

Characterization of coprecipitated ferroelectric $\text{Bi}_2\text{VO}_{5.5}$

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Abstract. Fine powders of orthorhombic bismuth vanadate ($\text{Bi}_2\text{VO}_{5.5}$) have been synthesized by coprecipitation method. Powder X-ray diffraction and electron microscopic techniques have been used to characterize these samples. The formation of the monophasic $\text{Bi}_2\text{VO}_{5.5}$ was confirmed. The compacted powders sintered at 1070 K have been characterized for their dielectric properties as a function of both temperature (300–900 K) and frequency (100 Hz–10 MHz) and found to be superior to those obtained by the conventional solid-state reaction route.

Keywords. Bismuth vanadate; coprecipitation; dielectric constant; Curie temperature.

Bismuth vanadate ($\text{Bi}_2\text{VO}_{5.5}$) has been found to be ferroelectric at room temperature. This oxide belongs to the $n = 1$ member of the well-known ferroelectric Aurivillius family of oxides with the general formula $[\text{Bi}_2\text{O}_2]^{2+}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ (Bush and Venevtsev 1986; Osipyan *et al* 1987; Borisov *et al* 1988; Varma *et al* 1990). We have been investigating the structural, dielectric and ferroelectric properties of this material in both polycrystalline (ceramic) and single-crystalline states for some time (Varma *et al* 1990; Prasad and Varma 1991, 1993, 1994). Interestingly, we found that the dielectric properties of $\text{Bi}_2\text{VO}_{5.5}$ ceramic strongly depend on its microstructural features (Prasad *et al* 1994). It is well known that the microstructural characteristics of ferroelectric ceramics do depend on the method by which they are prepared. Therefore, we thought it was worth investigating the dielectric and ferroelectric properties of the title compound synthesized by a different route. In this communication, we report the results concerning with the synthesis and characterization of the ceramic obtained by the coprecipitation route. The present results are compared with those obtained for ceramics prepared by the conventional solid-state reaction route.

Fine powders of bismuth vanadate $\text{Bi}_2\text{VO}_{5.5}$ were obtained by the coprecipitation of bismuth oxycarbonate $(\text{BiO})_2\text{CO}_3$ and ammonium metavanadate (NH_4VO_3) solutions. Initially, the solutions of $(\text{BiO})_2\text{CO}_3$ and NH_4VO_3 were prepared in dilute HCl. The pH of the solutions was optimized to obtain clear solutions. The actual amounts of Bi_2O_3 and V_2O_5 present in $(\text{BiO})_2\text{CO}_3$ and NH_4VO_3 solutions were estimated prior to the final mixing. Then appropriate amounts of $(\text{BiO})_2\text{CO}_3$ and NH_4VO_3 solutions were mixed thoroughly. A few drops of ammonium hydroxide (NH_4OH aq.) were added to the mixture for the precipitation to take place. After completion of the precipitation, the precipitate was washed with distilled water and filtered. The residue was dried at 420 K for 2 h. The dried powder was subjected to the following heat treatment: 670 K for 12 h, 970 K for 12 h, and 1020 K for 12 h, with intermediate grinding operations. The flow chart for the synthesis of $\text{Bi}_2\text{VO}_{5.5}$ powders by the coprecipitation route is shown in figure 1.

The evolution of the required phase through various intermediate products during the process was followed by X-ray powder diffraction studies using a Philips X-ray

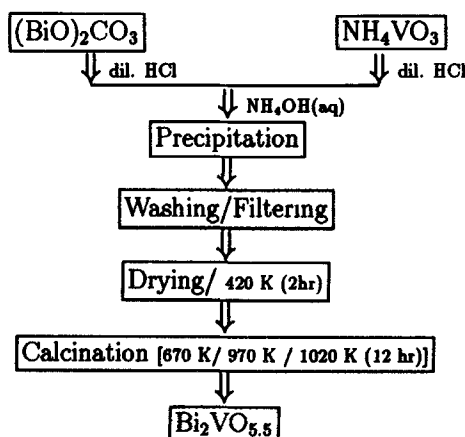


Figure 1. Flow diagram for the synthesis of $\text{Bi}_2\text{VO}_{5.5}$ powders by the coprecipitation method.

