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Dielectric and Optical Properties of $Bi_{12}SiO_{20}$ Crystals Doped with Zn and Cd and Co-Doped with P

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Abstract: Single crystals of $Bi_{12}SiO_{20}$ (BSO) Zn- and Cd-doped and co-doped with P were grown by the Czochralski technique and segregation coefficients were determined. The dielectric permeability ϵ and dielectric loss tan δ were measured at room temperature in two frequency ranges: 10^3–10^7 and 10^3–10^5 Hz. Dopants were found to decrease the dielectric permeability in the whole frequency range and P, Zn+P and Cd+P doping increased dielectric loss in the frequency range 10^3–10^5 Hz. Transmission and reflection spectra were taken in the range 0·38–0·85 μm and absorption was calculated. P, Zn+P and Cd+P doping shifted transmission spectra to the shorter wavelengths and drastically reduced the transmission shoulder region as well as the absorption coefficients.

1 INTRODUCTION

BSO crystals are of special interest due to their application as dynamic holographic recording media[1,2] and as spatial light modulator devices.[3–5] The dielectric properties of undoped BSO crystals were studied by Reddy *et al.*[6] and weak dielectric permeability dependence on frequency was established in the 10^3–10^7 Hz range. Al, P and V doping produced crystal bleaching and drastically changed optical absorption.[7] Mn- and Cr-doped specimens exhibited a strong photochromic effect under illumination and altered absorption.[8]

2 EXPERIMENTAL DETAILS

The crystals were grown from a stoichiometric melt by the Czochralski technique in a standard, resistively heated puller. High purity (impurity content below atomic absorption sensitivity) Bi_2O_3, SiO_2, P_2O_5, CdO and ZnO were used for synthesis and doping. Synthesis and growth were carried out in pure Pt crucibles.

To measure dielectric properties, specimens sized 10 × 10 × 0·7 mm were fabricated and Pt electrodes were deposited using cathode sputtering. Dielectric permeability and loss were measured on a P 5083 AC RLC bridge in the range 10^2–10^5 Hz and Hewlett-Packard 4275 A Multi-frequency RLC bridge.

Optical transmission and reflection spectra were measured at room temperature using a Perkin-Elmer 330 spectrophotometer. Absorption α was determined from transmission and reflection data in the range 0·38–0·85 according to the formula[9]

$$\alpha = -\frac{\ln T}{d} - \frac{2R}{d}\left[1 + \frac{R}{2}\left(1 - \frac{T^2}{(1-R)^4}\right)\right]$$

where T is transmission, R reflection and d specimen thickness.

3 RESULTS AND DISCUSSION

Figure 1 shows typical BSO crystals doped with Zn, Cd, Zn+Cd and Cd+P grown under optimal conditions. It was established that optically homogeneous inclusion-free crystals were obtained when the solid–liquid interface was maintained slightly convex to the melt. Dopant segregation coefficients are listed in Table 1. P addition to the melt changed Zn and Cd segregation in the crystals. P segregation coefficient in co-doped crystals was

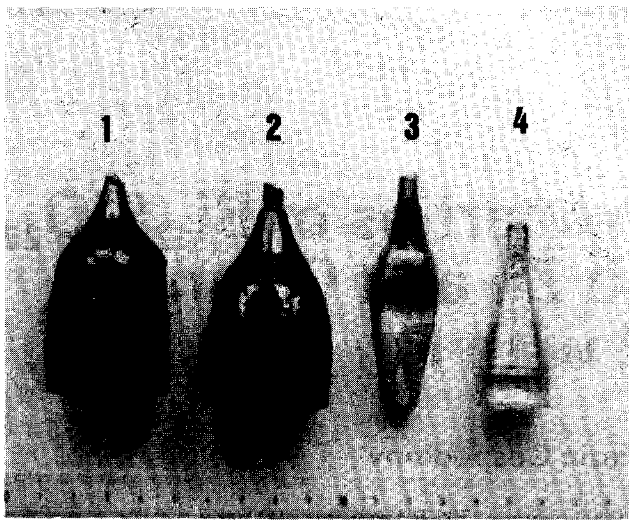

Fig. 1. Four doped BSO crystals: (1) BSO : Cd, (2) BSO : Zn, (3) BSO : Cd+P and (4) BSO : Zn+P.

found lower than established in Ref. 7 and comparable to the value reported in Ref. 10 for the case of BSO co-doped with P and first group transition elements.

