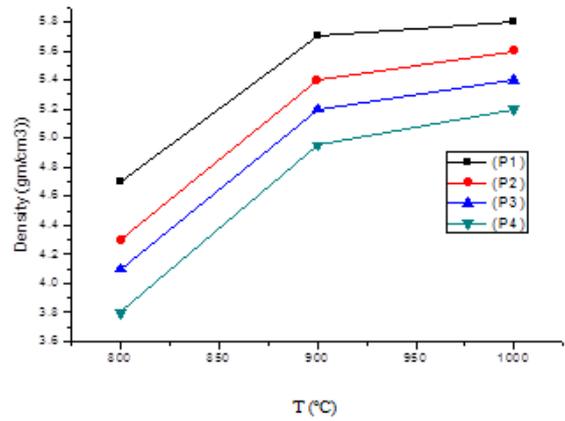


Fig.2 Influence of sintering temperature on the density of the prepared samples.

Figure 3 indicate the compositional dependence of the water absorption and shrinkage % at temperature of 1000°C. Better densification of BaTiO_3 ceramics can be obtained by adding Pr_6O_{11} in current ZrO_2 . This is because the presence of closed pores was minimized. Sample (P₄) of $x = 0.6$ mol% which fired at temperature of 1000 °C for 1/2 h recorded the minimum water absorption and maximum shrinkage %. Test results clearly indicated that minimum water absorption and improved densifications are realized in all samples subjected to fired temperature of 1000 °C for 1/2 h.

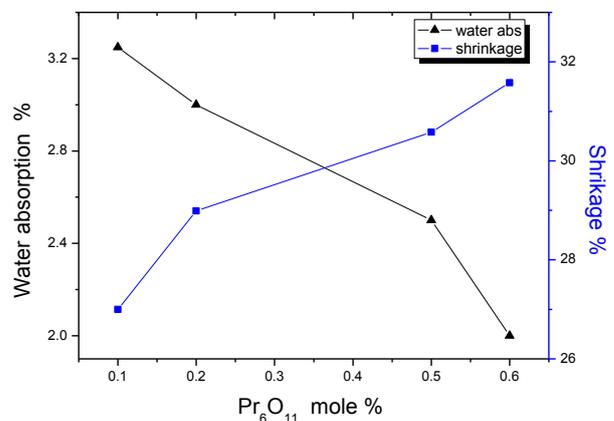


Fig. 3 Compositional dependence of the water absorption % and shrinkage % of the prepared samples.

Figure 4 shows the x-ray diffraction patterns of the prepared samples. All compositions possess pure structure without any secondary phase to complete dissolution of the present dopants oxides in the lattice which form solid solution.

The average crystallite size (D) BaZrTiO_5 ceramics has been calculated from x-ray data using Scherrer's equation [22, 23] and was found to increase with increasing Pr_6O_{11} content. The larger crystallite size may be due to the bridging of fine particles that formed

the continuous grain boundary networks [24]. The maximum size of crystal was appeared in sample P₃ as illustrated in Fig.5. Further increase of Pr₆O₁₁ causes a decrease in the crystalline size of the sample P₄ this may be attributed to the presence of some secondary phases of Pr₂O₃ at the grain boundaries which delays the growth of grains and creates an external pressure on the grains [25].

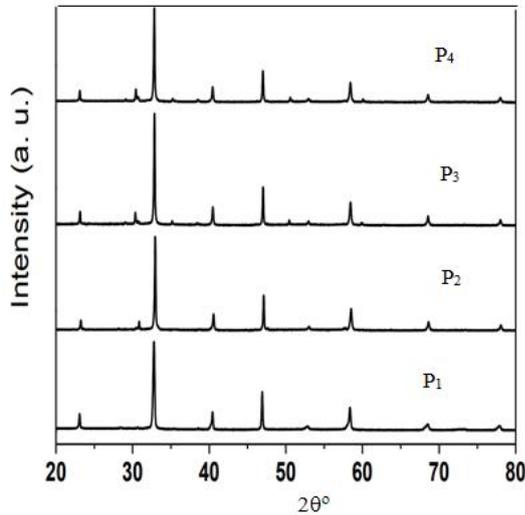


Fig. 4 XRD of the prepared samples.

