Properties of unconventional lithium bismuthate glasses

S. Hazra,* S. Mandal,† and A. Ghosh
Solid State Physics Department, Indian Association for the Cultivation of Science, Calcutta-700 032, India
(Received 9 May 1997)

Unconventional bismuthate glasses containing lithium oxide have been prepared by a conventional melt-quench technique. X-ray diffraction, scanning electron microscopy, and differential thermal analysis show that stable binary glasses of composition $x\mathrm{Li_2O}$-$(100\text{-}x)\mathrm{Bi_2O_3}$ can be achieved for $x=20-35$ mol %. Systematic variation of the glass-transition temperature, density, and molar volume observed in these glasses indicates no significant structural change with composition. Differential thermal analysis and optical studies show that the strength of the glass network decreases with the increase of $\mathrm{Li_2O}$ content in the glass matrix with a small deviation for the extra stable $30\mathrm{Li_2O}$-$70\mathrm{Bi_2O_3}$ glass composition. Studies of Raman spectra and molar volume ensure that all glasses are built up of $[\mathrm{BiO_6}]$ octahedral units, while the influence of $\mathrm{Li^+}$ ions in the glass matrix is also confirmed from optical, Raman, and electrical studies. Wide transmitting window in the optical region having sharp cutoffs in both ultraviolet-visible and infrared regimes may make these glasses useful in spectral devices. High dielectric values in these glasses compared to glasses formed with conventional glass former can be attributed to the influence of the high polarizability of the unconventional network forming cations, $\mathrm{Bi^{3+}}$. [S0163-1829(97)08937-6]

I. INTRODUCTION

Glasses based on heavy-metal oxides such as $\mathrm{Bi_2O_3}$ have wide applications in the field of glass ceramics, layers for optical and optoelectronic devices, thermal and mechanical sensors, reflecting windows, etc.[1] However, most of the bismuthate glasses studied so far are multicomponent, some of which are the precursor for the high-T_c superconductors.[2,3] The study of binary glasses based on unconventional $\mathrm{Bi_2O_3}$ as a unique network former is scarce,[4,5] because $\mathrm{Bi_2O_3}$ does not form glass by itself. It has been pointed out[6] that bismuth ions are highly polarizable and that cations may exist in the glass network in $[\mathrm{BiO_3}]$ pyramidal units in the presence of conventional glass-forming cations such as $\mathrm{P^{5+}}$, $\mathrm{Si^{4+}}$, $\mathrm{B^{3+}}$, etc. Recent study of bismuth cuprate glasses[5] also shows the glass-forming ability of $\mathrm{Bi^{3+}}$ ions in the presence of transition-metal copper ions. The network of these glasses is also built up of $[\mathrm{BiO_3}]$ pyramidal units, while multicomponent bismuth cuprate glasses are built up of both $[\mathrm{BiO_6}]$ octahedral and $[\mathrm{BiO_3}]$ pyramidal units.[7] The glass-forming ability of $\mathrm{Bi^{3+}}$ ions in the presence of alkali ions is not well studied so far. However, these glasses, if formed, will be useful candidates for spectral devices[6,8,9] and optical switches.[1] Structural and conductivity studies of bismuth cuprate glasses[5,10] reveal that the copper ions occupy the network-forming positions and are unable to diffuse through the host matrix, unlike the alkali ions in most conventional network-modified glasses.[11] The role of alkali ions in the unconventional network system is, however, not known, which will be an interesting aspect for the glass structure.

In this paper, we report the glass formation and the physical properties of the lithium bismuthate system and the role of $\mathrm{Li^+}$ ions in unconventional glass formation.

