JOURNAL OF MATERIALS SCIENCE 29 (1994) 2691–2696

Grain size effects on the dielectric properties of ferroelectric $Bi_2VO_{5.5}$ ceramics

K. V. R. PRASAD, A. R. RAJU, K. B. R. VARMA
Materials Research Centre, Indian Institute of Science, Bangalore 560012, India

Dielectric properties and microstructural characteristics of ferroelectric bismuth vanadate ($Bi_2VO_{5.5}$) ceramics exhibiting grain sizes of 7, 10, 20 and 25 μm have been studied. Microstructural studies indicate the presence of ferroelectric 90° domain patterns on the surface as well as in the bulk of the coarse-grained ceramics. The dielectric constant and the loss tangent both at room temperature and in the vicinity of the Curie temperature have been found to increase with increasing grain size. The Curie temperature (725 K) is found to shift slightly (by about 7 K) towards higher temperatures as the grain size increases (7–25 μm). The magnitude of the dielectric anomaly around 725 K is found to be higher for coarse-grained ceramics. The dielectric constant and the loss have been found to decrease with increase in frequency (1–100 kHz) for all the ceramics studied. The increase in dielectric constant with increasing grain size is attributed to a decrease in thickness of the relatively more insulating grain boundary layer.

1. Introduction

Bismuth vanadate ($Bi_2VO_{5.5}$) is an interesting ferroelectric compound: it belongs to the $n = 1$ member of the Aurivillius family of oxides with the general formula $Bi_2A_{n-1}B_nO_{3n+3}$. and has relatively low Curie temperature, 710 K [1–3]. Previous studies by the present authors pertaining to the structural, dielectric, pyroelectric and ferroelectric properties of bismuth vanadate confirm the Curie temperature (T_c) to be around 725 K [4, 5]. Borisov *et al.* [2] have indicated that this compound undergoes phase transitions in the region 500–600 K and near 710 and 840 K, based on their dielectric and thermal property studies, and suggested that it goes to an antiferroelectric state at 710 K. Although we have confirmed the high-temperature (840 K) phase transition by differential scanning calorimetric and X-ray studies, we could not establish it by other means, namely by dielectric, pyroelectric and ferroelectric studies, owing to the high conductivities associated with these ceramics above 800 K. High-temperature X-ray powder diffraction studies indicate that $Bi_2VO_{5.5}$ undergoes a phase transition at 725 K from orthorhombic to non-centrosymmetric tetragonal, and subsequently goes to centrosymmetric tetragonal at 840 K [6]. These observations are consistent with those of Abraham *et al.* [7].

In the process of making the above measurements, it was noticed that at 725 K, the values of the dielectric constants and the magnitude of the dielectric anomaly depend on the sintering temperature and the duration of sintering. This observation has prompted the present systematic investigations to visualise the influence of sintering temperature and time, and the corresponding grain size effects, on the dielectric properties of $Bi_2VO_{5.5}$ ceramic. This paper presents the results obtained from dielectric and microstructural studies carried out on $Bi_2VO_{5.5}$ ceramics of various grain sizes (7, 10, 20 and 25 μm).

2. Experimental procedure

Polycrystalline powdered samples of $Bi_2VO_{5.5}$ were prepared by heating a stoichiometric mixture of reactor grade Bi_2O_3 and V_2O_5 up to ~ 770 K initially, and then at 1070 K for about 24 h with intermediate grinding steps. The X-ray powder diffraction pattern obtained for the resulting compound confirmed the formation of $Bi_2VO_{5.5}$ [4]. Pellets of diameter 10 mm and thickness 1.5 mm were made by pressing the prereacted powders at room temperature and sintering them at 1070 K for various durations (16, 24, 36 and 52 h). Sintered pellets were ground, polished and etched with dilute HNO_3 (1:4). The microstructural studies were carried out using a Cambridge S360 scanning electron microscope. Quantitative elemental analysis has been carried out using LINK AN 10000 energy-dispersive spectroscopy (EDX) by employing ZAF-4 software. Gold electrodes were deposited on either side of the polished discs for making capacitance measurements. The dielectric constants were evaluated by taking the capacitance measurements as a function of both temperature (300–760 K) and frequency (1–100 kHz) with a signal strength of 0.1 V r.m.s using a Hewlett Packard multifrequency LCR meter model 4274 A.

