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LOW TEMPERATURE SINTERED ELECTRONIC CERAMIC BODIES FOR INDUSTRY AND ENGINEERING

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ABSTRACT

In the present investigation, several samples of pure barium zirconate and barium zirconate doped with various mol% lithia were prepared by the usual ceramic (high-temperature solid-state reaction) and sintering techniques. The preparation was followed by a careful program of X-ray diffraction and spectroscopic analyses. An extensive study has been made of the behavior of the dielectric constant and dielectric loss as a function of temperature, frequency, sintering temperature and mol% lithia dopant. From the results obtained, some selected samples have promising results, confirming their special importance in industry and engineering.

INTRODUCTION

Ceramic capacitors in engineering are manufactured to meet diverse property and service requirements. They often replace expensive mica capacitors. Ceramics with a high dielectric constant play a large role in the manufacture of condensers with a large capacitance and the abilities to withstand high temperatures. In particular, substance ferroelectricity exists in a definite temperature range or below a certain temperature (Curie point) above which paraelectrics take over. In different cases, the Curie point may range from 10 K to several hundred K. Previous studies carried out by Blokhim and Shuvaev [1] on the *L*-emission and *K*-absorption of Zr and *L*-absorption spectra of Ba in $BaZrO_3$ showed that the chemical bond prevailing, which is believed to be responsible for electrical ordering, is substantially covalent. Stetson and Schwartz [2] reported a dielectric constant $\epsilon = 32$ for $BaZrO_3$ at 25°C and frequency 1 Mc s^{-1} for a specimen sintered at 1450°C for 2 h. Koenig and Jaffe [3] reported a value of 40.5 for the dielectric constant of $BaZrO_3$ ceramics. Novoselev et al. [4] gave a value of 20 for the dielectric constant of $BaZrO_3$. They found that after four

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months, the dielectric constant of same material decreases by 9%. It was reported earlier by Novosiltsev and Khodakov [5] that mixing $BaTiO_3$ with $BaZrO_3$ gave a solid solution of very high dielectric constant. In a previous publication [6] the present authors found on mixing titania additives with $BaZrO_3$ the dielectric constant exhibits a pronounced increase with the increase of Ti^{4+} ions until 20 wt.% TiO_2 additives is obtained.

The major goal of the present work is to determine the optimum conditions for synthesizing ceramic insulators which have a high dielectric constant, and are suitable for condensers used at low-to-high frequency as well as at relatively high temperatures.

EXPERIMENTAL

Material synthesis and sample preparation

Barium zirconate ceramic was prepared by intimate mixing of an equimolar ratio of $BaCO_3$ and $ZrO_2(1:1)$ [7] using a high speed magnetic stirrer and bidistilled water for 4 h. The product was dried overnight at 150°C, pulverized in an agate mortar, dried, calcined at 1000°C for 3 h, pulverized, and fired at 1200°C for 4 h. The material thus prepared was subjected to careful X-ray diffraction and spectroscopic analysis to ensure the correct preparation and degree of purity. The prepared $BaZrO_3$ was then dry mixed with Li_2CO_3 (0.5–40 mol%) in order to give Li_2O–$BaZrO_3$ mixtures. Li_2CO_3 is used as a source of fresh active Li_2O. All the starting materials were of pure chemical grade (BDH, 99.82%). The mixtures were pressed into cylindrical pellets, fired for 1/2 h, ground and sintered for 1 h at a suitable temperature program ranging from 1450 to 750°C depending on the amount of lithia added (see Table 1).

The materials thus prepared were subjected to X-ray diffraction and spectroscopic analyses to evaluate the phase formed and the degree of purity. The indications of a well sintered sample are that it seems hard and bright, and there is a disappearance of cracks from its surface. Sintered pure barium zirconate was found to be white in color, whereas sintered samples containing Li_2O have a greenish color which darkens with the increasing molar ratio of Li_2O. The two opposite surfaces of each pellet (disk) were polished and an

TABLE 1

Molar percentages of lithia in barium zirconate and the most suitable sintering temperature (°C)

Mol% Li_2O	0.0	0.5–1.0	2	3	5	10–15	20	30	40
Sintering temp. (°C)	1450	1400	1350	1300	1200	1100	950	850	750

area 0.59 cm in diameter painted with graphite paste, a small enough area to prevent current surface leakage and to achieve a good contact area for the dielectric measurements.

X-ray diffraction measurements

The room temperature X-ray diffraction patterns of pure and lithia-doped barium zirconate samples were conducted using a Seifert horizontal diffractometer, Cu K_α radiation and Ni filter.