II. EXPERIMENT

Glassy samples of compositions $x\mathrm{Li_2O}$-$(100\text{-}x)\mathrm{Bi_2O_3}$ ($x=20$, 25, 30, 35 mol %) were prepared using reagent-grade chemicals $\mathrm{Bi_2O_3}$ and $\mathrm{Li_2CO_3}$. The mixtures of these chemicals taken in alumina crucibles were calcined at 450 °C for 2 h and then melted at 900–1000 °C for 30 min in an electric furnace. Glassy samples were obtained by quenching the melts using two copper plates. All samples were transparent and yellow in color and showed hygroscopic nature. X-ray-diffraction patterns of the samples as prepared and heat treated at different temperatures for different durations of time were recorded in an x-ray diffractometer (Seifert, model XRD 3000 P). The scanning electron micrographs of the polished surfaces of the prepared as well as the heat-treated samples were taken in a scanning electron microscope (Hitachi, model S-415A). A thick (~150 Å) gold coating on the polished surface of the sample was done by vacuum evaporation for the conducting layer function before taking the micrographs. The density of the as-prepared samples was measured at room temperature by the liquid displacement method. Differential thermal analysis of the as-prepared samples was performed in an air atmosphere using a thermal analyzer (Shimadzu, model DT-40). Optical spectra of the prepared samples were also recorded at room temperature in a UV-VIS scanning spectrophotometer (Shimadzu, model UV-2101 PC) in the wavelength range 200–800 nm. Infrared spectra of the prepared samples in the bulk form were recorded at room temperature in a spectrophotometer (NICOLET, model MAGNA IR 750, series II) in the wave number range 400–4000 $\mathrm{cm^{-1}}$. Raman spectra were recorded at room temperature in the wave number range 200–1000 $\mathrm{cm^{-1}}$ by a double monochromator (Spex, model 1403) fitted with a holographic grating of 1800 groves/mm and a cooled photomultiplier tube of Hamamatsu Photonics, Japan. The samples were excited by an $\mathrm{Ar^+}$-ion laser (Spectra Physics, model 2020-05) at a power of 250 mW. The scattered light was focused onto the entrance slit of width of 4 $\mathrm{cm^{-1}}$. For electrical measurements, gold electrodes were deposited on both surfaces of the samples. ac conductivity was measured above room temperature using a precision RLC meter

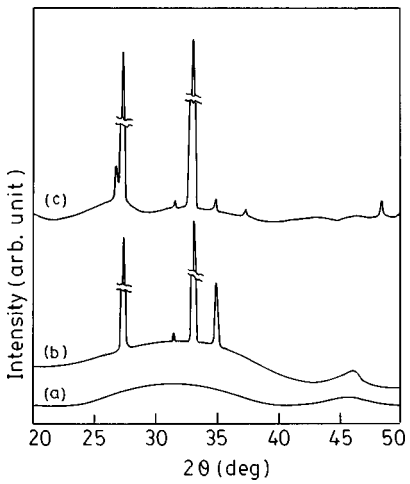

FIG. 1. X-ray-diffraction patterns of different samples: (a) $30Li_2O$-$70Bi_2O_3$ sample as prepared, (b) $30Li_2O$-$70Bi_2O_3$ sample heat treated at 340 °C, and (c) $30Li_2O$-$70Bi_2O_3$ sample heat treated at 400 °C.

(QuadTech, model 7600) in the frequency range 10^2-10^6 Hz.

III. RESULTS AND DISCUSSION

A. Glass formation and thermal analysis

X-ray-diffraction (XRD) patterns of the powdered samples as prepared and heat treated at different temperatures are shown in Fig. 1. A broad diffuse scattering at low angles observed [in curve (a) of Fig. 1] for the as-prepared sample is the indication of long-range structural disorder. The absence of microstructure of the prepared sample observed from a scanning electron micrograph shown in Fig. 2(a) indicates the amorphous and homogeneous nature of the sample. Similar behavior is also observed for other as-prepared samples.

Peaks have been observed [in curves (b) and (c) of Fig. 1] for the glasses heat treated above T_c, which is the indication of the formation of the crystalline phase(s). However, none of the existing crystal structure for different lithium bismuthates,[12] such as $LiBiO_3$, Li_3BiO_4, Li_5BiO_5, Li_7BiO_6, etc., is similar to our heat-treated samples. Also, the heat-treated samples do not resemble any one of the different stable (α and δ) and/or metastable (β and γ) phases of Bi_2O_3,[13] indicating that it crystallizes to some other unknown phase(s). Microstructures observed in the electron micrograph, Fig. 2(b), are due to the crystalline behavior of the heat-treated samples.