diffractometer (PW 1050/70) with Cu K_α radiation. The X-ray diffraction patterns of the powders, heat-treated at different temperatures, 420 K, 670 K, 970 K and 1020 K, are shown in figure 2. The X-ray diffraction pattern for the powder dried at 420 K (figure 2a) exhibits the peaks corresponding to only the BiOCl crystalline phase. It is interesting to note that at this stage there are no peaks corresponding to the vanadium pentoxide (V_2O_5). This would imply that the vanadium-containing compound in the dried powders could be present in an amorphous phase (Bullot *et al* 1984). The powder heated at 670 K showed the presence of BiVO_4 along with BiOCl phase (figure 2b). This observation suggests that part of BiOCl would have reacted with amorphous V_2O_5 to give rise to BiVO_4 phase. On further heating the powder at 970 K the formation of $\text{Bi}_2\text{VO}_{5.5}$ phase apart from BiOCl and BiVO_4 is indicated (figure 2c). The powder pattern obtained for the sample heated at 1020 K (figure 2d) confirms the formation of the monophasic $\text{Bi}_2\text{VO}_{5.5}$ with the cell parameters $a = 3 \times 5.528(1)$, $b = 5.607(1)$ and $c = 15.276(3)$ Å.

For carrying out dielectric studies, the powders of $\text{Bi}_2\text{VO}_{5.5}$ were cold pressed into pellets of 12 mm diameter and 2 mm thickness under a compacting pressure of ~ 500 MPa. The compacted samples were sintered in air at 1070 K for 24 h and then furnace cooled to room temperature. The apparent density of the sintered specimens was measured by Archimedian method. The results of the density measurements along with that of the sample obtained by the solid-state reaction route are given in table 1. The theoretical density of the $\text{Bi}_2\text{VO}_{5.5}$ is reported to be ~ 7.814 g/cm³ (Osipyan *et al* 1987).

Transmission electron microscopic (TEM) studies were carried out using a JEOL 200 CX microscope. The selected area electron diffraction (SAED) pattern obtained along [001] confirms the formation of $\text{Bi}_2\text{VO}_{5.5}$ (figure 3). It is evident from figure 3 that the present sample also exhibits superlattice spots (tripling of the mean cell parameters) along both the directions of the basal plane (a and b) in contrast to the data obtained by X-ray diffraction studies. The occurrence of superlattice spots along

