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RAPID COMMUNICATION

SrB_4O_7:$Bi_2VO_{5.5}$ — A novel nanocomposite

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Abstract. Glass composites of strontium tetraborate, SrB_4O_7 (SBO) with bismuth vanadate, $Bi_2VO_{5.5}$ (BiV) of the composition $(1-x)$ SBO–x BiV ($0 \leqslant x \leqslant 0.75$), have been synthesized. X-ray powder diffraction and electron microscopy indicate as-quenched composites to be amorphous and the annealed samples showed the presence of nanometer sized particles of BiV dispersed in the glassy matrix of SBO. The dielectric constant of these composites increases with increase in the volume fraction of BiV, at 300 K. The measured dielectric constant of the composite very nearly obeys the Maxwell's relationship. Optical transmission studies confirm a steady shift in the optical absorption edge towards longer wavelengths with increase in x.

Keywords. Strontium tetraborate; bismuth vanadate; nanocomposites; dielectric.

Ferroelectric particles dispersed in a glassy dielectric matrix have been known to exhibit electro-optic (Borrelli 1967) and nonlinear optical (NLO) properties such as second harmonic generation (SHG) (Tanaka *et al* 1995). Strontium tetraborate, $SrO \cdot 2B_2O_3$ (SBO) is a recently reported NLO material of the borate series belonging to the orthorhombic crystal system (Oseledchik *et al* 1994). The application of single crystals of this material is restricted because of the absence of phase-matching for SHG for $\lambda < 1.06\,\mu$m. The glass forming capability and the network structure of SBO glass have been reported (Akasaka *et al* 1993) in the literature. Therefore, we thought that it is worth exploring the possibility of exploiting SBO glass as a matrix material for NLO applications (Shankar and Varma 1995). On the other hand, bismuth vanadate, $Bi_2VO_{5.5}$ (BiV) is an interesting ferroelectric belonging to a $n = 1$ member of the Aurivillius family of perovskite oxides (Varma *et al* 1990). The use of BiV for NLO applications in the visible region of the electromagnetic spectrum is restricted because of the fact that its transmission cut-off on the lower wavelength side is 650 nm. Hence it is not possible to utilize BiV for converting 1064 nm radiation into 532 nm. Nevertheless, we believe that it may be a good and efficient NLO material in the IR region, which is yet to be examined. In the present communication, we report the structural and dielectric studies carried out on the composite with the specific composition $0.6(SrB_4O_7) - 0.4(Bi_2VO_{5.5})$, though the samples have been synthesized for x ranging from 0 to 0·75.

Samples, for the present study, were prepared from a mixture of pre-reacted SrB_4O_7 (SBO) and $Bi_2VO_{5.5}$ (BiV) in molar ratios, according to the stoichiometry $(1-x)$ SBO–x BiV. The homogeneous mixture was melted in an electrically heated furnace at 1100°C for 1h and then the melt was poured on a brass plate and was pressed to obtain flat plates. The as-quenched and annealed samples were examined by X-ray powder diffraction (XRD) technique at room temperature using the CuK_α radiation. Electron diffraction and microscopic studies were carried out using a high resolution JEOL 200CX microscope. Differential thermal analysis (DTA) measurements were carried out from room temperature to 900°C at a heating rate of 10°C/min for a chip of the as-quenched sample weighing ≈ 20 mg. The density of the sample was determined by