Figure 3 shows a differential thermal analysis (DTA) curve for a typical composition. A glass transition temperature (T_g) followed by two crystallization temperatures (T_c) is observed in Fig. 3. The presence of the glass transition temperature as well as the amorphous nature of the samples having compositions xLi_2O-$(100-x)Bi_2O_3$, where $x = 20-35$ mol %, proves the glass-forming ability of the Bi^{3+} (heavy-metal) ions in the presence of Li^+ (alkali) ions. A large difference ($\Delta T \geqslant 45$ °C) between the glass-transition temperature and crystallization temperature is the indication of the stability of the glass. However, the sharp peaks corresponding to crystallization temperatures indicate the fast

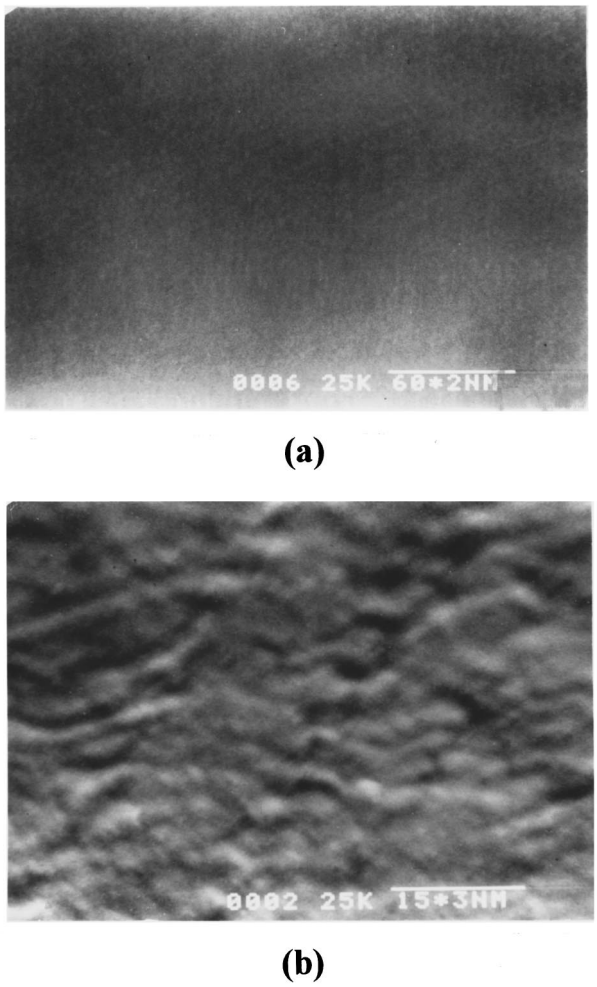

FIG. 2. Scanning electron micrographs of different samples: (a) $30Li_2O$-$70Bi_2O_3$ sample as prepared and (b) $30Li_2O$-$70Bi_2O_3$ sample heat treated at 340 °C.

growth kinetics of the individual phases. The values of T_c, T_g, and ΔT are shown in Table I for all glass compositions. The decrease of glass transition temperature with the increase of Li_2O concentration shown in the inset of Fig. 3

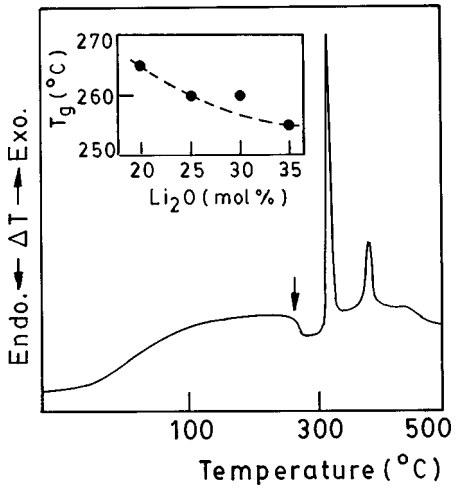

FIG. 3. Differential thermal analysis curve of $30Li_2O$-$70Bi_2O_3$ glass composition. Inset shows the variation of T_g with the Li_2O content in the glass composition.

TABLE I. Different physical parameters obtained from density and DTA curve for the lithium bismuthate glasses.

