

Dielectric properties of BaTiO₃ modified with ZrO₂

N M MOLOKHIA and M A ISSA

Physics Department, Faculty of Science, Riyadh University, Riyadh, Saudi Arabia

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Abstract. The dielectric constant and loss tangent of BaTiO₃ with ZrO₂ additives have been studied. The loss tangent was less ranging between 0.16 for pure BaTiO₃ and 0.05 for samples containing 5% ZrO₂. The dielectric constant at Curie temperature decreased with increasing ZrO₂ concentration up to 0.4%. The volume resistivity measurements illustrate a peak value at a certain range of temperatures for each composition.

Keywords. Dielectric properties; loss tangent; dielectric constant.

1. Introduction

The discovery of the usefulness of BaTiO₃ has led to enormous efforts towards study in the properties of ceramic bodies with modified composition. Jonker and Kwestroo (1958) studied the system (BaO:TiO₂:ZrO₂) and mentioned that small amounts of ZrO₂ stabilize two new BaTiO₃ phases, Ba₂Ti₅O₁₂ and Ba₂Ti₉O₂₀. Smalenskii and Isupov (1954) mentioned that substantial replacement of Ti⁺⁴ by Zr⁺⁴ causes depression of the Curie point below room temperature. However, slight replacement (below 10%) causes a rise in the orthorhombic tetragonal transition temperature, so that the orthorhombic phase becomes stable at room temperature. A solid solution slightly deficient in Ba⁺² (produced by adding ZrO₂ rather than BaZrO₃) was found preferable for obtaining high coupling factor and lowered dielectric constant (Brajer *et al* 1952). Gallagher (1963) worked on the system of Zr-doped BaTiO₃ where Zr replaced Ti up to 10 mole %. He mentioned that the dielectric constant of BaTiO₃ decreases continuously with ZrO₂ additives. Polandov and Mylov (1964) studied the dielectric properties of polycrystalline solid state solution Ba(Ti_{0.9}, Zr_{0.1})O₃ in weak electric fields. It was established that with increase of pressure, the curves giving the dependence $E=f(t)$ were shifted toward lower temperature.

The purpose of this investigation was to determine the effect of low concentrations of ZrO₂ on the dielectric properties of BaTiO₃ as well as to fabricate a highly insulating material with good dielectric properties.

2. Experimental procedure

BaTiO₃ used in this work was prepared by mixing BaCO₃ with TiO₂ by the usual ceramic methods (Payne and Tennery 1965). The x-ray diffraction patterns for the prepared BaTiO₃ indicated that the reaction went to completion and the tetragonal

BaTiO₃ is the only crystalline phase present. The prepared compositions with ZrO₂ additives were pressed into small tablets 1.2 cm diameter and 0.1 cm thickness and fired at 1400°C for 10 hr. The specimen after being silver-coated were placed in a holder having spring loaded contacts ready for electrical measurements.

The dielectric constant and the loss tangent were measured with a capacitance bridge with 0.5 V r.m.s. signal at a frequency of 1490 c.p.s. across the specimens. The structure and lattice parameters of the specimens were determined by room-temperature using x-ray diffraction powder technique. Measurement of volume resistivity was carried out by a two probe method of placing a known voltage across the specimen and measuring the current with nanoammeter.

3. Experimental results

The temperature dependence of the dielectric constant for compositions from 0 to 5% ZrO₂ in BaTiO₃ was measured. Figure 1 illustrates the results of two samples of 0.4 and 4% ZrO₂. Comparing with pure BaTiO₃, it is clear that the addition of ZrO₂ decreases the dielectric constant of BaTiO₃ but not linear. Figure 2 represents the variation of the dielectric constant with ZrO₂ percentage at different temperatures.

The effect of an applied electric field on the dielectric constant of the sample 0.4% ZrO₂ at different temperatures is shown in figure 3. On increasing the applied field to 6 kV/cm, the dielectric constant at Curie temperature increased by nearly 50%.

The loss tangent of pure BaTiO₃ improves on adding ZrO₂. It decreases from 0.16 for pure BaTiO₃ to 0.05 in the samples with 5% ZrO₂ at room temperature. The results of tan δ for different samples are included in table 1.