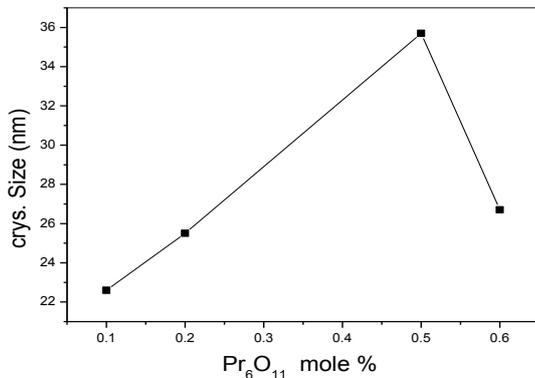


Fig. 5 Variation of the crystallite size with Pr₆O₁₁ mol %

The effect of increasing temperature on endothermic, weight loss and exothermic reaction were examined by the aid of TGA thermograms method for all the prepared samples, Fig. 6. A marginal weight loss of about 1% was observed in the TGA curve in the range between 100 and 300°C. This is attributed to the liberation of adsorbed moisture found in the sample as a result of the ultra-fine nature of the as prepared sample. Strong endothermic was also revealed around at this temperature. A wide exothermic peak was recorded in the temperature region between 300°C and 600°C. In this region, the third loss in weight was noticed by burning Pr-based material in TGA curve. The existence of small exothermic peak in TG pattern at 258 °C can be due to intermediate reaction steps

among the precursor material which leads to the creation of compound at a phase where mass loss reaches a saturation level. Thus the best appropriate temperature for calcinations to prepare the samples by a solid- state technique looks to be about 560°C.

The SEM of the samples P₁ and P₃ are shown in figure 7. SEM images show BaO grains are tend together and presence of pores of various sizes indicating a kind of volatilization, also Zr, Ti and Pr go into solid solution in the BaO grains.

Figure 8 shows the relation between V and I for all investigated samples in the present work. Figure 8 confirm the non linear, non- Ohmic current field characteristics of the prepared samples. The I-V relation of the samples P₁, P₄ is placed as an inset of Fig.8 to clarify the the non-Ohmic behaviour of the samples. It is clear that all investigated samples show nonlinear I-V characteristics.

Also the breakdown field was measured as function of Pr₆O₁₁ mol% and the obtained results are shown in figure 9. This figure shows that as Pr₆O₁₁ mol% increases the breakdown field improved and attained its maximum value at 0.5mol % Pr₆O₁₁ (Sample P₃).

The increase of the breakdown field with increasing Pr₆O₁₁ concentration is attributed to, the addition of small amount of Pr₆O₁₁ may causes a thicker grain boundaries phase which reported elsewhere[26] which increases the effective barrier between the electrodes. Further addition of Pr₆O₁₁ above 0.5 mol % causes suppression of grain growth, as shown in Fig.5, and Pr₆O₁₁ generates secondary phases at the grain boundaries and the valency state of praseodymium is changed into Pr₂O₃ leading to change the donor concentration and decreasing the number of active barriers between the two electrodes and consequently the breakdown field decreases [25].

The dielectric constant of all the samples was measured as a function of frequency ranged from 1 to 20 kHz and the obtained results are shown in Fig.10. It was found that, the dielectric constant (ϵ') of all samples decreases with increasing frequency as shown in Fig.10. The sample P₄ which containing 0.6 mol% Pr₆O₁₁ represents the maximum value of dielectric constant. As frequency increases the magnetic dipoles can not flow the variation of the electric field direction and consequently the dielectric constant decreases with the frequency.