Dielectric permeability ϵ frequency dependence at room temperature for undoped and Cd-, Zn- and P-doped crystals is shown in Fig. 2. The frequency dependence of ϵ for Zn+P and Cd+P co-doped crystals coincided with measured data for P-only doped specimens, and for this reason the latter is not shown in Fig. 2. Compared to undoped specimens Zn-, Cd-, P-, Zn+P- and Cd+P-doped material showed lower ϵ values by 12–15% in the frequency range 10^3–10^6 Hz. In the range 10^6–10^7 Hz this difference was less than 5%. Doped crystals exhibited weaker frequency dependence of ϵ than undoped material in the whole range studied.

The higher permeability values in undoped and Zn-, Cd-, P-, Zn+P-, Cd+P-doped crystals at lower frequencies reveal the presence of charged defects, which can be related to space-charge polarization. ϵ relative change is not large in the whole frequency range of consideration, which supports the conclusion that defect density in our BSO material is not high.

Table 1. Melt concentration Y_m and segregation coefficients k in Zn-, Cd- and P-doped and Zn+P- and Cd+P-co-doped BSO crystals

Dopant A	Additional dopant B	Concentration in the melt Y_m (mol %)		Segregation coefficient k	
M_A	M_B	M_A	M_B	M_A	M_B
Cd	—	2·18	—	0·06	—
Cd	P	2·81	3·76	0·06	2·20
Zn	—	6·68	—	0·01	—
Zn	P	6·68	5·47	0·01	2·31

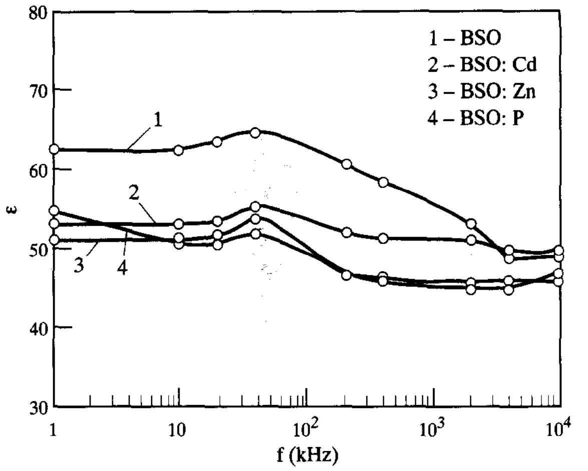

Fig. 2. Frequency dependence of the dielectric permeability: (1) BSO, (2) BSO : Cd, (3) BSO : Zn, (4) BSO : P.

Figure 3 shows the dielectric loss tan δ frequency dependence at room temperature. Zn and Cd doping slightly increased the loss factor as compared to undoped crystals. P impurity ions, which act as donors in BSO, strongly increase the loss factor, thus increasing conductivity. This can be attributed to free carrier generation.

Figure 4 presents optical transmission spectra of both pure and doped BSO. For all crystals the fundamental absorption edge lies at 0·38 μm. Zn and Cd dopants shift transmission to the shorter wavelengths and alter the transmission shoulder shape. Drastic changes are observed with P, Zn+P and Cd+P, where the transmission shoulder is distinguished faintly. Normally, transmission shoulder in $Bi_{12}SiO_{20}$ is related to lattice defects of the type considered by Oberschmid,[7] i.e. a Si vacancy in the SiO_4 tetrahedron. According to Refs 11 and 12 about 10% of the Si sites in the tetrahedral positions are substituted by Bi ions. These tetrahedral Bi atoms produce the transmission shoulder and

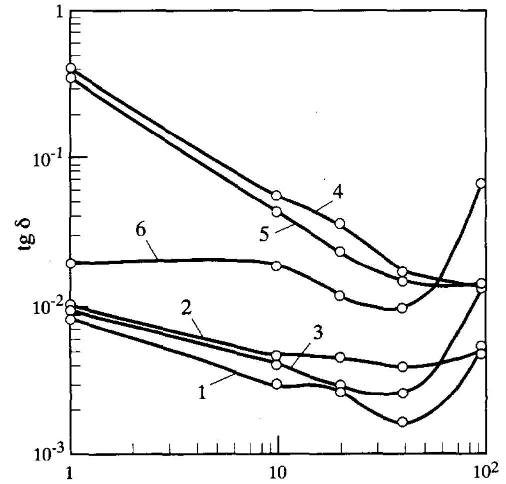

Fig. 3. Dependence of the dielectric loss tan δ on frequency: (1) BSO, (2) BSO : Cd, (3) BSO : Zn, (4) BSO : P, (5) BSO : Cd+P, (6) BSO : Zn+P.