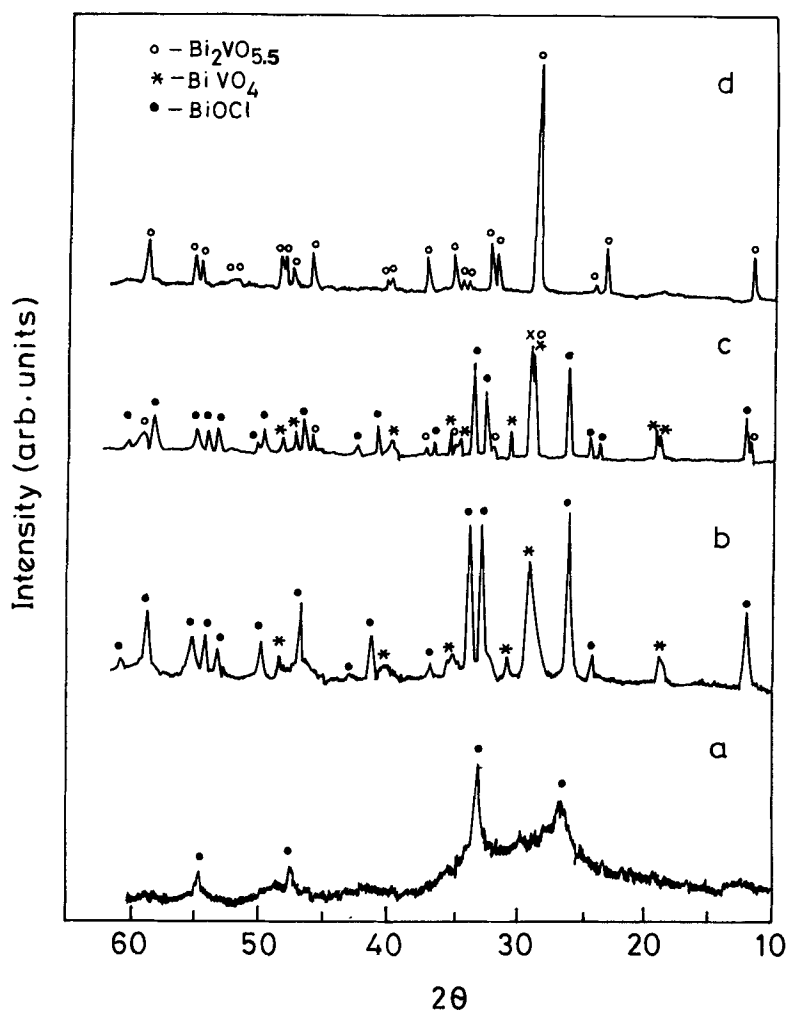


Figure 2. X-ray diffraction patterns of the powders heat treated at different temperatures: (a) 420 K for 2 h, (b) 670 K for 12 h, (c) 970 K for 12 h and (d) 1020 K for 12 h.

Table 1. Microstructural and dielectric data for $\text{Bi}_2\text{VO}_{5.5}$ ceramics obtained by the coprecipitation and solid-state reaction routes.

	Coprecipitation	Solid-state reaction
Av. grain size (μm)	~ 13	~ 14
Density (g/cm^3)	7.50	7.30
T_c (K)	735	728
ϵ_r (100 kHz)	105	90
$\tan \delta$ (100 kHz)	0.260	0.290
ϵ_r , max (at $\sim T_c$)	~ 8800	~ 6000

