DIELECTRIC ANISOTROPY IN PARTIALLY GRAIN-ORIENTED $\text{Bi}_2\text{VO}_{5.5}$ CERAMICS

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Ceramics obtained from quenching melts of prereacted polycrystalline $\text{Bi}_2\text{V}_{5.5}$ exhibit grain orientation ($\sim 55\%$). Microstructural studies carried out using scanning electron microscopy (SEM) on subsequently annealed ceramics show ferroelectric domains. These post-annealed ceramics possess dielectric anisotropies of about 1:1.2 at 300 K and 1:4.3 in the vicinity of the Curie temperature (~ 730 K) between the directions parallel and perpendicular to the quenching direction. The dielectric constants of the samples, obtained by quenching the melts, are higher than that of the post-annealed ceramics. Electrically poled and thermally cycled samples of both as-quenched and post-annealed exhibit ferroelectric hysteresis loops at 300 K.

1. INTRODUCTION

Grain-oriented ceramics of the Aurivillius family of oxides are of considerable interest from the piezoelectric applications point of view [1-4]. The piezoelectric and ferroelectric properties of high density and large degree of grain-oriented ceramics were reported to be close to that of single crystals [5]. Many techniques have been employed to achieve grain-orientation in ceramics of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and related materials [4, 6-9]. These techniques include hot-pressing, hot-forging and hot-rolling, etc. These are, in general, expensive and non-conventional. Holmes [10] has developed dense (92% of theoretical), highly oriented ($> 95\%$) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics using a simple technique that consisted of molten-salt synthesis, tape-casting, followed by conventional sintering. Bismuth vanadate ($\text{Bi}_2\text{VO}_{5.5}$) is reported to be $n = 1$ member of the Aurivillius family of ferroelectric oxides [11-13]. We have been making attempts to prepare fine-grained ceramics of this compound via a glass route and characterize them for various physical properties. In the process, we have encountered with partially grain-oriented ceramics and thought these are worth examining for various physical properties. We report in this paper, the microstructural and dielectric properties of the post-annealed ceramics of $\text{Bi}_2\text{VO}_{5.5}$ obtained by splat-quenching the melts.

2. EXPERIMENT

Partially grain-oriented ceramics of $\text{Bi}_2\text{VO}_{5.5}$ were obtained by splat-quenching the melts. In this technique, a platinum crucible of capacity 100 cc was charged with the prereacted powder of $\text{Bi}_2\text{VO}_{5.5}$. The details about the preparation of the starting polycrystalline $\text{Bi}_2\text{VO}_{5.5}$ powder were given elsewhere [13]. The crucible

containing the charge was transferred to a vertical resistive (SiC) furnace. The temperature of the furnace was raised to 1400 K, which is well above its melting point. The melt was kept at this temperature for about 2 hours. Subsequently, it was poured onto a brass plate and quickly pressed using another brass block. Plates of average area $20 \times 20 \text{ mm}^2$ and 3-4 mm in thickness were obtained. Henceforth, the direction parallel to the thickness is termed as the pressing direction. These plates were post-annealed at 1070 K for 24 hours.

The X-ray powder diffraction studies were carried out on the as-quenched and post annealed ceramics to confirm the existence of $\text{Bi}_2\text{VO}_{5.5}$ phase using a Phillips X-ray diffractometer (PW 1050/70) with a $\text{CuK}\alpha$ radiation. Scanning electron microscopic (SEM) studies were carried out on both as-quenched and post-annealed ceramics using a Cambridge S360 scanning electron microscope. The dielectric constant measurements were carried out on the gold-electroded and subsequently silvered specimens. The capacitance, and the dielectric loss ($\tan \delta$) were monitored as a function of temperature with an HP 4274A multifrequency LCR meter at 100 kHz with a signal strength of 0.5 Vrms. The ferroelectric hysteresis loop studies were carried out at 300 K using a modified Sawyer-Tower circuit with a switching frequency of 50 Hz.