Glass composition Li_2O (mol %)	Glass composition Bi_2O_3 (mol %)	Density (g cm^{-3})	Molar volume (experimental) (cm^3 mol^{-1})	Molar volume (ideal packing) (cm^3 mol^{-1})	T_g (°C)	T_c (°C)	ΔT (°C)
20	80	8.28	45.74	44.85	265	310, 360	45
25	75	8.14	43.85	42.97	260	315, 370	55
30	70	8.03	41.74	41.10	260	320, 380	60
35	65	7.98	39.26	39.22	255	310, 360	55

ensures the formation of nonbridging oxygen in the glasses, which increases with the increase of Li_2O content. A systematic small variation of glass transition temperature also indicates no significant structural change with composition. However, a small deviation observed in both T_g and ΔT for the $30Li_2O$-$70Bi_2O_3$ glass composition can be attributed to the extra stability of the glass.

B. Density and molar volume

The measured density of the glass samples is shown in Table I. The experimental molar volume of the glasses has been estimated from the molecular weight and density. The corresponding molar volume for ideal close packing is also calculated, simply by summing up the molar volumes of the crystalline Bi_2O_3 (52.36 cm^3) and Li_2O (14.84 cm^3)in the molar ratio. Both of these values have been enlisted in Table I for comparison. The variations of density as well as the molar volume of the glasses, shown in Fig. 4, are small and are consistent with the composition. The monotonic variation of these quantities also indicates no significant change of structural unit with composition. The experimental molar volume and the molar volume for ideal close packing are almost the same, which indicates that the glass structure may be formed by the same $[BiO_6]$ units as that of α-Bi_2O_3.

C. Optical spectra

Figure 5 shows the optical spectrum of a typical glass composition in the ultraviolet-visible (UV-VIS) region. A distinct cutoff has been observed in Fig. 5. Other glass compositions also have the similar behavior. However, the values of the cutoff wavelength (λ_c) for different glass compositions are slightly different and are shown in Table II. The optical band gap (E_{opt}) has been estimated from this cutoff wavelength and is also listed in Table II. The variation of optical band gap with composition is shown in the inset of Fig. 5, which shows that the optical band gap increases slightly with an increase of Li_2O content in the bismuthate glasses with a small deviation for the $30Li_2O$-$70Bi_2O_3$ glass composition. It has been reported earlier[13] that bismuth oxide in the form of thin film shows an optical band gap in the range 2.5–2.6 eV. So it is evident that the introduction of Li^+ ions in the bismuth oxide network increases the optical band gap (Table II). However, the presence of a sharp cutoff in these glasses may make them useful in the spectral devices.

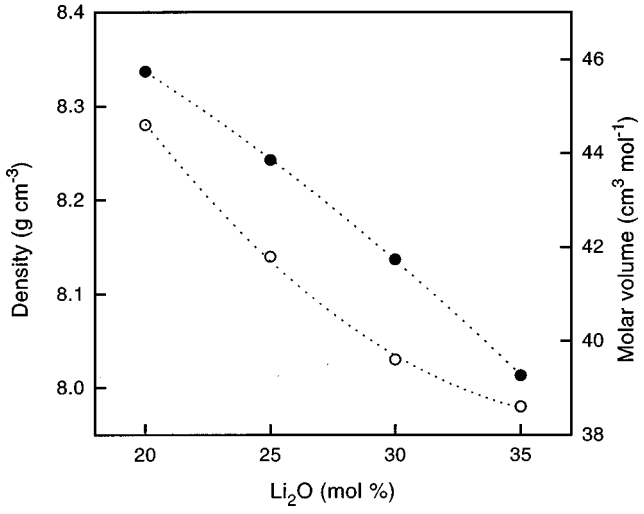

FIG. 4. Variation of density (○) and molar volume (●) with the Li_2O content in the glass composition.