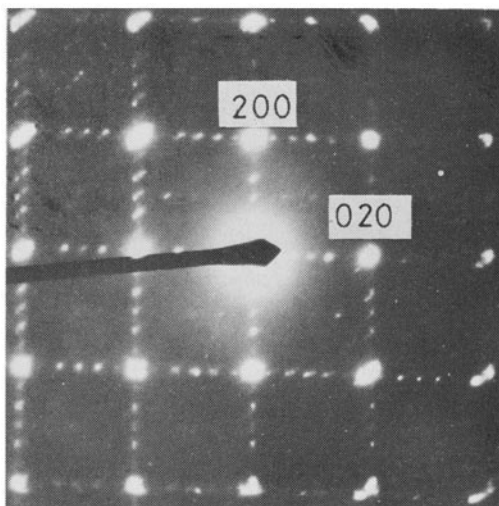


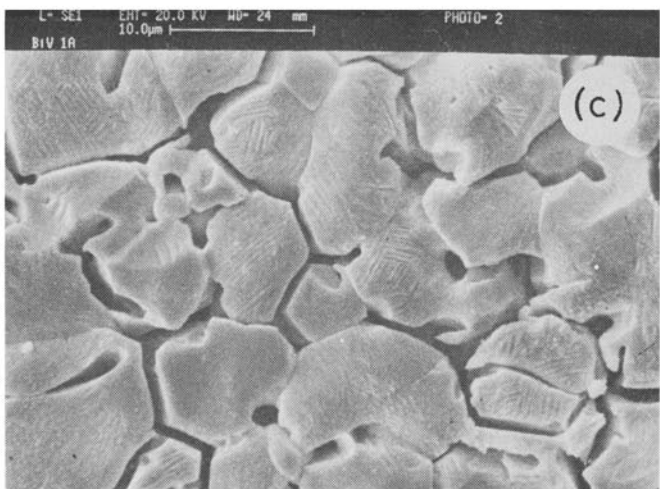
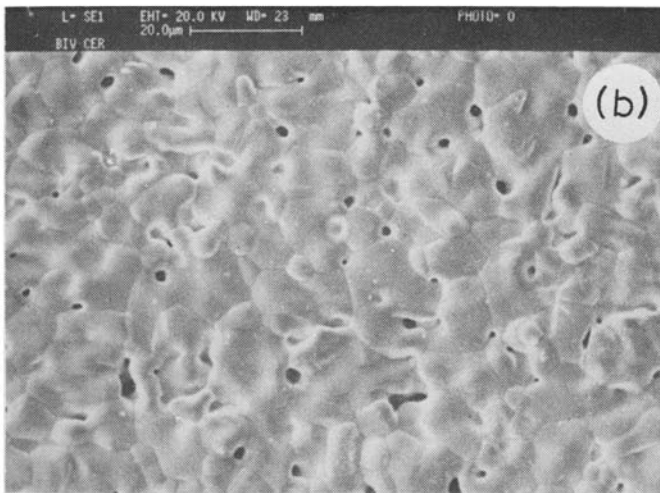
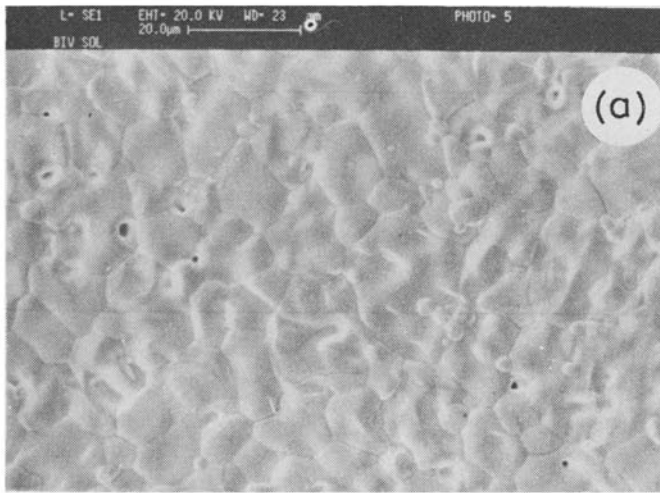
Figure 3. SAED pattern of $\text{Bi}_2\text{VO}_{5.5}$ recorded along $[001]$ indicating superlattice spots in both the directions of the basal plane.

both a and b directions in electron diffraction patterns are attributed to the presence of 90° domains. This observation is consistent with that of the earlier results reported by Varma *et al* (1990). Therefore, it should be noted that the superstructure exhibited by $\text{Bi}_2\text{VO}_{5.5}$ ceramic does not seem to depend on the method of preparation. The origin for the superstructure is attributed to the oxygen vacancy ordering (Varma *et al* 1990).

Scanning electron microscopic (SEM) studies were carried out using a Cambridge S360 scanning electron microscope. Scanning electron micrographs of unetched samples prepared by the coprecipitation and the solid-state reaction routes are shown in figures 4a and b. The average grain size as determined by the line intercept method for the sample prepared by the coprecipitation route is $\sim 13 \mu\text{m}$, and that of the ceramic prepared by the solid-state reaction route is $\sim 14 \mu\text{m}$ though it was sintered under similar conditions. The chemically etched (with dil. HNO_3) ceramic obtained by the coprecipitation route reveals the presence of ferroelectric domain patterns (figure 4c) which are similar to that of ceramics prepared by the conventional solid-state reaction route (Prasad *et al* 1994).