3. RESULTS AND DISCUSSION

The X-ray powder diffraction patterns recorded for the as-quenched, post-annealed and conventionally fired (by solid state reaction route) ceramics are shown in Fig. 1(a-c). It is clear from Fig. 1a that the as-quenched sample is crystalline. It is evident from the diffraction patterns (Fig. 1(a-c)) that the intensities of the (00 l) reflections (*viz.*, (002) and (006)) of as-quenched and post-annealed samples are higher than those of the sample obtained by solid state reaction route. This would imply that most of the grains of the as-quenched ceramics are oriented along the c -direction. However, the intensity of the reflection (020) in Fig. 1b is higher than that of as-quenched and conventionally fired ceramics suggesting that post-annealing promotes the growth of non c -oriented grains as well. The degree of the grain orientation in these ceramics was calculated based on X-ray diffraction patterns (in the 2θ range 10° - 40°), using the X-ray orientation factor method proposed by Lotgering [14].

Lotgering orientation factor, which is a measure of the degree of orientation, is given by

$$f = \frac{(p - p_0)}{(1 - p_0)}$$

Where

$$p = \frac{\sum I_{(00l)}}{\sum I_{(hkl)}}$$

FIGURE 1 X-ray diffraction patterns for (a) as-quenched, (b) post-annealed and (c) conventionally fired $\text{Bi}_2\text{VO}_{5.5}$ ceramics.

for a given oriented ceramic
and

$$p_0 = \frac{\sum I_{(00l)}}{\sum I_{(hkl)}}$$

for a given non-grain oriented ceramic (in the present case as sintered ceramic obtained by conventional solid state reaction route). The orientation factors, f for the as-quenched and post-annealed specimens are found to be 0.55 and 0.53. It suggests that more than 50% of the grains are oriented along the c -direction.

The scanning electron micrographs of unetched as-quenched, post-annealed, and conventionally fired (non-grain oriented) ceramics are shown in Figs. 2a, b and c, respectively. Fig. 2b reveals a rectangular, bar-shaped or lenticular-shaped grain morphology as compared to that of as-quenched sample shown in Fig. 2a. The average grain size as determined by the line intercept method, for post-annealed

FIGURE 2 Scanning electron micrographs of unetched (a) as-quenched, (b) post-annealed and (c) conventionally fired $\text{Bi}_2\text{VO}_{5.5}$ ceramics.

ceramic is about $100\ \mu\text{m}$ in length and $35\ \mu\text{m}$ in diameter. The growth rate of individual grains in the plane normal to the pressing direction appears to be high. Scanning electron micrograph (Fig. 2b) confirms the presence of good orientation, as was concluded by X-ray diffraction studies. The arrays of the crystallites are oriented parallel to the basal facets of the plates. Such a texture appears to be common to all the materials of the Aurivillius family of oxides.

The domain studies were carried out on chemically etched post-annealed ceramics. The scanning electron micrographs (Figs. 3a and b) show complex banded (lamellar)-type domain patterns on individual grains. These domain patterns are identical to those obtained by the solid state reaction route reported earlier [15]. The domain density is found to be very high when compared to the conventionally fired ceramics. The micrographs obtained for the specimens etched

FIGURE 3 Scanning electron micrographs of post-annealed $\text{Bi}_2\text{VO}_{5.5}$ ceramics (a) etched with dilute HCl and (b) etched with dilute HNO_3 revealing complex banded type domain patterns on individual grains.