3. Results and discussion

Scanning electron micrographs of etched ceramics of $Bi_2VO_{5.5}$ sintered at 1070 K for various durations

0022-2461

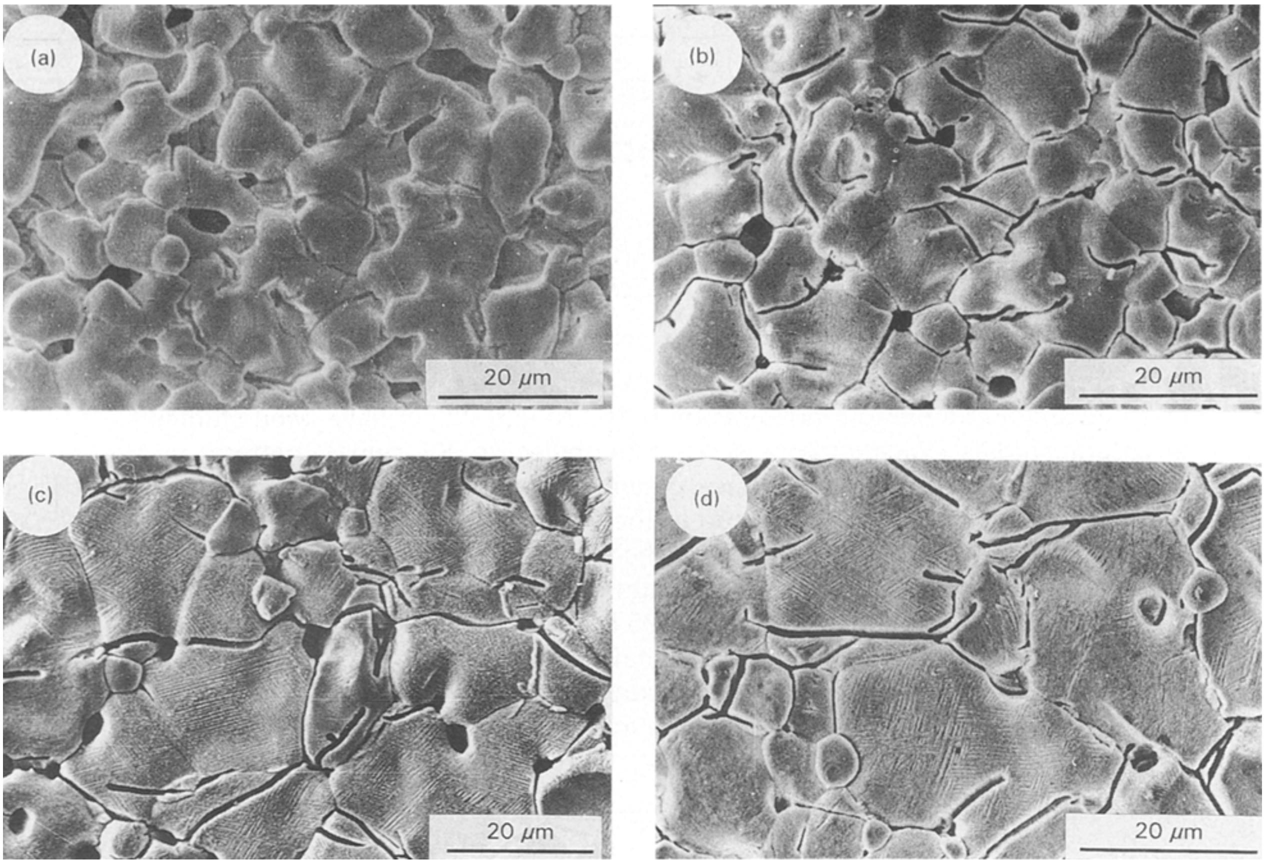

Figure 1 Scanning electron micrographs of etched ceramics of $Bi_2VO_{5.5}$ sintered at 1070 K for various durations (a) 16, (b) 24, (c) 36 and (d) 52 h.