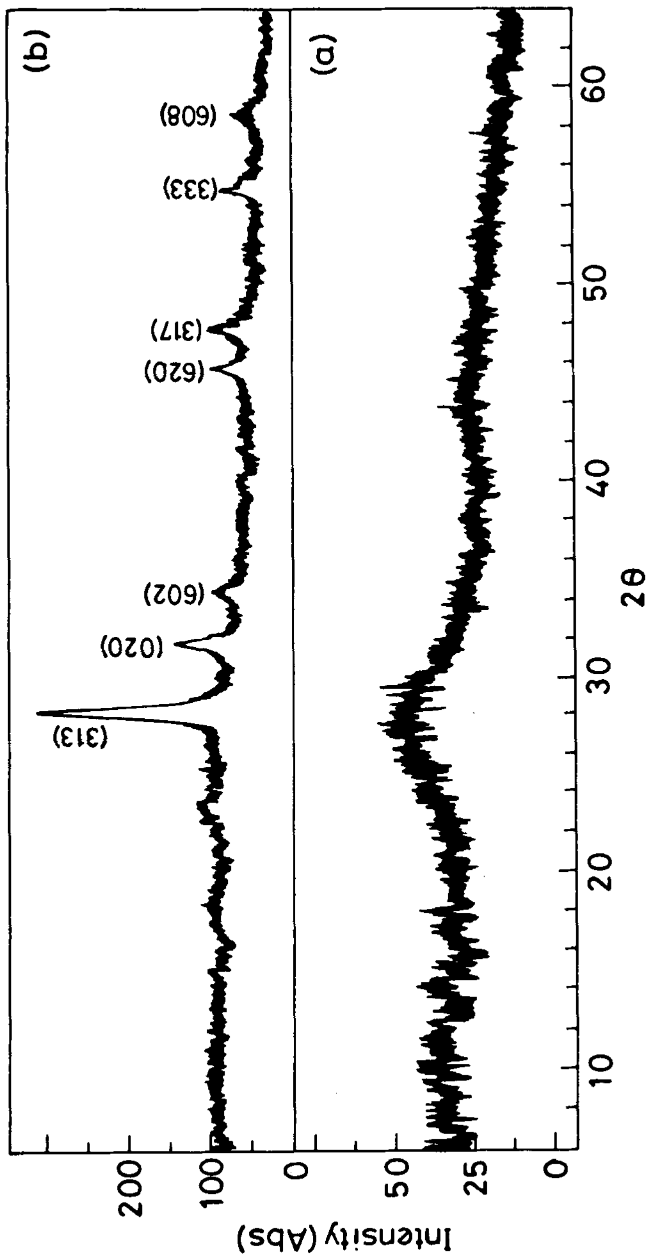

Figure 1. The X-ray diffraction pattern of the 0·60 SBO–0·40 BiV composite (**a**) as-quenched and (**b**) annealed.

the Archimedes method and calculated using the formula:

$$\rho = \frac{a}{(a-b)} \times 0.86,$$

where ρ is the density of the sample, a the weight of the sample in air, b the weight of the sample in xylene and 0·86 is the density of xylene.

The dielectric measurements were performed, in the 100 kHz–10 MHz frequency range, using HP 4194A Impedance/Gain-Phase Analyser. For the purpose of dielectric constant measurements, gold was sputtered on either side of the annealed plates. Subsequently silver epoxy was employed to bond the leads to the samples.

The amorphous nature of the as-quenched sample was confirmed by X-ray powder diffraction studies (figure 1a). X-ray powder diffraction analysis of the glass annealed at 500°C for 12 h shows strong Bragg peaks (figure 1b) corresponding to the crystalline BiV phase with the lattice parameters $a = 16.84$, $b = 5.607$, and $c = 15.3$ Å, suggesting that BiV precipitates out at a temperature well below the T_g (563°C) of the glass. The electron microscopy of the as-quenched sample ($x = 0.4$) showed both SBO and BiV to be amorphous. The BiV particles are finely distributed in the SBO matrix (figure 2a). The high resolution lattice image obtained for the annealed sample of the composition $x = 0.4$ is shown in figure 2b. The fringe spacing, observed in the BiV spherical particle (shown in the inset) is 7·6 Å, corresponding to one-half the value of the c-parameter of bismuth vanadate. This result is consistent with that of the X-ray data.

DTA performed on the as-quenched sample (figure 3) indicates a glass transition temperature (T_g) of 563°C and a crystallization temperature (T_{cr}) of 689°C. The large difference ($\delta T = 126$°C) between T_g and T_{cr} accounts for the thermal stability of the 0·60 SBO–0·40 BiV glasses. Physical property measurements were performed on glasses annealed at 500°C ($< T_g$) for 12 h. The density of the annealed sample was measured to be 4·14 g/cm^3 and the volume fraction of BiV present in the SBO glass was evaluated to be ≈ 0.24 based on the knowledge of the densities of pure SBO glass and polycrystalline BiV.

No evidence for the dispersion of the dielectric constant (ε_r) with frequency (100 kHz–10 MHz) was found; ε_r of the annealed sample of the composition 0·60 SBO–0·40 BiV, measured at a frequency of 100 kHz (12·94) was almost the same (within experimental accuracy) as that measured at 1 MHz (12·75). The measured dielectric constant could be predicted based on Maxwell's model (9), in which spherical particles of the material which has higher dielectric constant (ε_{rd}) are dispersed in a matrix of lower dielectric constant (ε_{rm}):

$$\varepsilon_r = \frac{V_m \varepsilon_{rm}(2/3 + \varepsilon_{rd}/3\varepsilon_{rm}) + V_d \varepsilon_{rd}}{V_m(2/3 + \varepsilon_{rd}/3\varepsilon_{rm}) + V_d},$$

where ε_r is the dielectric constant of the sample, V_m and V_d are the volume fractions of the matrix (SBO) and the dispersed phase (BiV).

The value of ε_r obtained using the above equation is 13·9 for 0·60 SBO–0·40 BiV sample. It is comparable with the experimental value of 12·75 at 1 MHz. This indicates that the sample under study is only a fine physical mixture of BiV and SBO and the polarization mechanism could be of Maxwell–Wagner type. The variation of ε_r with the volume fraction of the BiV phase present in the SBO glass, is shown in figure 4. As expected, the ε_r of the composite increases with increasing BiV volume fraction.

