

INVESTIGATION OF THE ACTION OF HIGH TEMPERATURE TITANIA ADDITIONS ON THE ELECTRIC AND DIELECTRIC PROPERTIES OF BARIUM ZIRCONATE CERAMICS

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(Received 14 October 1982)

ABSTRACT

The effects of titania additions on the electrical conductivity and dielectric properties is investigated, at room and elevated temperatures, for barium zirconate refractory.

Measurements of the temperature dependence of electrical conductivity indicate that the introduction of Ti^{4+} ions in the barium zirconate lattice takes place in four stages. The dielectric constant increased with the increase of titania up to 20 wt.% TiO_2 , falls to a minimum at 30 wt.% TiO_2 and rises again up to 40 wt.% TiO_2 . A mechanism is suggested for the solid state reaction of the system $BaZrO_3-TiO_2$.

INTRODUCTION

It was reported by Novosil'tsev and Khodakov [1], that mixing of $BaTiO_3$ with $BaZrO_3$ gave a solid solution of a very high dielectric constant. The aim of the present work is to evaluate solid solutions containing the $BaZrO_3-TiO_2$ system and the effect of high temperature titania additions on the electric and dielectric properties of barium zirconate.

EXPERIMENTAL

Material preparation

The starting materials were analytically pure grades of barium carbonate, zirconia and titania (AR from B.D.H. > 99.89%). $BaZrO_3$ was prepared by thorough mixing of an equimolecular ratio of $BaCO_3$ and ZrO_2 , followed by calcination at $1000^\circ C$ and firing at $1200^\circ C$ for 2 h as a soaking period. The $BaZrO_3$ thus obtained and the TiO_2 used for the preparation of ceramic

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mixes were both identified by chemical and X-ray analyses.

Ceramic mixes of BaZrO₃ and TiO₂ were prepared using TiO₂ in varying ratios from 1% up to 40% by weight. Each mix was thoroughly mixed and ground in an agate mortar for 3 h to ensure homogeneous distribution of TiO₂ in the BaZrO₃ powder. A few drops of bidistilled water were added to the ground powder as a binder and discs of 1.5 cm diameter and 0.3 cm thick were pressed at 22650 kg cm⁻² in a stainless steel die. The pressed discs were then sintered at 1400°C for 6 h as a soaking period and then allowed to cool to room temperature in 24 h.

Identification of the prepared samples

The prepared samples of BaZrO₃ and modified BaZrO₃ having 1, 2, 3, 5, 10, 20, 30 and 40 wt.% TiO₂ were analysed spectroscopically using a Carl Zeiss d.c. arc spectrograph and by X-ray diffraction using a Philips X-ray diffractometer with CuK_α radiation.

Electrical conductivity measurements

Several specimens of each composition were polished and painted on both flat surfaces with silver paste for the purpose of conductivity measurements and also for dielectric measurements. The conductivity was measured by means of a two probe, d.c. method using 300 V under a vacuum of 10⁻³ mm, Hg. An electrometer was used to measure the current and voltage. The temperature dependence of the current in the range 220°C to room temperature was studied a few hours after applying the high voltage. Constancy of current was achieved after 3 h. This period (3 h) was enough to remove any absorption current.

Dielectric constant measurements

For studying the dielectric constant, specimens were placed in the cell. The variation of the dielectric constant as a function of temperature was recorded at intervals of 5°C, using a Tesla BM 4006 capacitance bridge at a constant frequency of 800 Hz s⁻¹ and 3.5 V.

The electrical conductivity and dielectric constant measurements were taken three times for each temperature equilibration, to ensure good, repeatable results.

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of electrical conductivity, $\sigma(\text{ohm}^{-1} \text{cm}^{-1})$, as a function of temperature and titania additions.

Plotting values of $\log \sigma$ vs. $1000/T$, a straight line could be obtained at relatively high temperatures. From this relation the activation energy for conduction (eV) was calculated (see Fig. 3) in accordance with the method given previously [2].