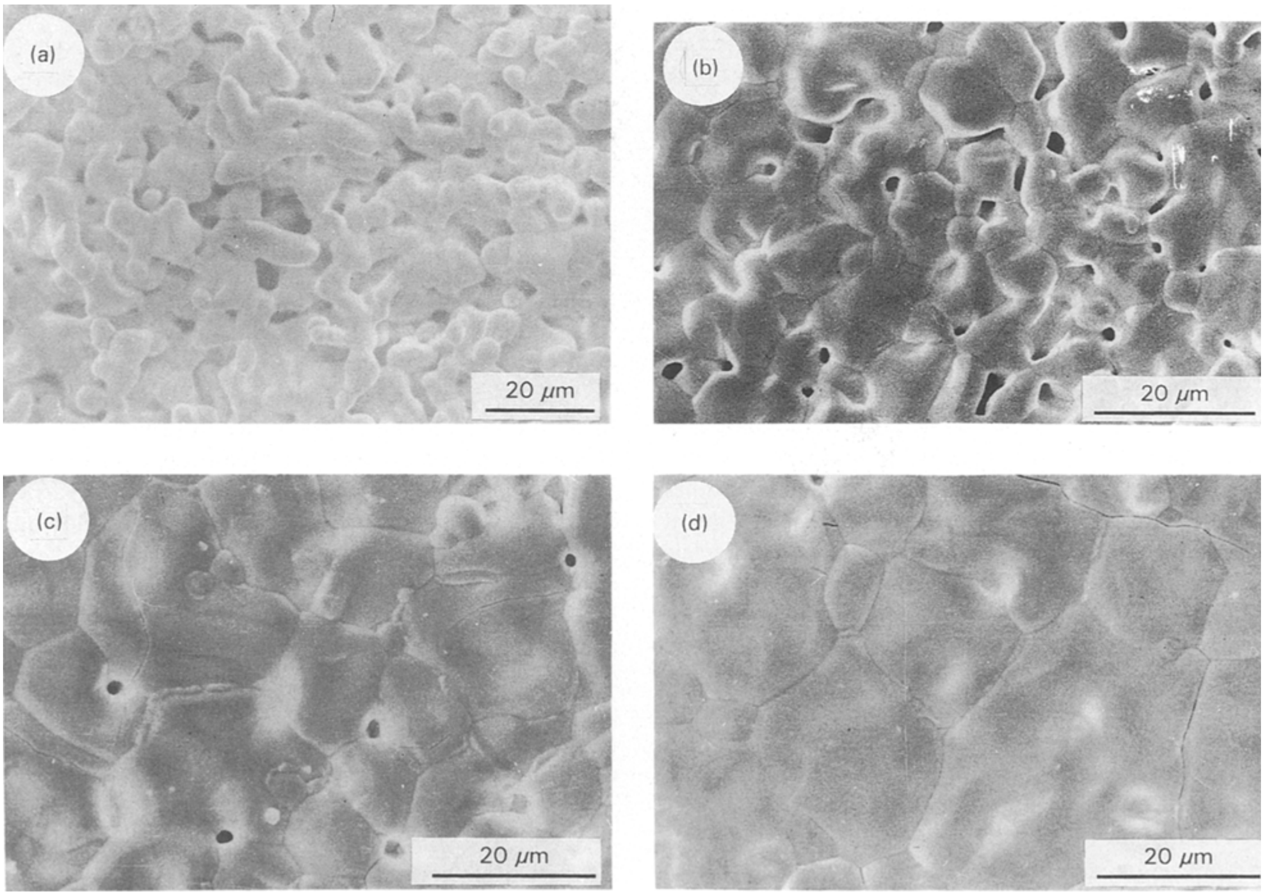

Figure 2 Scanning electron micrographs of unetched ceramics of $Bi_2VO_{5.5}$ sintered at 1070 K for (a) 16, (b) 24, (c) 36 and (d) 52 h.

(16, 24, 36 and 52 h) are shown in Fig. 1, and those obtained for unetched ceramics are shown in Fig. 2. It is clear from these figures that there is a progressive change in the shape and size of the grains as the sintering time increases. It is evident from Fig. 1 that the size of the grain increases with increasing sintering time. The average grain size has been determined for etched ceramics by the line intercept method. The grain size increases almost linearly with increasing sintering time and almost attains a saturated value of 25 μm (Fig. 3). The grain size does not seem to increase significantly beyond this point. These grains are mostly not six-sided, suggesting that the grain boundary energies are unequal, which implies the existence of intergranular stresses [8]. It is known that the complicated domain patterns form in order to minimize these intergranular stresses. In fact, the electron micrographs shown in Fig. 1b–d reveal banded structures on individual grains. The series of parallel lines could result from an alternation between two positions of the 'c'-axis 90° apart. The fine black-and-white stripes seen on individual grains could be ferroelectric 90° domains. Figs 4a and b show the characteristics of the enlarged versions of the domain patterns observed on particular grains in Figs 1c and d, respectively. The presence of a similar domain pattern in the fractured surface of the 52 h sintered ceramic is depicted in Fig. 4c. These domain patterns have only been observed on etched samples. The domain patterns are not distinctly visible in the samples containing grain sizes of 7 μm and below.