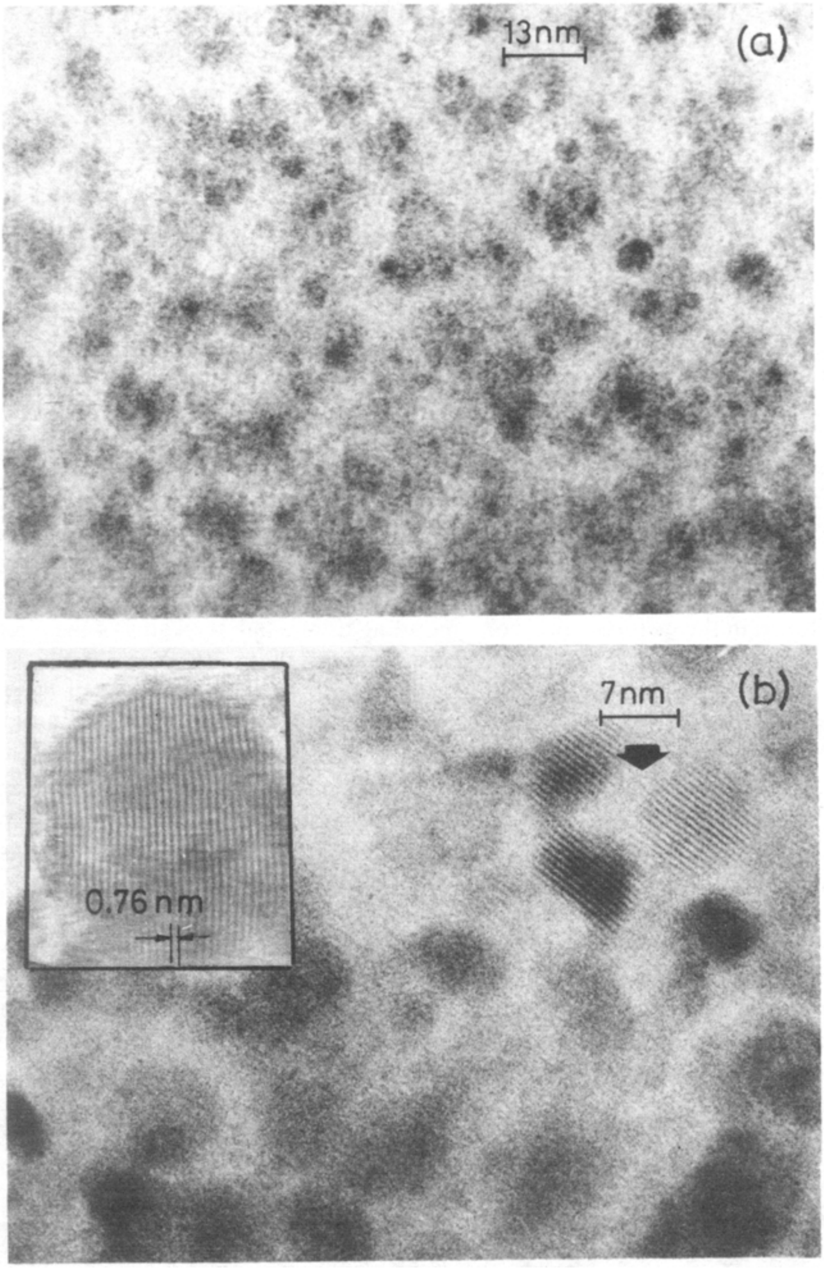

Figure 2. Transmission electron micrograph of the 0·60 SBO–0·40 BiV composite (**a**) as-quenched and (**b**) annealed. The inset shows the lattice image of a single BiV particle.

The transparent SBO glass becomes pale yellow for $x = 0{\cdot}15$ and transforms to reddish grey for $x = 0{\cdot}4$. The optical transmission spectra obtained for the compositions $(1 - x)$ SBO–x BiV ($0 \leqslant x \leqslant 0{\cdot}5$) in the spectral range of 300 nm to 2500 nm is shown in figure 5. The cutoff shifts towards longer wavelength side with increase in x (figure 6).

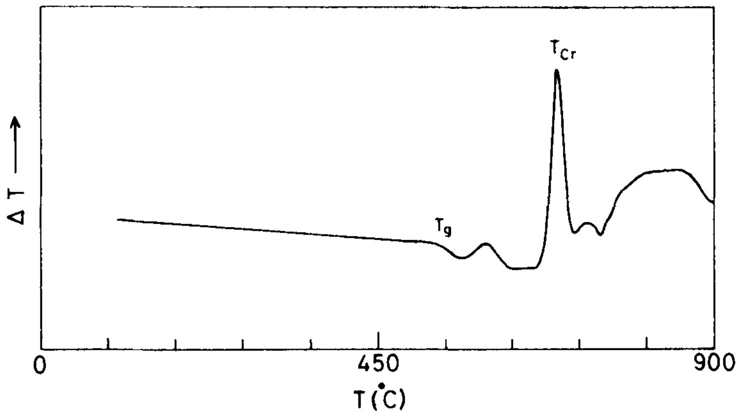

Figure 3. The DTA trace of as-quenched 0·60 SBO–0·40 BiV glass.