X-ray measurements indicate that the crystal structure of BaTiO₃ is the same throughout our modified compositions. The lattice parameter of BaTiO₃ agreed

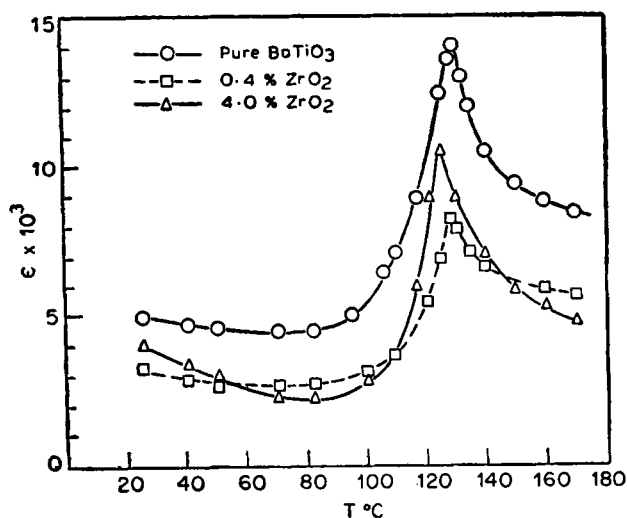


Figure 1. Variation of the dielectric constant with temperature

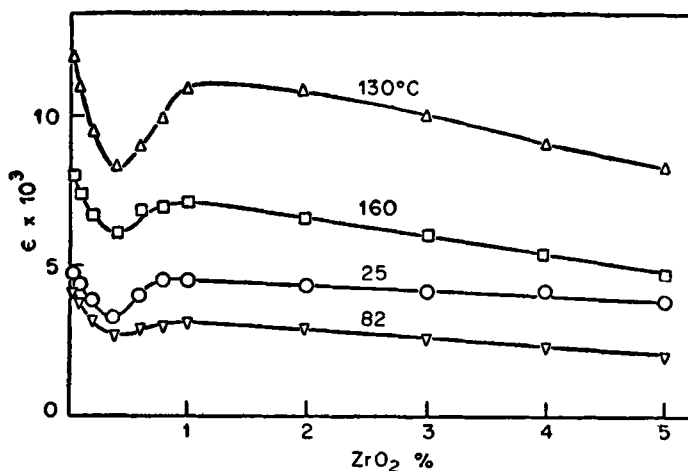


Figure 2. Dependence of dielectric constant on ZrO_2 additives

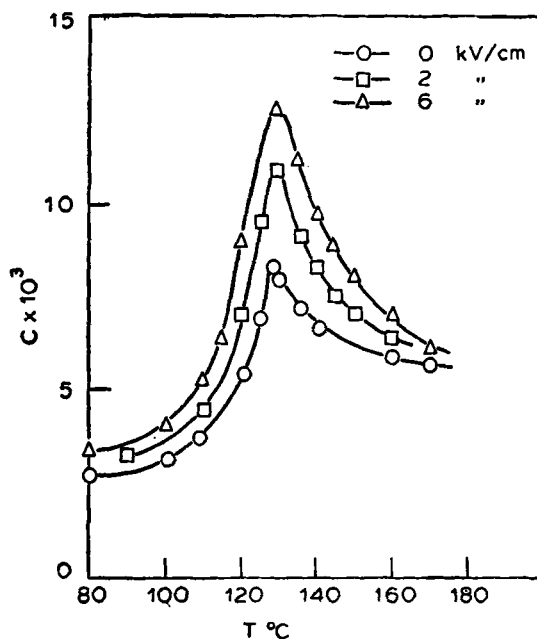


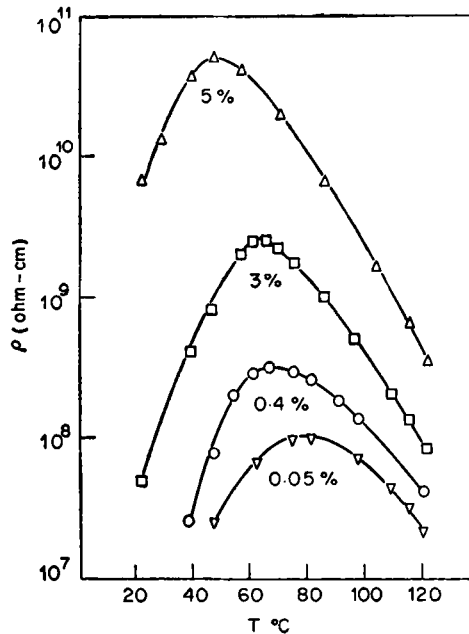
Figure 3. Effect of d.c. field on the temperature dependence of the dielectric constant for 0.4% ZrO_2 in BaTiO_3

well with the results of Megaw (1957), ($a_0 = 3.985 \text{ \AA}$ and $c_0 = 4.02 \text{ \AA}$). As shown in table 1, the lattice parameter increases with ZrO_2 additives.

The volume resistivity for each specimen was measured at different temperatures covering the phase transition from cubic to tetragonal structure. Figure 4 illustrates the resistivity variation for the samples 0.05, 3 and 5% ZrO_2 in BaTiO_3 . All curves show resistivity maxima at different temperatures.

Table 1. Compositions and properties of BaTiO₃ containing ZrO₂

Composition	tan δ at 25°C, 1490 Hz	Lattice constant	
		a ₀ (Å)	c ₀ (Å)
BaTiO ₃	0.160	3.985	4.020
(BaTiO ₃) _{99.95} (ZrO ₂) _{0.05}	0.033	3.992	4.032
(BaTiO ₃) _{99.9} (ZrO ₂) _{0.1}	0.030	3.995	4.036
(BaTiO ₃) _{99.6} (ZrO ₂) _{0.4}	0.041	4.006	4.068
(BaTiO ₃) ₉₅ (ZrO ₂) ₅	0.047	4.003	4.072
(BaTiO ₃) ₉₇ (ZrO ₂) ₃	0.047	4.012	4.108
(BaTiO ₃) ₉₅ (ZrO ₂) ₅	0.050	4.019	4.150

Figure 4. Volume resistivity for different percentages of ZrO₂ in BaTiO₃ at different temperatures

It is clear that the addition of ZrO₂ causes an increase in the volume resistivity in the investigated range of temperatures as also a shift in the maximum resistivity peak to lower temperatures.

4. Discussion