The sintered ceramic samples were gold electroded and subsequently silvered for dielectric constant measurements. The capacitance and the dielectric loss ($\tan \delta$) were monitored as a function of frequency (100 Hz–10 MHz) using a HP 4194A impedance/gain phase analyser at a signal strength of 0.5 V (rms). The temperature response (300–900 K) of the capacitance and the loss tangent was monitored using a HP 4274A multifrequency LCR meter at 100 kHz with the same signal strength. For this purpose, the samples were heated at the rate of 1–1.5 K/min.

Figure 4. Scanning electron micrographs of unetched samples obtained by (a) the coprecipitation and (b) the solid-state reaction routes. (c) Scanning electron micrograph of chemically etched ceramic prepared by the coprecipitation route revealing the ferroelectric domain patterns on individual grains.



The variation of the dielectric constant and the loss tangent as a function of the temperature for $\text{Bi}_2\text{VO}_{5.5}$ ceramic obtained by the coprecipitation route is shown in figure 5. On heating, the dielectric constant ϵ_r increases with increasing temperature and exhibits a broad maximum around 600 K and later shows a sharp maximum at 735 K. Subsequently, it exhibits yet another broad maximum around 840 K. The occurrence of a broad maximum around 600 K could be associated with second-order type of transition. The dielectric anomalies observed around 735 K and around 840 K are consistent with the DSC data, shown in figure 6. The nature of these transitions has already been established earlier in the case of both poly- and single-crystalline samples and reported elsewhere (Prasad and Varma 1993, 1994). The loss tangent increases with increase in temperature and rises sharply beyond 600 K. The frequency

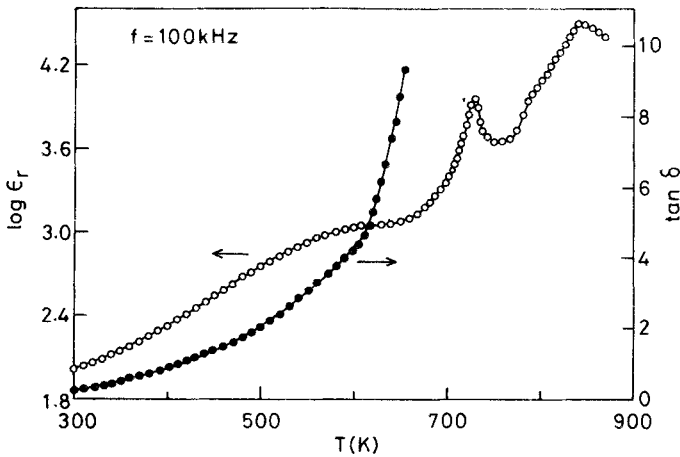


Figure 5. Temperature variation of the dielectric constant (ϵ_r) and the dielectric loss ($\tan \delta$) of $\text{Bi}_2\text{VO}_{5.5}$ ceramic.

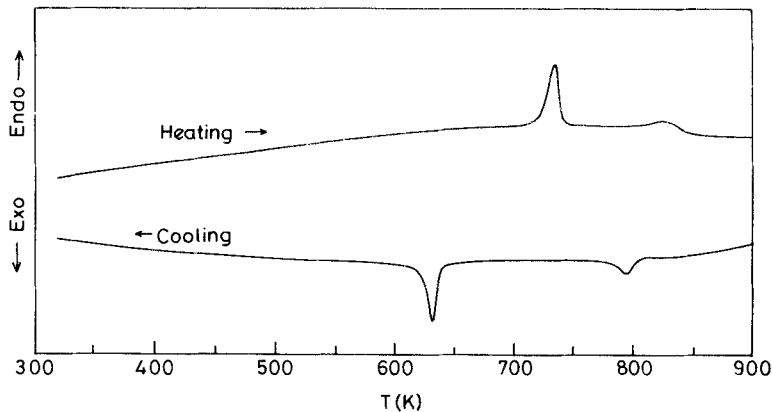


Figure 6. Differential scanning calorimetric curves of $\text{Bi}_2\text{VO}_{5.5}$ ceramic obtained by the coprecipitation route.