TABLE 1

The microstructural and dielectric data for grain oriented and non-grain oriented $\text{Bi}_2\text{VO}_{5.5}$ ceramics

	Grain oriented ceramic		Non-grain oriented ceramic
	As-quenched	Post-annealed	
Av. grain size (μm)	~ 1.2	~ 100 in length ~ 35 in dia	~ 14
Density (gm/cm^3)	~ 7.36	~ 7.50	~ 7.30
ϵ_r at 300 K (100kHz)	$\epsilon_{r\parallel} 165$	$\epsilon_{r\parallel} \sim 105$ $\epsilon_{r\perp} \sim 90$	~ 90
ϵ_r at T_c (100kHz)	— —	$\epsilon_{r\parallel} \sim 13,000$ $\epsilon_{r\perp} \sim 3000$	~ 6000
P_r (C/cm^2)	1.04×10^{-8}	4.47×10^{-8}	2.25×10^{-8}
E_c (V/cm)	1066	600	650

with dil. HCl and dil. HNO_3 are shown in Figs. 3a and b, respectively. The nature of the domain pattern for these ceramics seems to be independent of the etchants used.

The apparent density of the specimens was measured by the Archimedian method and the results are tabulated in Table 1. It is evident from Table 1 that the density of the grain oriented ceramic is higher than those of as-quenched and conventionally fired ceramics. It should be noted here that the theoretical density of the $\text{Bi}_2\text{VO}_{5.5}$ is reported to be $\sim 7.814 \text{ gm}/\text{cm}^3$ [12]. The dielectric properties of post-annealed ceramics have been studied parallel ($\epsilon_{r\parallel}$) and perpendicular ($\epsilon_{r\perp}$) to the pressing direction. The room temperature dielectric constants in the direction parallel and perpendicular to the pressing are 105 and 90 respectively, while the dielectric constant of the as-quenched ceramic measured along the pressing direction is 165. Unfortunately, no dielectric constant studies could be conducted perpendicular to the pressing direction on as-quenched samples. In the crystal structure of $\text{Bi}_2\text{VO}_{5.5}$, the perovskite-like layers are parallel to the a and b axes and are separated by the Bi_2O_2 layers along the c -axis. The easy-polarization axis, therefore, lies in the c -plane; thus, the dielectric constant along every direction in c -plane is higher than that along other directions. The results indicated in Fig. 1 suggest that more than 50% of the c -axis-oriented crystallites are arranged parallel to the pressing direction. The temperature variation of the dielectric constant for both the grain oriented ceramic as well as conventionally (solid state synthesis route) fired ceramic is shown in Fig. 4. The dielectric constant measured parallel to the pressing direction is found to be higher than that measured perpendicular to the pressed direction. Also, it is higher than that of a conventionally fired ceramic both at room temperature and in the vicinity of the Curie temperature (730 K). The anisotropy in dielectric constant increases with increasing temperature. At the Curie temperature, the ratio of dielectric constants reaches a maximum value of 1:4.3 ($\epsilon_{r\perp} = 3000$ and $\epsilon_{r\parallel} = 13,000$). The temperature

FIGURE 4 The temperature variation of the dielectric constant for both the grain-oriented (post-annealed) as well as conventionally fired ceramics.

FIGURE 5 The temperature variation of the dielectric loss for both the grain-oriented (post-annealed) as well as conventionally fired ceramics.

variation of the loss tangent ($\tan \delta$) for post-annealed and conventionally fired ceramics is shown in Fig. 5. The loss tangent increases with increase in temperature and rises sharply above 600 K in both the cases. The as-quenched, post-annealed, and conventionally fired ceramics exhibit ferroelectric hysteresis loops at 300 K. The remnant polarisation (P_r) and coercive field (E_c) obtained from the hysteresis loop studies are given in the Table 1. The P_r for post-annealed ceramics is higher than that of as-quenched and coventionally fired samples.

4. SUMMARY

In summary, partially grain oriented ($\sim 55\%$) ceramics of $\text{Bi}_2\text{VO}_{5.5}$ have been prepared by splat-quenching technique. The post-annealed ceramics are found to

exhibit dielectric anisotropy not only at room temperature but also in the vicinity of the Curie temperature. The dielectric anisotropy increases with increasing temperature. Microstructural studies confirm the presence of ferroelectric domains. The dielectric constants of as-quenched ceramics are higher than those of post-annealed ceramics.

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