The variation of the dielectric constant with temperature at 100 kHz for various grain sizes is shown in Fig. 5. The dielectric constant is found to increase with increasing temperature in all cases, and is found to increase with increasing grain size not only at room temperature but also at the Curie temperature. The values of the dielectric constants and the loss tangent, along with the density measurements carried out at room temperature, as a function of grain size are given in Table I. The density is found to increase with increasing grain size. It should be noted that all the dielectric constant measurements have been carried out on the ceramics which were of strictly equal dimensions, the only variable parameter being the grain size. It is found that the Curie temperature (725 K) shifts slightly towards high temperature with an increase in grain size, as in the case of $BaTiO_3$ [9]. This has been confirmed independently by differential scanning calorimetric (DSC) studies carried out on ceramics of various grain sizes (Fig. 6). The upward shift in T_c as the grain size increases may be attributed

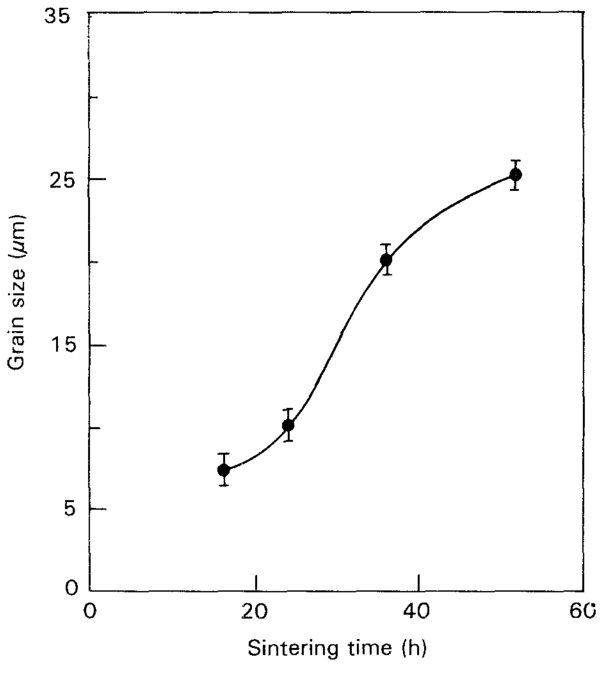

Figure 3 Variation of the average grain size as a function of sintering time at 1070 K for $Bi_2VO_{5.5}$ ceramics.