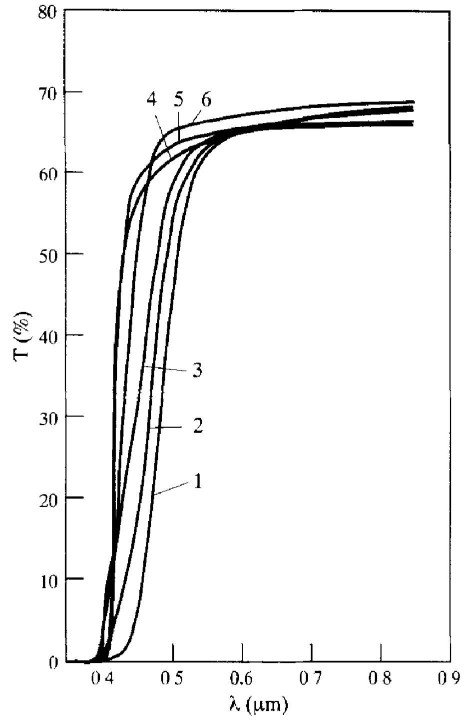

Fig. 4. Transmission spectra of doped BSO crystals: (1) BSO, (2) BSO:Zn, (3) BSO:Cd, (4) BSO:P, (5) BSO:Zn+P, (6) BSO:Cd+P.

hence the yellowish coloration. Zn, Cd and P ions are supposed to partially occupy vacant tetrahedral positions, which causes the bleaching dopant effect.

Zn and Cd dopants alter absorption in the shoulder region only slightly as compared to the undoped material shown in Fig. 5. Marked reduction in absorption in the shoulder region is observed in the case of Zn+P and Cd+P doping. P lattice incorporation is supposed to decrease the density of some types of structural imperfection in BSO.

4 CONCLUSIONS

This paper shows that Zn, Cd, P, Zn+P and Cd+P doping of $Bi_{12}SiO_{20}$ crystals decreases dielectric permeability and increases dielectric loss at room temperature. P doping shifts the optical transmission spectrum to the blue wavelengths and reduces markedly the transmission shoulder and absorption. Reducing absorption in the operable optical range in holographic recording is important as absorption α determines the usable long wavelength boundary. In holographic recording, increasing the operational wavelength enhances the device diffraction efficiency.

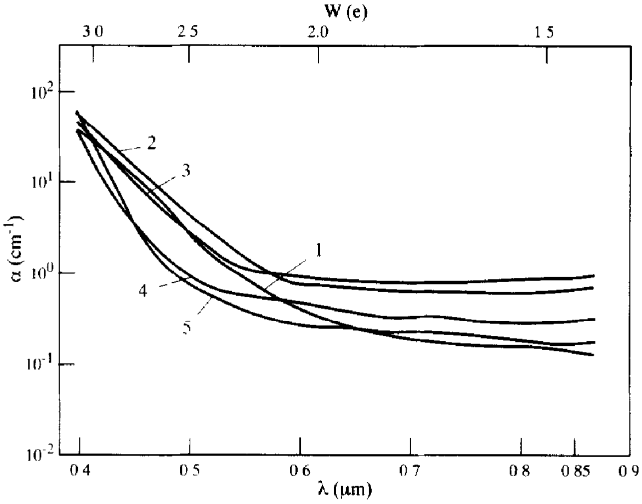

Fig. 5. Dependence of the absorption coefficient on wavelength: (1) BSO, (2) BSO:Zn, (3) BSO:Cd (4) BSO:Zn+P (5) BSO:Cd+P.

The strong increase of electric conductivity in P-doped crystals allows their use as epitaxial substrate material upon which high resistivity undoped BSO can be grown for the fabrication of thin film space–time light modulators.

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