Dielectric measurements

The temperature dependence of dielectric constant, ϵ, and dielectric loss, tan δ, were conducted as a function of frequency and mol% of lithia added. The oven used for high temperature measurements was gradually heated (DC voltage) and the readings were taken frequently after 15 min for each temperature equilibration. The insulation between the holder was teflon to insure good insulation and minor current leakage. For measuring the capacitance of the sample and the dielectric loss tangent, the cell leads were connected to a Scherring bridge (Fig. 1). The Scherring bridge [8,9] has the advantage of a greater accuracy in the medium range of frequency as used in

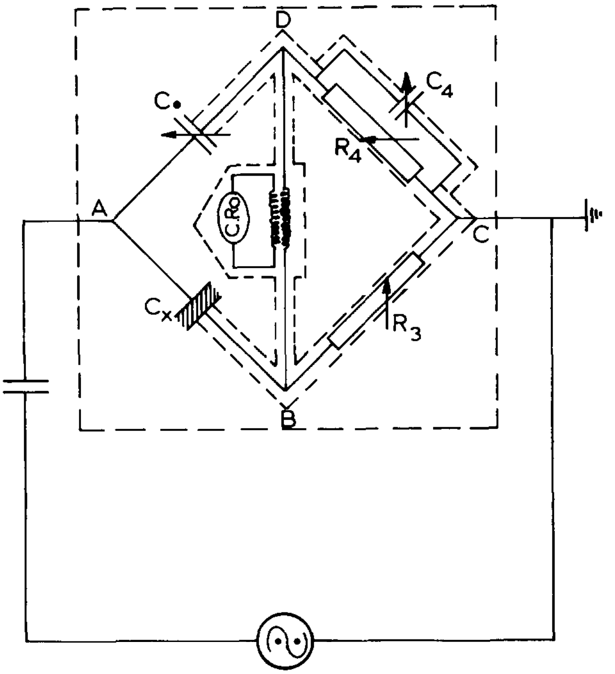

Fig. 1. Schematic diagram of the Scherring bridge used for dielectric measurements.

the present study. The dielectric loss, $\tan \delta$, could be calculated from,

$$\tan \delta = 2\pi f C_4 R_4 \times 10^{-6} \tag{1}$$

where f = frequency of the bridge supply (c s^{-1}), C_4 = reading obtained for capacitance (μF), R_4 = the shunting resistance (ohms). In deriving the above equation, the actual dielectric constant, ϵ, is assumed to be an ideal capacitance connected in parallel with a pure resistance, whereas the capacitance C_x of the specimen is calculated from the equation

$$C_x = C_0 R_4/R_3 \frac{1}{1 + \tan^2 \delta} \tag{2}$$

where C_0 = a fixed capacitor (air capacitor), R = a non-inductive variable resistance.

Values of $\tan^2\delta$ were neglected for $\tan \delta$ values less than 0.1. Therefore, the dielectric constant value is given by

$$\epsilon = \frac{3.6\pi C_x h}{S} \tag{3}$$

where h is the thickness of the specimen, and S is area of the parallel (painted) electrodes. The accuracy equals 0.00001 for capacitance measurements.

RESULTS AND DISCUSSION

Figure 2 shows the room temperature Cu K_α radiation X-ray diffraction patterns of pure barium zirconate and barium zirconate containing 0.5–40 mol% Li_2O. For different values of Bragg's angle, θ, the corresponding interplanar spacings, d, in Å, and the relative intensities of the main diffraction lines are summarized and recorded in Tables 2 and 3, together with the corresponding values given in the ASTM card index for $BaZrO_3$. Comparing the interplanar spacings and relative intensities deduced from the X-ray diffraction pattern as shown in Tables 2 and 3 with those of the ASTM card index, confirms the correct preparation and complete phase formation for $BaZrO_3$. For barium zirconate samples containing a small mol% Li_2O, the X-ray diffraction patterns show a gradual shift in the peak positions towards high θ values or small d spacings as the percentage of lithia increases to 30 mol%. At these percentages, and as a result of the greater affinity of Li_2O to ZrO_2 than BaO to ZrO_2, the high temperature solid-state reaction suggested may proceed as follows

$$BaZrO_3 + Li_2O \rightarrow Li_2ZrO_3 + BaO \tag{4}$$

At Li_2O mol% greater than 30 the excess lithium atoms are believed to occupy positions distributed throughout the barium zirconate lattice. This is explained by the high mobility of the lithium ion which acts as a flux giving