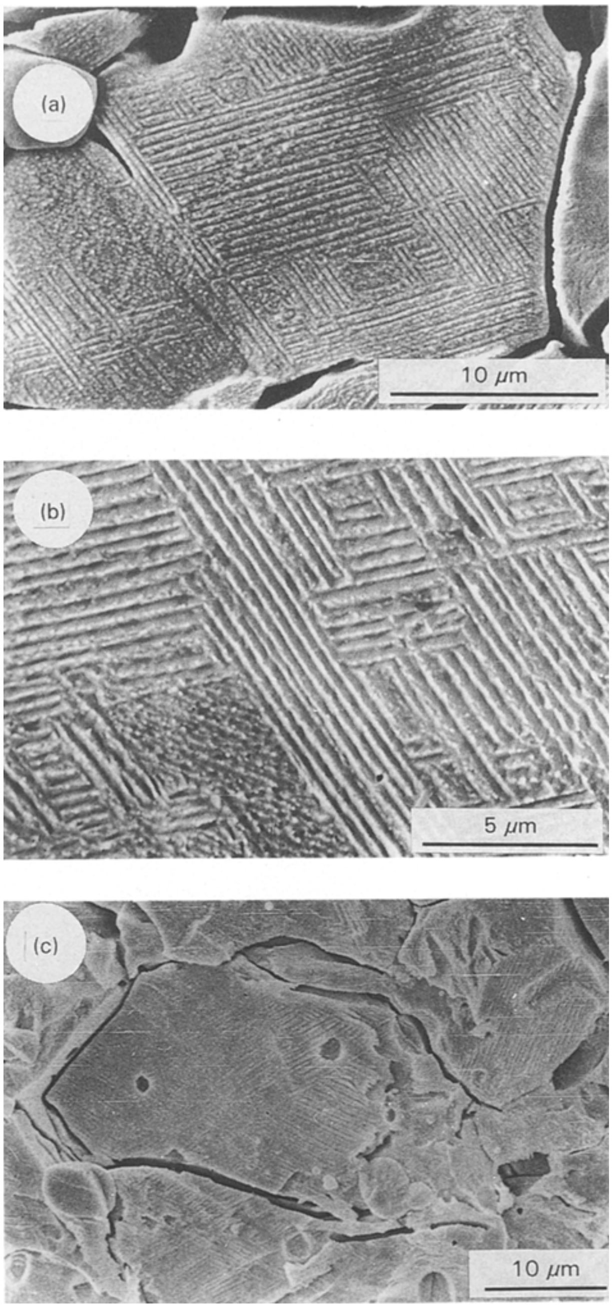

Figure 4 Scanning electron micrographs of enlarged versions of 90° domain patterns observed on individual grains of (a) Fig. 1c and (b) Fig. 1d. (c) Scanning electron micrograph obtained on etched fractured surface of $Bi_2VO_{5.5}$ ceramic sintered for 52 h.

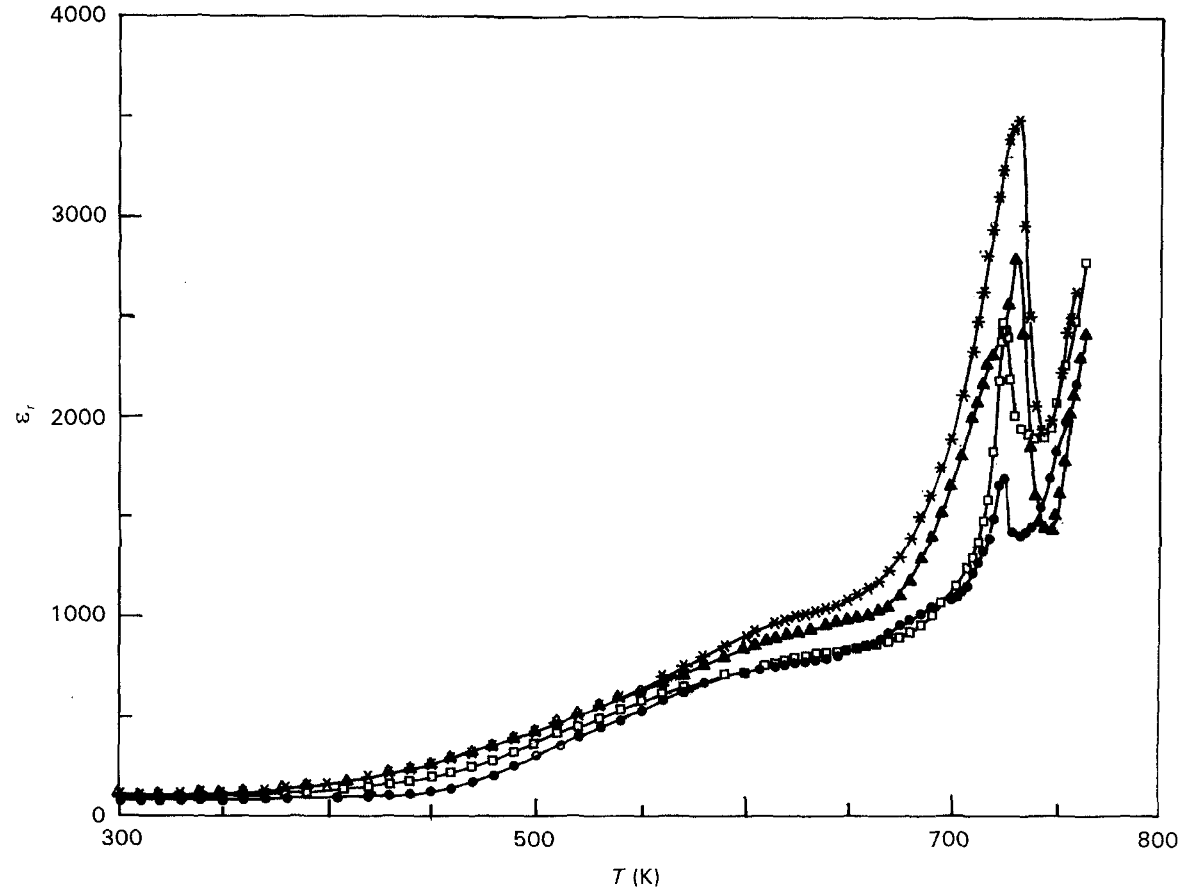

Figure 5 Variation of the dielectric constant as a function of temperature for $Bi_2VO_{5.5}$ ceramics of different grain sizes. ●, 16 h, ~ 7 μm; □, 24 h, ~ 10 μm; ▲, 36 h, ~ 20 μm; ✱, 52 h, ~ 25 μm. $F = 100$ kHz.