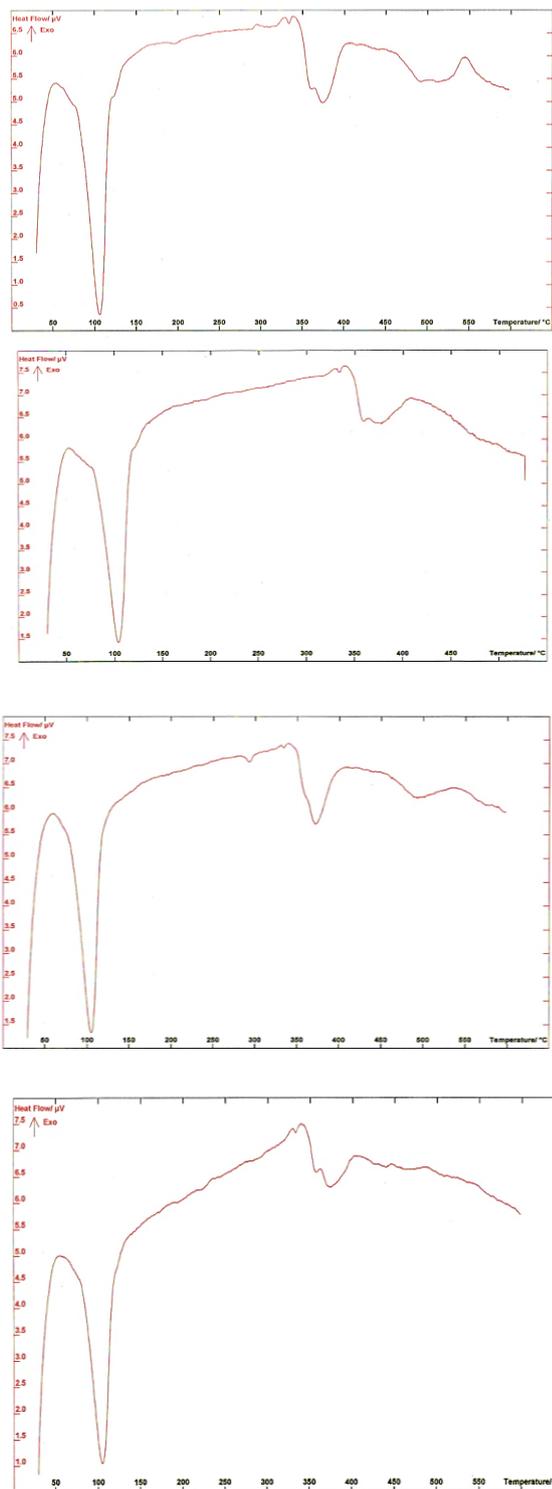


Fig. 6 TGA thermograms of all the prepared samples

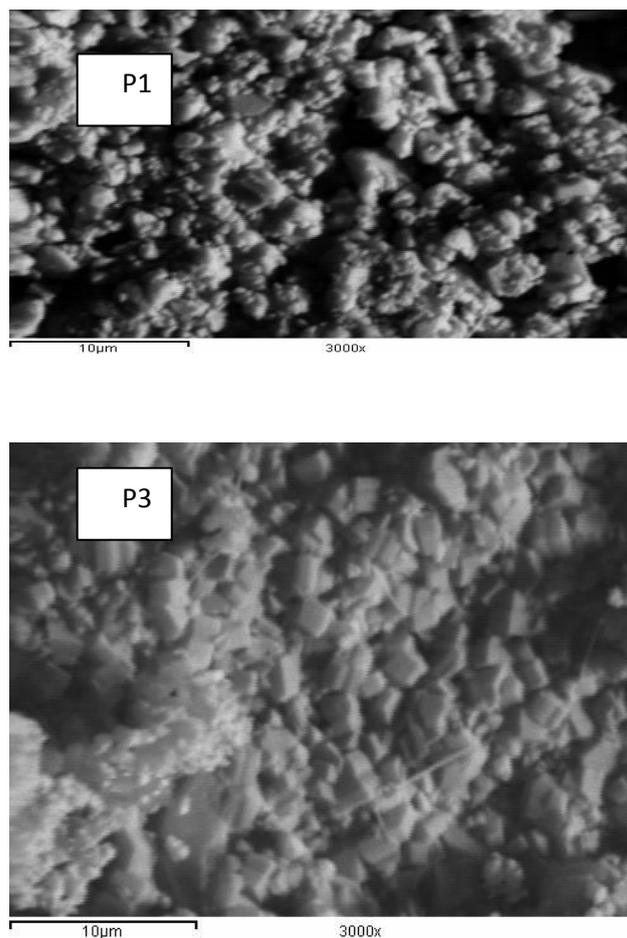


Fig.7 SEM images of the of the sample P₁ and P₃

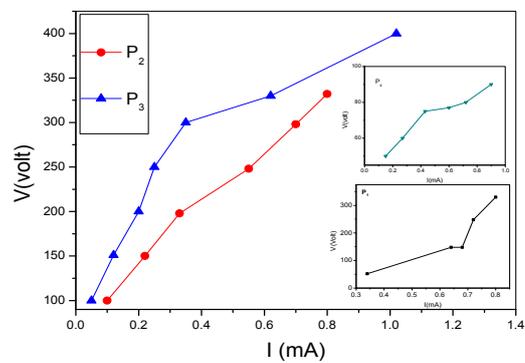


Fig. 8. (I -V) Characteristics of the prepared samples

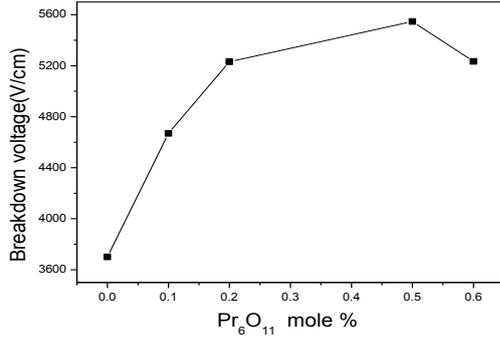


Fig. 9 Breakdown field as a function of Pr₆O₁₁ mole %

The role played by praseodymium oxide in this case is during firing the valency state of praseodymium is changed into Pr₂O₃ with the evolution of oxygen. The electronic interface states generation out grain boundaries is due to the evolution of such oxygen.