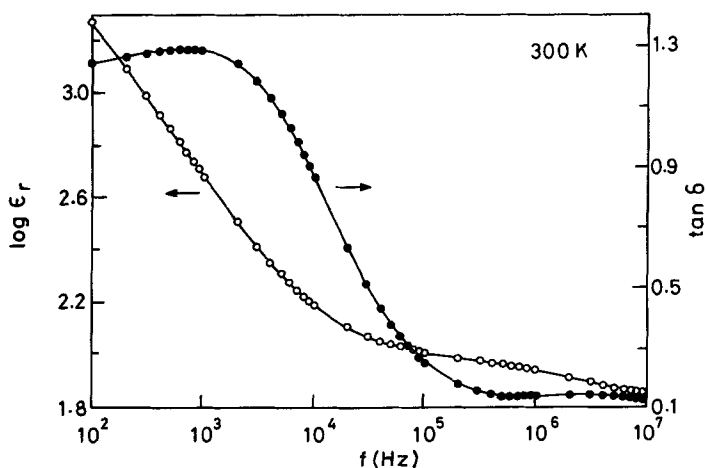


Figure 7. The frequency response of the dielectric constant and the dielectric loss of $\text{Bi}_2\text{VO}_{5.5}$ ceramic at 300 K.

response of the dielectric constant and dielectric loss is shown in figure 7. The dielectric constant at room temperature is found to decrease with increase in frequency till 10 MHz. The dielectric loss increases initially and exhibits a broad maximum around 1 kHz and subsequently decreases up to 5×10^5 Hz.

In order to compare the microstructural (grain size) and physical properties (dielectric) of $\text{Bi}_2\text{VO}_{5.5}$ ceramic obtained by both the coprecipitation and the solid-state reaction routes, they were sintered under the same conditions. The results pertaining to the microstructural and dielectric properties of these ceramics are given in table 1. The dielectric constant of the $\text{Bi}_2\text{VO}_{5.5}$ ceramic obtained by the coprecipitation route is higher both at room temperature and in the vicinity of the Curie temperature (T_c), ~ 735 K, compared to that of the ceramic obtained by the solid-state reaction route. However, the Curie temperature is higher by about ~ 7 K. The high dielectric-constant value for $\text{Bi}_2\text{VO}_{5.5}$ ceramic obtained by the coprecipitation route could be attributed to the high density (less porous) associated with it (figure 4a).

In summary, we have demonstrated the possibility of obtaining a monophasic, relatively dense ferroelectric $\text{Bi}_2\text{VO}_{5.5}$ by adopting a coprecipitation (soft chemistry) route. The present compound also exhibits superlattice spots corresponding to the tripling of the cell along the crystallographic axes a and b . It is noteworthy that the appearance of the superstructure is found to be independent of the method of preparation. The high dielectric constants and relatively low loss associated with the present ceramics could be of some interest from the capacitor applications point of view.

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References

- Borisov V N, Poplavko Yu M, Avakyan P B and Osipyan V G 1988 *Sov. Phys. Solid State* **30** 904
Bulot J, Cordier P, Gallais O, Gauthier M and Livage J 1984 *J. Non-Cryst. Solids* **68** 123
Bush A A and Venetsev Yu N 1986 *Russ. J. Inorg. Chem.* **31** 769
Osipyan V G, Savchenko L M, Elbakyan V L and Avakyan P B 1987 *Inorg. Mater.* **23** 467
Prasad K V R and Varma K B R 1991 *J. Phys. D. Appl. Phys.* **24** 1858
Prasad K V R and Varma K B R 1993 *Mater. Chem. Phys.* (in press)
Prasad K V R and Varma K B R 1994 *J. Mater. Sci.* (in press)
Prasad K V R, Raju A R and Varma K B R 1994 *J. Mater. Sci.* **29**
Varma K B R, Subbanna G N, Guru Row T N and Rao C N R 1990 *J. Mater. Res.* **5** 2718