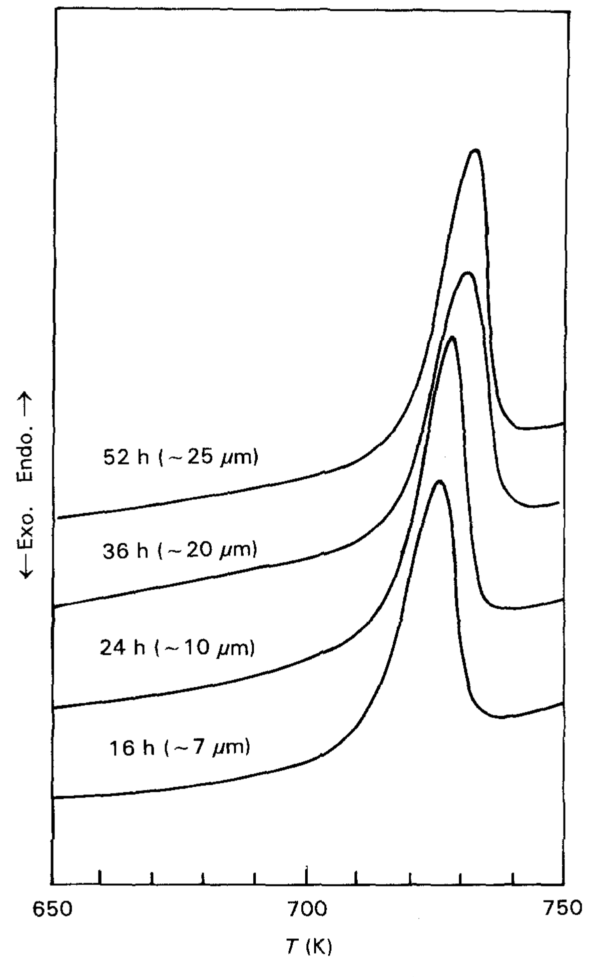

Figure 6 DSC traces of $Bi_2VO_{5.5}$ ceramics of various grain sizes.

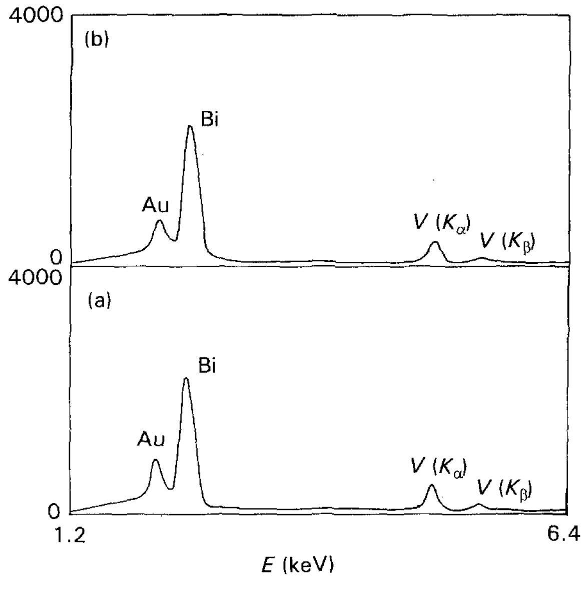

Figure 7 EDAX spectra for (a) grain, Bi:V (66.2:33.8) at %, and (b) grain boundary, Bi:V (71.3:28.7) at %, of the 52 h sintered $Bi_2VO_{5.5}$ ceramic.

to the decrease in internal stresses associated with the ceramics [10, 11]. The increase in dielectric constant with increasing grain size may be explained tentatively as follows. It is assumed that the grains are relatively more conducting as compared to the grain boundary layers; this is supported by experimental observations on the chemical composition of the grain boundary