D. Infrared spectra

The Fourier transform infrared (FTIR) spectrum for a typical glass composition is shown in Fig. 6. A sharp cutoff in the low-frequency region has been observed in the FTIR spectrum. Other glass compositions also have the similar spectra with a little variation in the cutoff frequency. The cutoff wave number ($\overline{\nu_c}$) for different glass compositions is shown in Table II. The fundamental vibrational frequency for a basic unit is expressed as $\nu=(1/2\pi)(k/\mu)^{1/2}$, where k is the field strength and μ is the reduced mass. This indicates

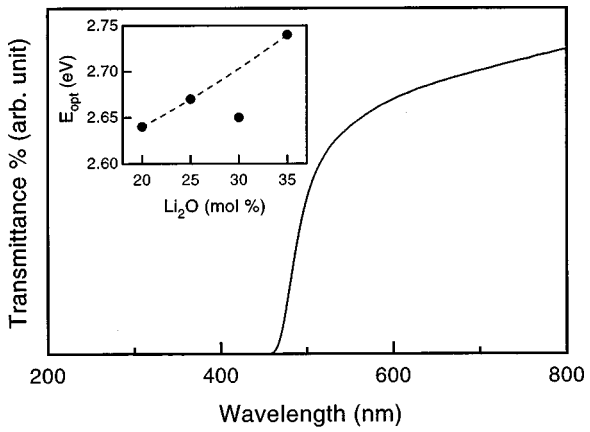

FIG. 5. Optical spectrum of $30Li_2O$-$70Bi_2O_3$ glass composition in the UV-VIS region. Inset shows the variation of E_{opt} with the Li_2O content in the glass composition.

TABLE II. Different physical parameters estimated from optical and IR spectra and electrical conductivity measurements for the lithium bismuthate glasses.

Glass composition Li_2O (mol %)	Bi_2O_3 (mol %)	λ_c (nm)	E_{opt} (eV)	$\overline{\nu_c}$ (cm^{-1})	ε_∞	σ_{dc} (at 200 °C) (Ω^{-1} cm^{-1})
20	80	469	2.64	1117	30	7.1×10^{-9}
25	75	464	2.67	1086	32	4.0×10^{-9}
30	70	467	2.65	1143	32	2.8×10^{-9}
35	65	453	2.74	1053	35	2.0×10^{-9}

that the larger the mass and the smaller the field strength, the smaller the IR cutoff frequency.[14] It can be noted that for the present glass system the cutoff frequency decreases slowly with the increase of the Li_2O content in the glass matrix shown in the inset of Fig. 6 with the same small deviation for the $30Li_2O$-$70Bi_2O_3$ glass composition as observed in the optical spectrum. The decrease of cutoff frequency in the lithium bismuthate glasses with the increase of Li_2O content and also in comparison to the PbO-Bi_2O_3 glasses (dashed curve of Fig. 6) indicates the strong influence of Li^+ ions in the glass matrix. As the introduction of the Li^+ ions in the glass network may decrease (or loosen), the field strength (or structure) of the basic vibrational BiO unit, hence the cutoff frequency can be decreased. Absorption near 3400 cm^{-1} due to the water band is observed in all glass samples indicating hygroscopic nature of the glasses.

The large transmission observed in these glasses in the wide frequency range, starting from UV-VIS to IR regimes, may make them useful as transmitting window. The width of the transmitting window also increases slowly with the increase of the Li_2O content in the glass compositions. However, the small deviation observed in both UV-VIS and IR cutoffs in the $30Li_2O$-$70Bi_2O_3$ glass composition may be due to the extra stability of this glass composition compared to other compositions, as expected from differential thermal analysis.

