Effect of Pr$_6$O$_{11}$ 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$_6$O$_{11}$ on the structure, dielectric and electrical properties of BaTiZrO$_5$ ceramics. Samples of general formula (99.2-x) BaO-xPr$_6$O$_{11}$-0.5TiO$_2$-0.3ZrO$_2$ (x = 0.1, 0.2, 0.5 and 0.6) named P$_1$, P$_2$, 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$_6$O$_{11}$ 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$_6$O$_{11}$ on breakdown field, dielectric constant, ac resistivity was investigated. Finally, it was found that, the substitution BaO by Pr$_6$O$_{11}$ improves the physical properties of BaTiZrO$_5$ ceramics by increasing their breakdown field, ac resistivity and dielectric constant that makes these ceramics useful in the technological applications.

Keywords: BaTiZrO$_5$ 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 is 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 BaTiO$_3$-R$_2$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 BaTiO$_3$-R$_2$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 ZrO$_2$, Pr$_2$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 ZrO$_2$, ZnO, 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$_3$) 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$_2$O$_3$) structure for Pr$_2$O$_3$. In addition, praseodymium oxide exhibits negligible hysteresis and excellent reliability characteristics. The partial replacement of Ti$^{4+}$ by Sn$^{4+}$ produces the BaTi$_{1-x}$Sn$_x$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$_6$O$_{11}$ on the structure, electrical and dielectric properties of BaZrTiO$_5$ ceramics is investigated.

II. EXPERIMENTAL

Samples of general formula (99.2-x) BaO-xPr$_6$O$_{11}$-0.5TiO$_2$-0.3ZrO$_2$ (x = 0.1, 0.2, 0.5 and 0.6) named P$_1$, P$_2$, P$_3$ and P$_4$ respectively were prepared by conventional ceramic method using high-purity oxide powders BaO, ZrO$_2$, TiO$_2$ and Pr$_6$O$_{11}$. 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 CuKα 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.

Figure 2 indicate the compositional dependence of the water absorption and shrinkage % at temperature of 1000°C. Better densification of BaTiO₃ ceramics can be obtained by adding Pr₆O₁₁ in current ZrO₂. 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.

Figure 3 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) BaZrTiO₅ ceramics has been calculated from x-ray data using Scherrer’s equation [22, 23] and was found to increase with increasing Pr₆O₁₁ 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].

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 Pr₂O₃ 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 Pr₂O₃ 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 follow 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 sample P₁ and P₃

Fig. 8. (I-V) Characteristics of the prepared samples
The role played by praseodymium oxide in this case is during firing the valency state of praseodymium is changed into Pr$_2$O$_3$ with the evolution of oxygen. The electronic interface states generation out grain boundaries is due to the evolution of such oxygen.

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\text{Pr}_6\text{O}_{11} \rightarrow 3\text{Pr}_2\text{O}_3 + \text{O}_2
\]

The relation between resistivity ($\rho$) 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 filed at any certain frequency increases with increasing frequency.

![Fig. 9](image9.jpg)

**Fig. 9** Breakdown field as a function of Pr$_6$O$_{11}$ mole %

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 Pr$_6$O$_{11}$ generate secondary phases of Pr$_2$O$_3$ which change the donor concentration at the grain boundaries [25]. The substitution of BaO by Pr$_6$O$_{11}$ improves the physical properties of BaTiZrO$_5$ ceramics by increasing their break down field and ac resistivity makes these ceramics useful in the technological applications.

![Fig. 10](image10.jpg)

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

![Fig. 11](image11.jpg)

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

![Fig. 12](image12.jpg)

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

IV. CONCLUSIONS

BaZrTiPrO$_8$ 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 Pr$_6$O$_{11}$ in the presence of TiO$_2$, ZrO$_2$ 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 Pr$_6$O$_{11}$ improved breakdown field a further addition above 0.5 mol% is negatively affected. It was found that, the substitution of BaO by Pr$_6$O$_{11}$ improves the physical properties of BaTiZrO$_5$ 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.

REFERENCES