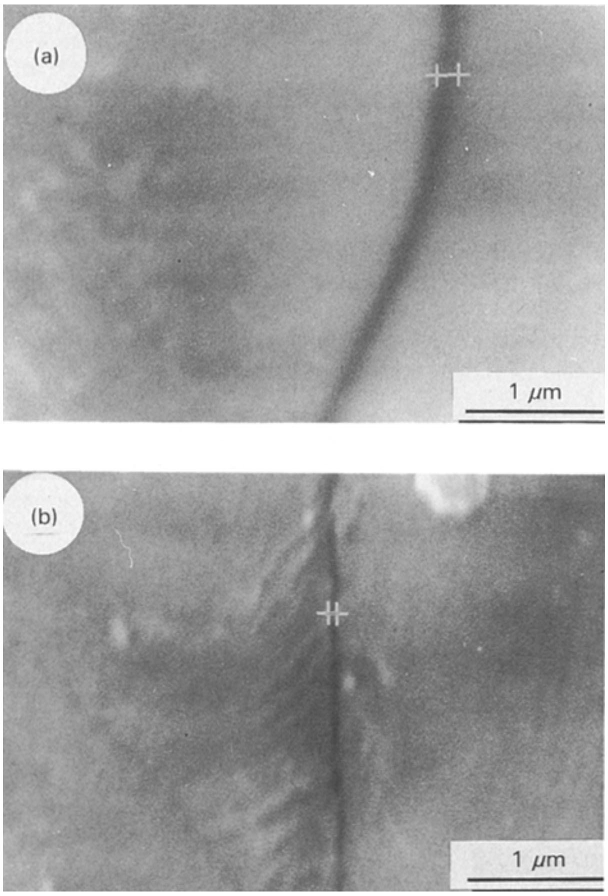

Figure 8 Scanning electron micrographs of the grain boundary of $Bi_2VO_{5.5}$ ceramic sintered at (a) 16 and (b) 52 h.

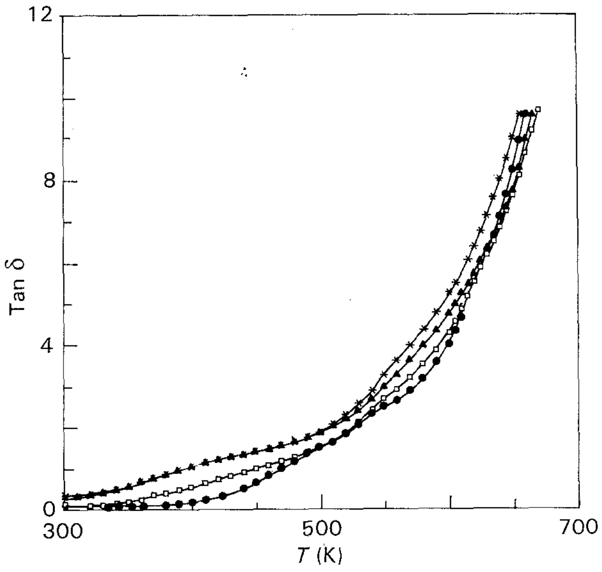

Figure 9 The loss tangent against temperature for various grain sizes of $Bi_2VO_{5.5}$ ceramic. ●, 16 h, ~ 7 μm; □, 24 h, ~ 10 μm; ▲, 36 h, ~ 20 μm; ∗, 52 h, ~ 25 μm. $F = 100$ kHz.