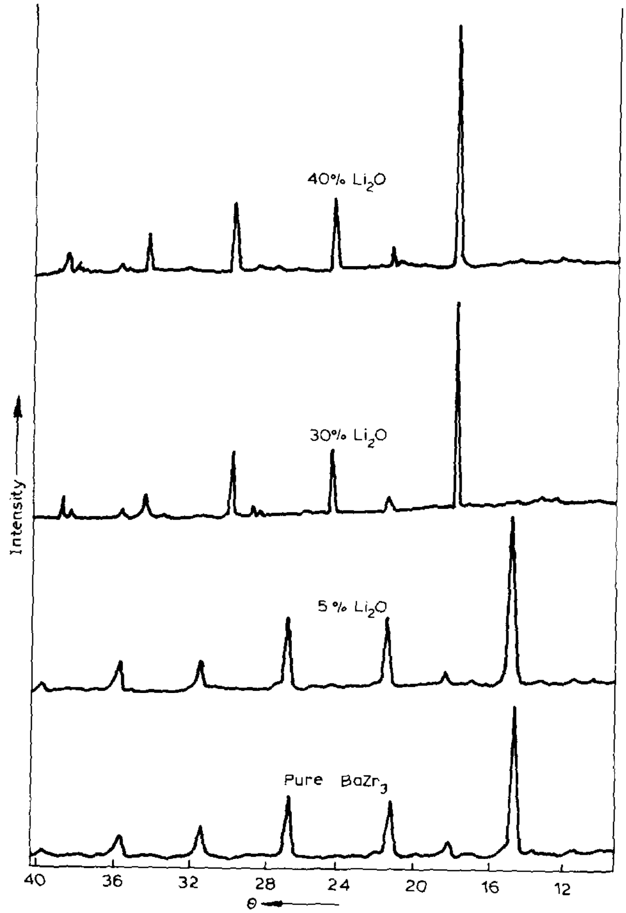

Fig. 2. Cu K_α X-ray diffraction patterns of barium zirconate sample and representative samples of barium zirconate containing lithia additives.

TABLE 2

Interplanar spacings, d, and relative intensities, I/I_0, for barium zirconate

The prepared $BaZrO_3$		ASTM card for $BaZrO_3$	
d (Å)	I/I_0	d (Å)	I/I_0
5.786	4	4.194	10
2.919	100	2.965	100
2.402	10	2.421	9
2.083	38	2.097	34
1.865	2	1.875	2
1.699	43	1.7116	37
1.472	21	1.4824	19
1.318	18	1.3258	17
1.207	4	1.2641	2
1.117	17	1.1206	16
1.038	2	1.0482	3
0.883	10	0.9883	9

TABLE 3

Interplanar spacings, d, and relative intensities, I/I_0, for lithia-doped barium zirconate

$BaZrO_3$ doped by 30 mol% Li_2O		$BaZrO_3$ doped by 40 mol% Li_2O	
d (Å)	I/I_0	d (Å)	I/I_0
2.493	100	2.479	100
2.097	8	2.102	9
1.854	34	1.857	28
1.549	34	1.548	30
1.367	14	1.365	17
1.237	14	1.240	11

rise to a glassy-like phase which acts as a sintering aid enhancing low temperature sintering. The glassy phase formed reflects itself by a rise in the diffractogram background at small θ values. For prolonged heating at each sintering temperature, it was proposed that the lithium zirconate formed exhibits partial decomposition to Li_2O–ZrO_2 solid solution (SS) in accordance with

$$Li_2ZrO_3 \rightarrow Li_2O\text{–}ZrO_2 \text{ (SS, white color)} \qquad (5)$$

This manifests itself in the gradual fading of the green color of the samples with prolonged heating at the sintering temperature and above until they become white again. This indicates that alkali zirconate is metastable and decomposes at these temperatures.

An alternate mechanism was suggested and established that the formation of $Li_2O:ZrO_2$(SS) takes place via lithium zirconate as an intermediate step.

Figures 3 and 4 show the temperature dependence of the dielectric constant of pure $BaZrO_3$, as well as for $BaZrO_3$–Li_2O compositions, at constant bridge supply frequencies of 10 and 50 kc s^{-1}, respectively. The values of the dielectric constant obtained at room temperature are in accordance with those given by earlier authors [2–4] for pure $BaZrO_3$. For $BaZrO_3$ containing lithia additives, the dielectric constant values are much higher than those for pure barium zirconate. This could probably be correlated with the induced polarization as well as solid-solution formation [5].