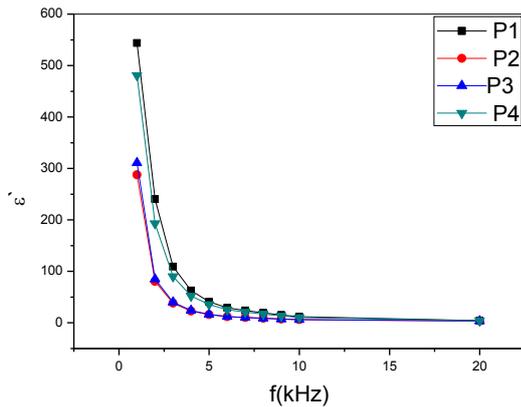
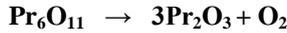


Fig. 10 Variation of the dielectric constant with the frequency for all the prepared samples.

The relation between resistivity (ρ) and frequency for all investigated mixes is illustrated in Fig. 11. The figure shows that as increases the resistivity decreases. This is because increasing frequency of the applied field liberates the charges trapped in deep traps and increases the conductivity and consequently the resistivity decreases also the the ionic response to the field at any certain frequency increases with increasing frequency.

The compositional dependence of the dielectric constant and ac resistivity is shown in Fig. 12. The figure shows that, as Pr₆O₁₁ content increases the ac resistivity increases and obtained its maximum value at 0.5 mol % of Pr₆O₁₁ then decreases. The increase of the resistivity and decreases of the dielectric constant are due to the increase in the thickness of the poor conductive grain boundaries with increasing Pr₆O₁₁ content. Also the increase in the ac resistivity is attributed to the

increase of the average crystallize size which causes an increase in the intragranular porosity of the samples [27, 28]. Above 0.5 mol% the resistivity decreases because some of Pr₆O₁₁ generate secondary phases of pr₂O₃ which change the donor concentration at the grain boundaries [25]. The substitution of BaO by Pr₆O₁₁ improves the physical properties of BaTiZrO₅ ceramics by increasing their break down field and ac resistivity makes these ceramics useful in the technological applications.

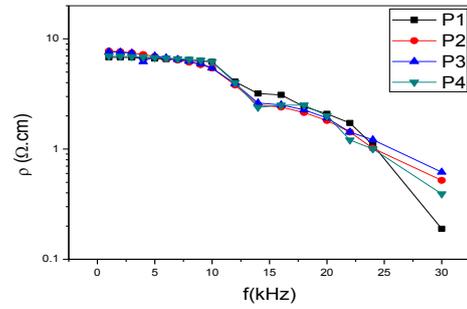


Fig.11 Effect of the frequency on resistivity of the prepared samples

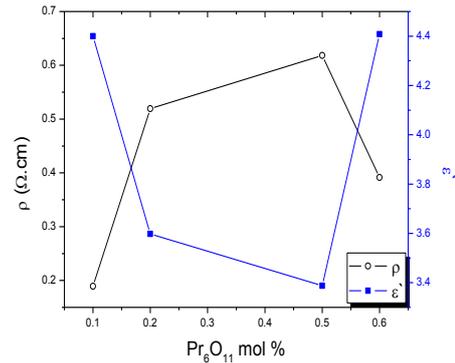


Fig.12 Compositional dependence of the dielectric constant and ac resistivity of prepared samples

IV. CONCLUSIONS

BaZrTiPrO₈ ceramic samples have been successfully prepared by (conventional ceramic method) solid state reaction and their structure; physical and dielectric, properties have been studied. Addition of Pr₆O₁₁ in the presence of TiO₂, ZrO₂ and BaO minimized the presence of closed pores and thus led to improved densification. Samples exposed to fired temperature of 1000°C for 0.5 hour recorded the minimum water absorption and the maximum shrinkage. Addition of Pr₆O₁₁ improved breakdown field a further addition above 0.5 mol% is negatively affected. It was found that, the substitution of BaO by Pr₆O₁₁ improves the physical properties of BaTiZrO₅ ceramics by increasing their break down field and ac resistivity while the dielectric constant decreases. The sample of 0.5 mol % has the highest breakdown field and ac

resistivity makes these ceramics useful in the technological applications.

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