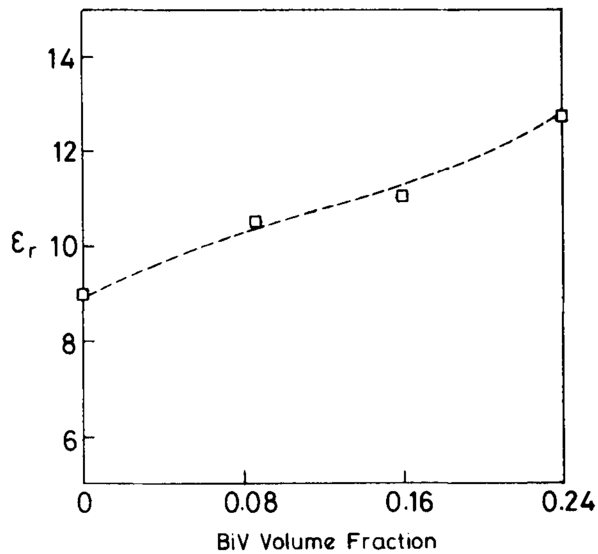

Figure 4. The variation of ε_r with BiV volume fraction, at 1 MHz.

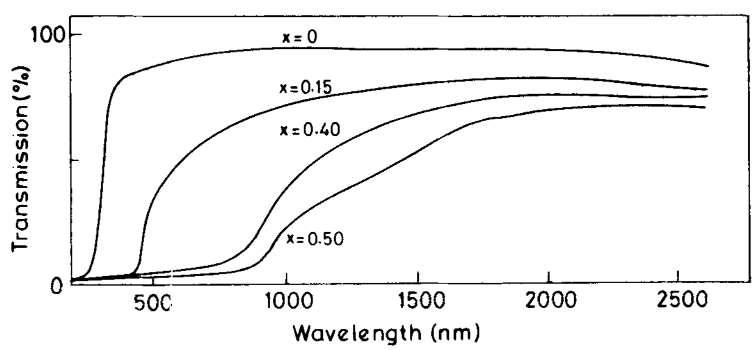

Figure 5. The optical transmission spectra of the $(1-x)$ SBO–x BiV composites for $0 \leqslant x \leqslant 0{\cdot}5$.

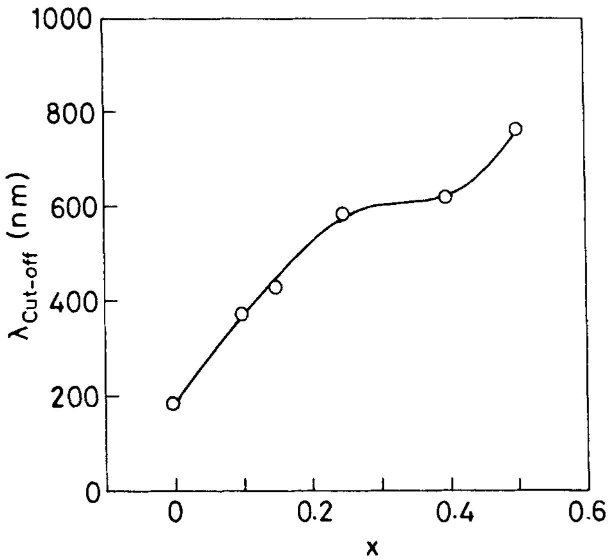

Figure 6. The variation of λ_{cutoff} with BiV concentration (x).

In conclusion, it is demonstrated that it is possible to fabricate transparent and coloured SBO–BiV composites, depending on the concentration of BiV. These composites may be of particular interest from the NLO device applications point of view. In fact, annealed transparent composites with nominal BiV concentration ($x < 0{\cdot}15$) have been found to exhibit second harmonic generation (SHG) of the 1064 nm radiation from a pulsed Nd:YAG laser. Quantitative measurements on these lines are in progress. For composites with higher concentrations of BiV ($x \geqslant 0{\cdot}25$) the SHG signal at 532 nm could not be detected as the λ_{cutoff} for these samples lie around this region and also the pèrcentage of transmission falls below 5. Nevertheless, these composites are worth considering for various applications in which higher ordér NLO processes are involved. These coloured transparent composites may also be used for electro-optic applications in the IR region.

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