In general, all compositions are characterized by a slight increase in the dielectric constant with temperature in the range 50–130°C, followed by a larger increase which exhibits itself to a greater or lesser extent for some compositions. However, there is one trend in common, namely an increase in the dielectric constant with temperature rise at both frequencies used (see Figs. 3 and 4). The increase in dielectric constant is much more pronounced for compositions with 0.5 mol% Li_2O in comparison with the pure $BaZrO_3$ sample. $BaZrO_3$, as a paraelectric insulator [3], has a dielectric constant which is nearly stable with temperature (see Fig. 3). In ferroelectric materials, on the other hand, ferroelectricity exists in a definite temperature range

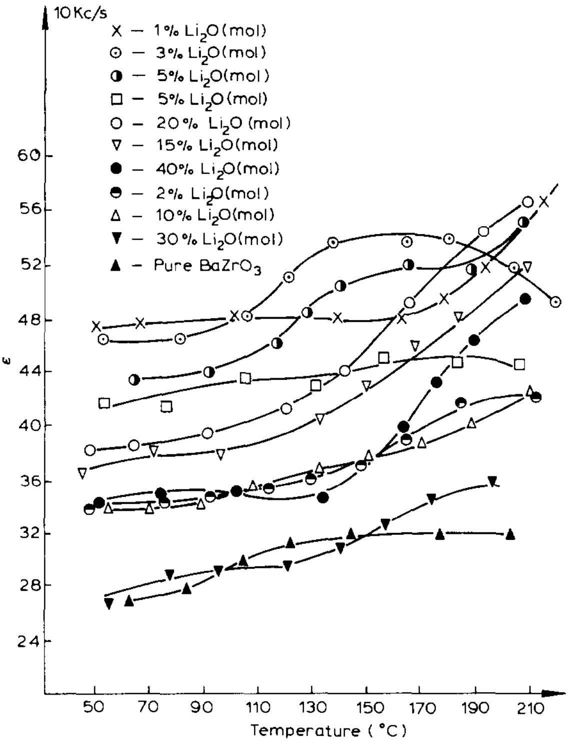

Fig. 3. An illustration of the temperature dependence of the dielectric constant (ϵ) of pure barium zirconate and barium zirconate containing lithia at 10 kc s^{-1}.

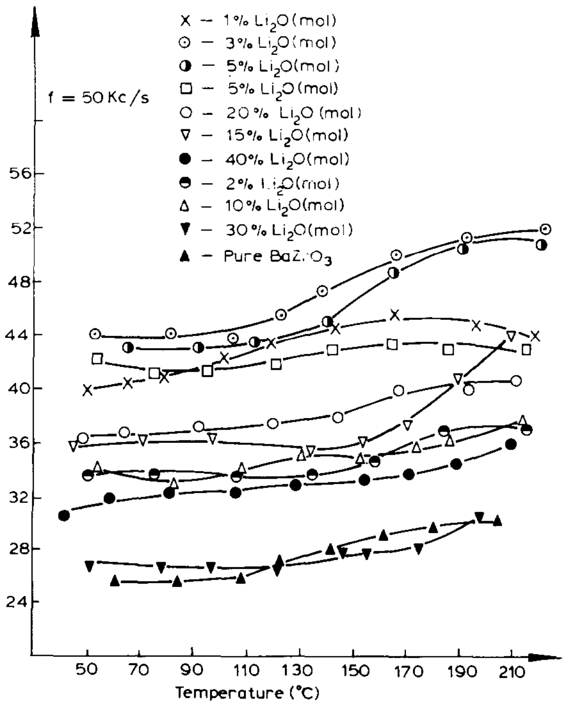

Fig. 4. An illustration of the temperature dependence of the dielectric constant (ϵ) of pure barium zirconate and barium zirconate containing lithia at 50 kc s^{-1}.

or below a certain temperature (the Curie point). In such materials, the dependence of the dielectric constant relation is maximum. Thus, as in Fig. 3, relating ϵ with temperature indicates that ϵ grows to a maximum beyond the range considered in the present investigation. This can be attributed to the fact that increasing Li_2O content in $BaZrO_3$ inverts the ceramic samples from paraelectrics to ferroelectrics in the range of temperature investigated as shown in Figs. 3 and 4.