E. Raman spectra

Figure 7 shows Raman spectrum of a typical glass composition consisting of broad peaks in the range 200–700 cm^{-1}. The broadening of the peaks is due to the disorderness. The superimposed broad peaks of the spectrum was deconvoluted into five peaks using a Gaussian distribution to find out the exact mode of vibrations. Other glass compositions also have the similar spectra with only slight deviation in their peak positions. Vibrational spectra of Bi_2O_3 and its derivatives studied by IR and Raman spectroscopy[15] indicate that bismuth does not form a simple structure. However, it is well known that bismuth ions can form $[BiO_3]$ pyramidal or $[BiO_6]$ octahedral units.[7,16] Pyramidal units have four fundamental vibrations, which are all Raman active, while octahedral units have six modes of vibrations, three of which are Raman active.[17] The five vibrations observed in the present glass system do not correspond with that observed for $[BiO_3]$ pyramidal units. The bands in the range 300–600 cm^{-1} can be assigned to symmetric stretching anion motion (i.e., vibration of bridging oxygen) in an angularly constrained Bi-O-Bi configuration.[18] The broad but strong band at ~380 cm^{-1} can be attributed to the Bi-O-Bi vibration of the $[BiO_6]$ octahedral units, while the weak band at ~628 cm^{-1} can be attributed to the Bi-O^- stretching vibration (i.e., vibration of nonbridging oxygen) of the $[BiO_6]$ octahedral units[18] modified in presence of Li_2O. This was also predicted from the molar volume estimation of these glasses. The presence of the $[BiO_6]$ octahedral units in lithium bismuthate glasses indicates that the coordination number of the glass-forming cation is higher than that of the copper bismuthate glasses reported earlier.[5]

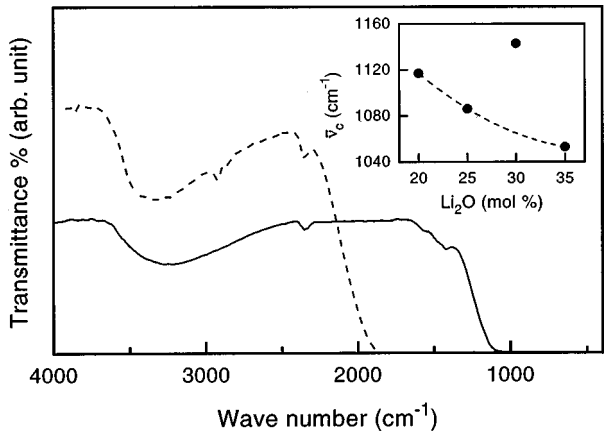

FIG. 6. FTIR spectra of $30Li_2O$-$70Bi_2O_3$ (solid curve) and PbO-Bi_2O_3 (dashed curve) glasses. Inset shows the variation of $\overline{\nu_c}$ with the Li_2O content in the lithium bismuthate glasses.

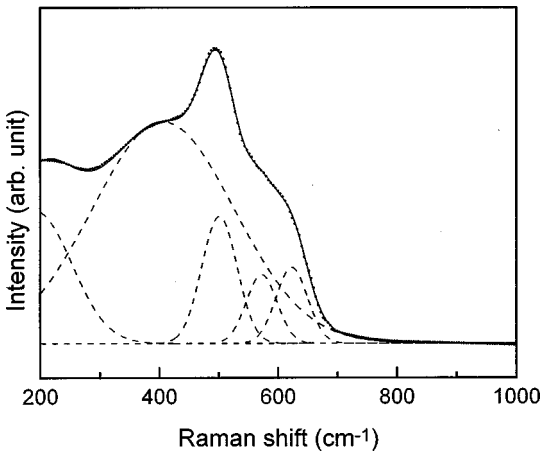

FIG. 7. Raman spectrum of $30Li_2O$-$70Bi_2O_3$ glass composition. Deconvoluted peaks are indicated by dashed curves.

F. Electrical conductivity

The ac loss and dielectric value of all the glass samples have been measured in the wide frequency range at high temperatures. A high dielectric constant has been observed for all glass compositions similar to copper bismuthate glasses[19] which may be due to the high polarizability of the unconventional network former Bi_2O_3.The dc conductivity (σ_{dc}) of the samples has been estimated from an ac complex impedance plot. The values of the high-frequency dielectric constants (ε_∞) and dc conductivity at 200 °C are shown in Table II. The low conductivity of these glasses compared to conventional lithium glasses may be due to that the some of Li^+ ions occupy the network-forming positions and are therefore unable to diffuse through the host matrix, unlike the alkali ions in most conventional network modified glasses.[11] This is a clear indication of the dominant role of Li^+ ions in unconventional glass formation, similar to Cu^+ ions in the copper bismuthate glasses.[10] However, the detailed electrical studies of these glasses are in progress, which will not only give conduction and relaxation mechanisms, but also its relation to the structure.