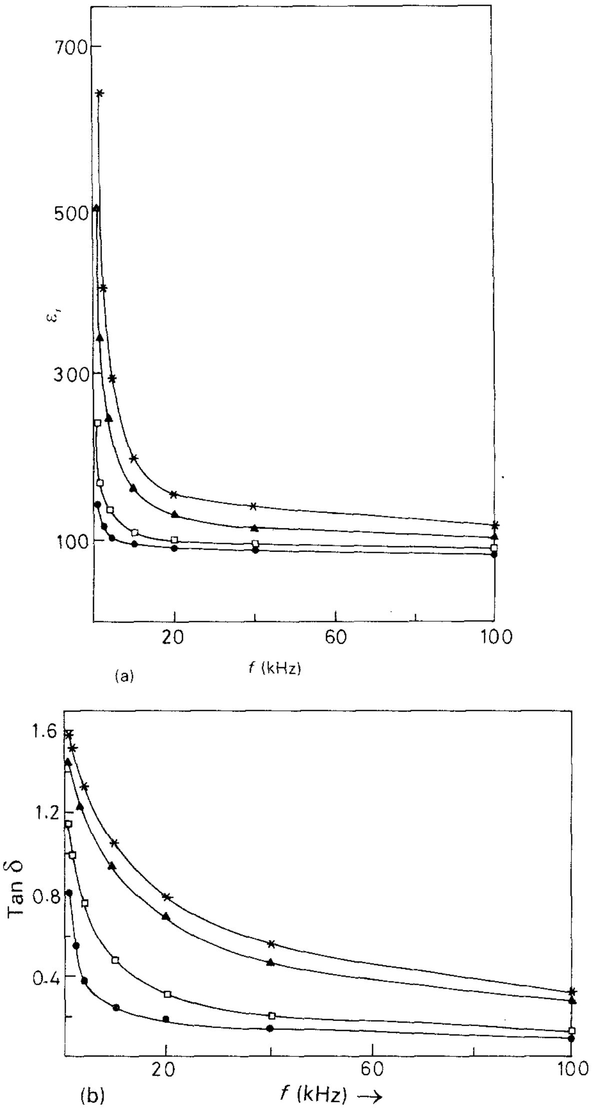

Figure 10 Frequency response of (a) the dielectric constant and (b) tan δ for various grain sizes of $Bi_2VO_{5.5}$ ceramic. ●, 16 h, ~ 7 μm; □, 24 h, ~ 10 μm; ▲, 36 h, ~ 20 μm; ∗, 52 h, ~ 25 μm.

TABLE I Variation of density, ε_r, tan δ and T_c as a function of grain size

Grain size (μm)	Density (gm cm^{-3})	ε_r (100 kHz)	tan δ (100 kHz)	T_c (K)
7	7.130	82	0.09	725
10	7.200	90	0.140	728
20	7.520	102	0.260	730
25	7.700	115	0.320	732

layer using SEM/EDAX studies (Fig. 7). It was found that the grain boundary layer is slightly rich in bismúth when compared to that of the grains. Also, it is noticed that the grain boundary layer thickness decreases as grain size increases (Fig. 8). This implies that the effective capacitance of the sample would increase with increasing grain size. As a result, the overall dielectric constant of the ceramic increases with increasing grain size.

The variation of the loss tangent (tan δ) at 100 kHz as a function of temperature of various grain sizes of the ceramics is shown in Fig. 9. The loss tangent is found to increase with increasing grain size at room temperature; it increases gradually up to about 500 K and thereafter rises sharply. Fig. 10 shows the variation of the dielectric constant and tan δ as a function of frequency for ceramics of different grain sizes. It is evident that both dielectric constant and tan δ decrease with increasing frequency for all the samples studied.

4. Conclusions

The grain size is found to increase (7–25 μm) with increasing sintering time at 1070 K. The presence of ferroelectric domains has been demonstrated on the surface as well as in the bulk of the ceramics. The dielectric constant is found to increase with increasing grain size both at 300 K and in the vicinity of the Curie temperature (725 K). The magnitude of the dielectric anomaly around 725 K is higher for coarse-grained ceramics of $Bi_2VO_{5.5}$. The Curie temperature shifts slightly (about 7 K) towards higher temperatures as the grain size increases. The increase in dielectric constant with increasing grain size is attributed to the decrease in grain boundary layer thickness.

Acknowledgements

The authors thank Professor Vikram Kumar and his group, Physics Department, for providing the experimental facilities to measure the capacitance. One of the authors (K.V.R.P.) is grateful to CSIR, Government of India, for financial support.

References

1. V. G. OSIPYAN, L. M. SAVCHENKO, V. L. ELBAKYAN and P. B. AVAKYAN, *Russ. J. Inorg. Mater.* **23** (1987) 467.
2. V. N. BORISOV, YU. M. POPLAVKO, P. B. AVAKYAN and V. G. OSIPYAN, *Sov. Phys. Solid State* **30** (1988) 904.
3. A. A. BUSH and YU. N. VENEVTSEV, *Russ. J. Inorg. Chem.* **31** (1986) 769.
4. K. B. R. VARMA, G. N. SUBBANNA, T. N. GURU ROW and C. N. R. RAO, *J. Mater. Res.* **5** (1990) 2718.
5. K. V. R. PRASAD and K. B. R. VARMA, *J. Phys. D: Appl. Phys.* **24** (1991) 1858.
6. K. V. R. PRASAD and K. B. R. VARMA, (to be published).
7. F. ABRAHAM, M. F. DEBREUILLE-GRESSE, G. MAIRESSE and G. NOWOGROCKI, *Solid State Ion.* **28–30** (1988) 529.
8. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to Ceramics" (John Wiley, New York, 1976).
9. J. PALETTO, G. GRANGE, R. GOUTTE and L. EYRAUD, *J. Phys. D: Appl. Phys.* **7** (1974) 78.
10. H. T. MARTIRENA and J. C. BURFOOT, *J. Phys. C* **7** (1974) 3182.
11. G. SAMARA, "Advances in High-pressure Research" (Academic Press, New York, 1969).

Received 26 January
and accepted 8 October 1993