The temperature dependence of the dielectric loss tangent (tan δ) of $BaZrO_3$ with various mol% Li_2O is graphically represented in Figs. 5 and 6 for the bridge supply frequencies of 10 and 50 kc s^{-1}, respectively. It is evident that the compositions with small Li_2O content (0.5–2 mol%) exhibit a maximum, which, for the same current frequency, shifts towards a higher temperature with an increase in lithia content. This maximum seems to fall off for the lower frequency values. In both Figs. 5 and 6, the behavior of the temperature dependence of dielectric losses for $BaZrO_3$ samples containing Li_2O is more or less constant up to 130°C. This is probably due to solid-solution formation [5] which forms a useful property for industry and engineering. At temperatures higher than 160°C there is a general increase of

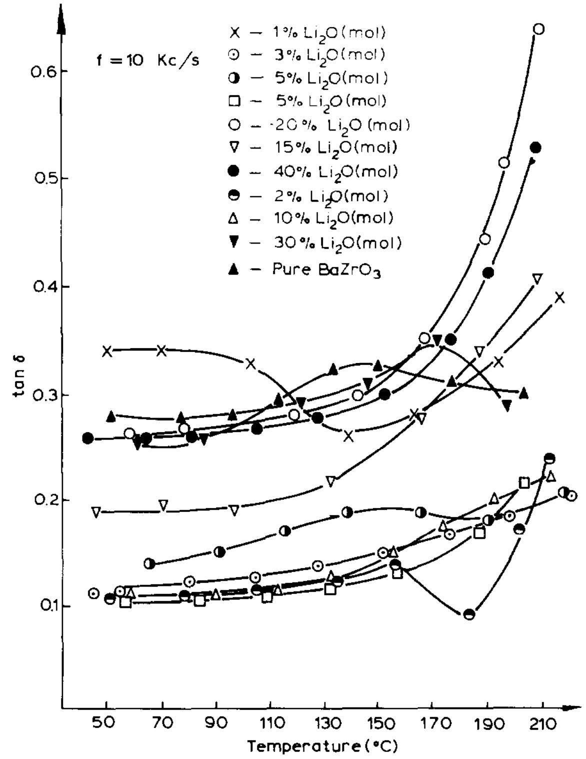

Fig. 5. The temperature dependence of the dielectric loss (tan δ) of pure barium zirconate and barium zirconate containing lithia at 10 kc s^{-1}.

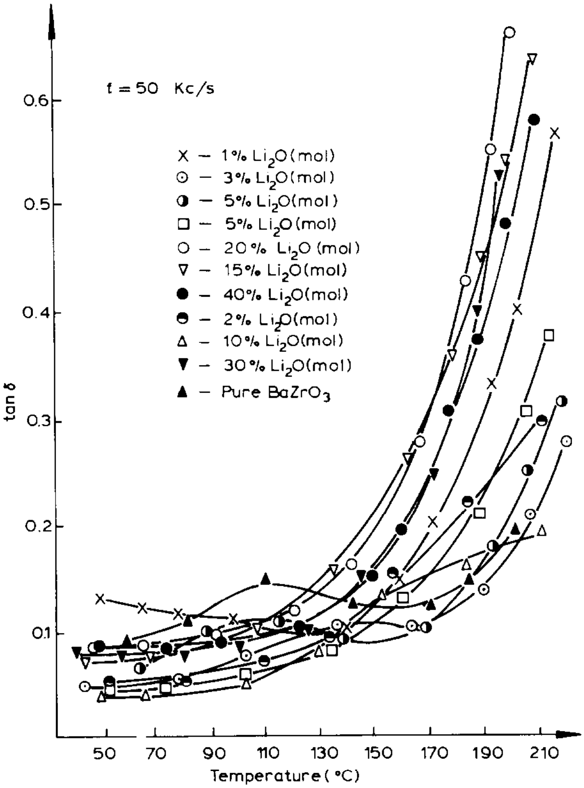

Fig. 6. The temperature dependence of the dielectric losses (tan δ) of pure barium zirconate and barium zirconate containing lithia at 50 kc s^{-1}.

dielectric loss with a rise in temperature for all Li_2O contents and frequencies used.

CONCLUDING REMARKS

From the results and discussion, the following interesting conclusions have arisen.

(1) Solid-state high-temperature interactions between lithia and barium zirconate may lead to the formation of Li_2O–ZrO_2 solid solution which takes place through the formation of lithium zirconate as an intermediate step.

(2) The variation of ϵ for the material investigated as a function of temperature showed that Li_2O additions slightly change the dielectric constant of $BaZrO_3$ in the range 50–130°C followed by a considerable increase at higher temperatures.

(3) The high temperature interaction of lithia with barium zirconate may

induce further permanent polarization elevating the dielectric constant values and giving rise to a constancy for the behavior of the dielectric loss as a function of temperature up to 130°C. These are useful properties for the final applications of materials investigated as ceramic capacitors and transducers.

(4) Dielectric data obtained indicate that some samples of lithia-doped barium zirconate suffer paraelectric → ferroelectric phase transitions. Furthermore, some compositions seem to have a Curie point beyond the investigated temperature range, promising results which are of special importance in industry and engineering.

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