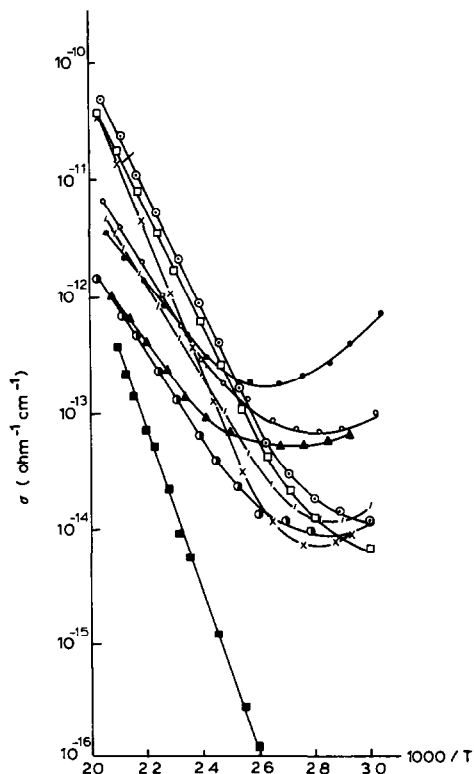


Fig. 1. A schematic representation for the variation of electrical conductivity of $\text{BaZrO}_3\text{-TiO}_2$ as a function of titania additions at various temperatures. ■, 0% TiO_2 ; ▲, 1% TiO_2 ; ●, 2% TiO_2 ; ▲, 3% TiO_2 ; ○, 5% TiO_2 ; ●, 10% TiO_2 ; ×, 20% TiO_2 ; □, 30% TiO_2 ; ○, 40% TiO_2 .

Pure barium zirconate has an electrical resistivity up to 1.03×10^{14} (ohm cm).

Since the materials possess a positive temperature coefficient of electrical conductivity (see Fig. 1), they have semiconducting behaviour in the temperature range investigated. As previously shown from measurements of the Seebeck coefficient [3], the materials have a *p*-type conduction mechanism, the holes being generated by ionization of cation vacancies in the Ba positions. At 3 wt. % TiO_2 , the electrical conductivity increased and the activation energy, ΔE (eV), decreased. At 5–10 wt. % TiO_2 , the electrical conductivity decreases again and the activation energy increases in the same direction. Beyond 10 wt. % TiO_2 , the conductivity falls, reaching a constant value at 20 wt. % TiO_2 . Beyond 20 wt. % TiO_2 a gradual increase in

conductivity values is once again observed with the subsequent decrease in values of the activation energy (see Fig. 3).

It can be seen that the decrease of the activation energy of current carriers

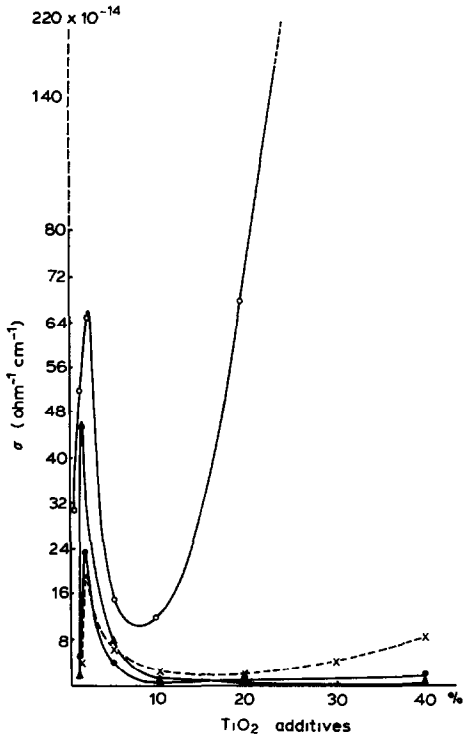


Fig. 2. The variation of the logarithm of electrical conductivity of $\text{BaZrO}_3\text{-TiO}_2$ as a function of titania additions. \blacktriangle , 70°C; \bullet , 90°C; \times , 115°C; \circ , 160°C.

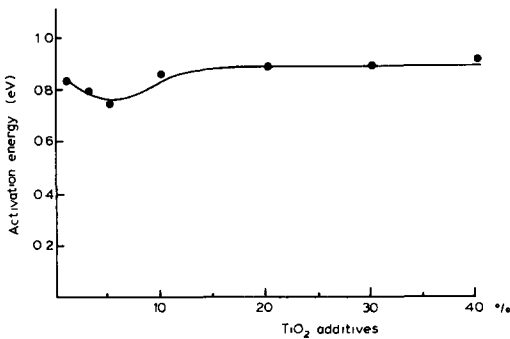


Fig. 3. The behaviour of the activation energy for conduction as a function of titania additions.

below 5 wt. % TiO_2 is accompanied by an increase of the number of current carriers corresponding to the conductivity of the materials. This may be attributed to a grain boundaries effect and/or phase segregation. The fact that the activation energy assumes different values depending on the concentration of defects, created during the preparation of the sample, is in conformity with other semiconducting materials [4].