IV. CONCLUSIONS

Stable ionic binary glasses using the heavy-metal oxide Bi_2O_3 as the unique network former have been achieved by the melt-quench technique. Systematic variation of different parameters indicates no significant structural change with composition. Sharp cutoffs both in the UV-VIS and IR regions and wide window of transmission between them may make these glasses useful in the spectral devices. The Raman and molar volume data ensure the presence of $[BiO_6]$ octahedral units in the present glass system unlike Bi_2O_3-CuO glasses where $[BiO_3]$ pyramidal units are present. The increase of the optical band gap and decrease of the IR cutoff frequency with the increase of lithium content may be attributed to the decrease of the strength of the glass structure. A small deviation of different physical properties of the $30Li_2O$-$70Bi_2O_3$ glass composition indicates the extra stability of this glass. The high value of the dielectric constant may be due to the influence of the highly polarizable network former Bi_2O_3.The influence of Li^+ ions in unconventional glass formation is also confirmed from UV-VIS, IR, Raman, and electrical studies.

ACKNOWLEDGMENTS

The authors would like to thank M. Ghosh and K. M. Mukherjee of the Spectroscopy Department, IACS, for their help in the optical and Raman studies. S.H. and S.M. acknowledge the University Grants Commission (India) for financial support.

*Author to whom correspondence should be addressed. Present address: Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Calcutta-700 064, India. Electronic address: shazra@hp1.saha.ernet.in

†Present address: ERU, Indian Association for the Cultivation of Science, Calcutta-700 032, India.

[1] D. W. Hall, M. A. Newhouse, N. F. Borrelli, W. H. Dumbaugh, and D. L. Weidman, Appl. Phys. Lett. **54**, 1293 (1989).

[2] T. Komatsu, R. Sato, K. Imai, K. Matusita, and T. Yamashita, Jpn. J. Appl. Phys., Part 1 **27**, L550 (1988).

[3] T. Minami, Y. Akamatsu, M. Tatsumisago, N. Tohge, and Y. Kowada, Jpn. J. Appl. Phys., Part 1 **27**, L777 (1988).

[4] Y. Dimitriev and V. T. Mihailova, J. Mater. Sci. Lett. **9**, 1251 (1990).

[5] S. Hazra and A. Ghosh, Phys. Rev. B **51**, 851 (1995).

[6] W. H. Dumbaugh, Phys. Chem. Glasses **19**, 121 (1978).

[7] H. Zheng, R. Xu, and J. D. Mackenzie, J. Mater. Res. **4**, 911 (1989).

[8] W. H. Dumbaugh, Phys. Chem. Glasses **27**, 119 (1986).

[9] H. Nasu, T. Ito, H. Hase, J. Matsuoka, and K. Kamiya, J. Non-Cryst. Solids **204**, 78 (1996).

[10] S. Hazra, S. Mandal, and A. Ghosh, J. Chem. Phys. **104**, 10041 (1996).

[11] D. L. Sidebottem, P. F. Green, and R. K. Brow, Phys. Rev. B **51**, 2770 (1995).

[12] N. Kumada, N. Takahashi, N. Kinomura, and A. W. Sleight, J. Solid State Chem. **126**, 121 (1996), and references therein.

[13] N. I. Medvedeva, V. P. Zhukov, V. A. Gubanov, D. L. Navikov, and B. M. Klein, J. Phys. Chem. Solids **57**, 1243 (1996), and references therein.

[14] A. Soufiane and M. Poulain, J. Non-Cryst. Solids **161**, 206 (1993).

[15] R. J. Betsch and W. B. White, Spectrochim. Acta A **43**, 505 (1978).

[16] R. Iordanova, Y. Dimitriev, V. Dimitrov, S. Kassabov, and D. Klissurski, J. Non-Cryst. Solids **204**, 141 (1996).

[17] K. Nakamoto, *Infrared and Raman Spectra of Inorganic Compounds* (Wiley, New York, 1963).

[18] A. A. Kharlamov, R. M. Almeda, and H. Heo, J. Non-Cryst. Solids **202**, 233 (1996).

[19] S. Hazra and A. Ghosh, J. Phys.: Condens. Matter **9**, 3981 (1997).