The results show that the dielectric constant of BaTiO₃ is nonlinear with ZrO₂ additives in the range 0 to 1%. This can be explained on the basis of how the Zr atoms diffuse in BaTiO₃ lattice. It seems that the Zr⁴⁺ atoms occupy an interstitial positions up to a concentration of 0.4% ZrO₂ in a disordered way. This effect will

disturb the polarization and the dielectric constant will decrease. Further addition of ZrO₂ to BaTiO₃ lattice will let the Zr⁺⁴ atoms substitute Ti⁺⁴ atoms giving rise to an ordered distribution of charges and the dielectric constant increases again.

As shown in figure 3, the domain structure of BaTiO₃ is affected by this addition of ZrO₂. The increase in dielectric constant at Curie temperature can be attributed to the reorientation of 90° domains under the effect of the applied field. The variation of loss tangent with additives is not like that of dielectric constant; it is nearly linear and decreased continuously with additives.

The resistivity maximum at a certain range of temperature is one of the properties of a semiconductor material. Introducing the Zr atoms in BaTiO₃ lattice does not change this behaviour. This means that the Zr atoms introduced has no effect on the energy band scheme of BaTiO₃ lattice. According to Tennary and Cook (1961), there is a narrow conduction band in BaTiO₃ which splits into sub-bands in the ferroelectric phase owing to the fact that Ti ion is not located at the centre of the oxygen octahedron. The addition of Zr atoms to BaTiO₃ lattice will cause an excess charge carriers moving through these sub-bands. Increasing the temperature of the samples will give enough energy to the conduction electrons to leave their atoms and the resistivity increase.

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