At low concentrations of TiO_2 , corresponding to high conductivity, the activation energy has a minimum value. This was in agreement with the authors' previous explanation [5], that at these concentrations of TiO_2 , the

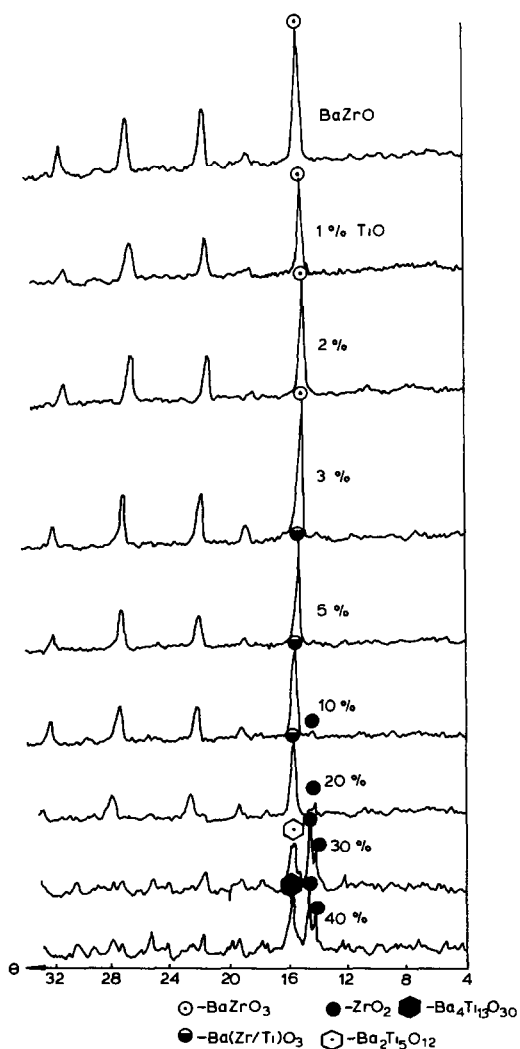


Fig. 4. A diagrammatic representation for the X-ray diffraction patterns of pure BaZrO_3 and BaZrO_3 containing TiO_2 (1–40 wt. %) fired at 1400°C for 6 h.

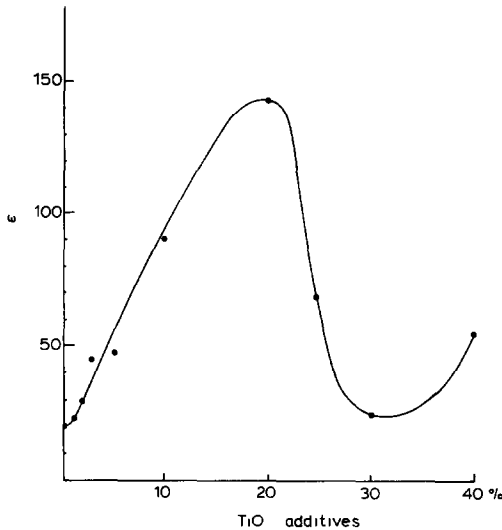


Fig. 5. A diagram showing the variation of the dielectric constant of barium zirconate as a function of titania additions.

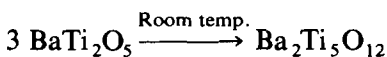
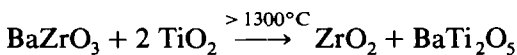
process whereby loosely bound (free) electrons of Ti^{4+} ions may fill up the barium vacancies originally present, must have a small activation energy. This explanation was in accordance with that previously given by Koenig and Jaffe [6].

At 20–40 wt. % TiO_2 (Fig. 3) the activation energy shows a nearly constant value, which was thought to be due to the formation of a solid solution which in turn may lead to formation of a new compound.

The results obtained from X-ray diffractograms and the temperature dependence of the dielectric constant as a function of TiO_2 additions are shown in Figs. 4 and 5, respectively. To explain the observed behaviour, it is important to recall the fact that BaZrO_3 is non-ferroelectric [3]. The introduction of TiO_2 into the lattice of BaZrO_3 must therefore be the factor responsible for the effect represented in Fig. 5.

Megaw [7] pointed out that the polarization of BaTiO_3 is due to the movement of Ti^{4+} ions. For BaZrO_3 , the zirconium ionic radius, 0.87 Å, is larger than the 0.64 Å titanium ion. Thus, the addition of TiO_2 to pure BaZrO_3 contributes to an increase in the dielectric constant as some Ti^{4+} ions distribute themselves on the zirconium sublattice. The dielectric constant reaches a maximum at 20 % TiO_2 , corresponding to the maximum limit for solid solution formation between barium zirconate and titania.

At concentrations of TiO_2 higher than 20 %, a subsequent decrease occurs in the dielectric constant. This is believed to be due to the formation of BaTi_2O_5 [8] according to the reaction



The dielectric constant is lower, based on the mixture of ZrO_2 , $BaTi_2O_5$ and the remaining unreacted component (see Fig. 4). The characteristic X-ray diffraction peaks for pure ZrO_2 appeared at $2\theta = 28.2^\circ$, $d = 3.16 \text{ \AA}$ and $2\theta = 31.3$, $d = 2.94 \text{ \AA}$ [9,10] for the sample containing 30 wt. % TiO_2 , and were similar for the sample containing 40 wt. % TiO_2 .

At 40 wt. % the observed increase in the dielectric constant may be correlated with other compounds richer in titania, such as $BaTi_3O_7$ [11]. This compound formation may take place through lattice imperfection, causing more polarization and hence a high dielectric constant would be obtained.

Therefore, this could be further explained by assuming that Ti^{4+} ions may enter the barium zirconate lattice in three stages. In the first stage, Ti^{4+} ions occupy firstly the positions of interstitial vacancies, thus introducing further free negative charges into the lattice associated with each atom. The occupation of Ti ions in barium vacancies continues until all the barium vacancies are occupied. This substitution is confirmed by the slow, continuous shifts and broadening of the X-ray peaks (see Fig. 4). This was further proved by the increased value of the dielectric constant as more polarization exists (Figs. 5 and 6).

In the second stage, Ti^{4+} ions enter the barium zirconate lattice substitutionally, replacing the Zr^{4+} ion positions forming $Ba(Ti, Zr)O_3$
 $BaZrO_3 + TiO_2 \rightarrow Ba(Zr, Ti)O_3$

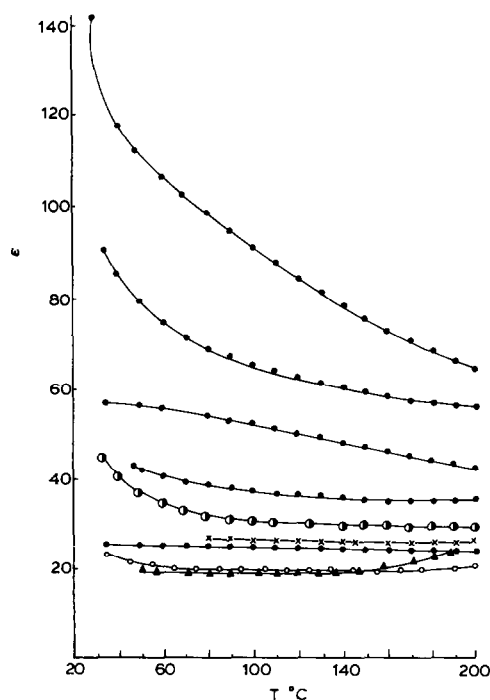


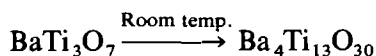
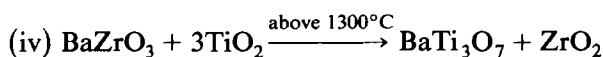
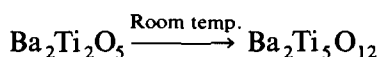
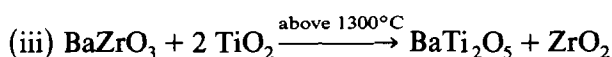
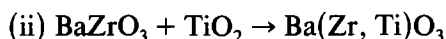
Fig. 6. A representation showing the variation of the dielectric constant for barium zirconate as a function of temperature at various titania additions.

The resultant Ba(Zr, Ti)O₃ solid solution has a high electrical resistivity causing a decrease of the measured electrical conductivity and an increase of the activation energy for conduction. The formation of this solid solution was proved by the appearance of a broad maximum in the curve (Fig. 5), representing the variation of dielectric constant as a function of % TiO₂ additions.

CONCLUSION

Our results of electrical conductivity, activation energy, X-ray diffraction and dielectric measurements were in good conformity and prove that the high temperature solid state reaction mechanism of barium zirconate with titania takes place in four stages. The four stages are given.

(i) At first, Ti⁴⁺ ions may fill up the barium vacancies which were present originally and continue until all vacancies are filled.



In a short time, using up to 20 wt % TiO₂, complete solid solution formation may take place. A mechanism was suggested for the high temperature solid state reaction of the system BaZrO₃-TiO₂.

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