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Influence of molybdenum ions on spectroscopic and dielectric properties of ZnF_2–Bi_2O_3–P_2O_5 glass ceramics

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ABSTRACT

Glasses doped with different concentrations of MoO_3 (ranging from 0 to 10 mol %) in the system ZnF_2–Bi_2O_3–P_2O_5 were crystallized and characterized by X-ray diffraction(XRD), scanning electron microscopy (SEM) and differential thermal analysis (DTA) techniques. The presence of $BiPO_4$, α-$Zn_3(PO_4)_2$, Bi_2MoO_6, γ-Bi_2MoO_6, $Bi_2Mo_2O_9$, $MoOPO_4$, α-$ZnMoO_4$ microcrystalline phases were exposed by XRD and SEM studies. The DTA indicated that the surface crystallization prevails over the bulk crystallization as the concentration of the crystallizing agent is increased. Spectroscopic properties (FTIR, Raman, optical absorption and ESR) at room temperature and dielectric properties (dielectric constant, loss tanδ, ac conductivity) over a range of frequency and temperature are studied. The IR and Raman spectra exhibit bands due to MoO_4 and MoO_6 units in structural groups in addition to various conventional phosphate groups. The existence of Mo^{5+} state in addition to Mo^{6+} state in these glass ceramic samples has been identified by the optical absorption, ESR and magnetic susceptibility studies. The variations observed in all these properties with the concentration of the crystallizing agent have been analyzed in the light of different oxidation states and environment of molybdenum ions in the glass ceramic network.

1. Introduction

Glass-ceramic materials are expected to have good mechanical, electrical and thermal properties, high chemical durability and very low coefficient of thermal expansion. By monitoring crystallization temperature and using appropriate nucleating agents the characteristics of these materials can be adjusted so as to exhibit excellent physical properties [1,2].

Among various glass ceramics, zinc bismuth phosphate glass ceramics are being widely used as fast ion conducting materials, laser hosts, energy storage devices and in solid state batteries [3–5]. Amid different crystallizing agents, MoO_3 is expected to be a more effective mineralizer, particularly in the glass systems like bismuth phosphate that exhibits non-linear optical properties. In fact, in several glass matrices, molybdenum oxide has been successfully used as a crystallizing catalyst [6,7]. The molybdenum ions exist in two valence states viz., Mo^{5+} and Mo^{6+} and participate in the glass network with octahedral (MoO_6) and tetrahedral (MoO_4) structural units [8,9]. Additionally, the presence of molybdenum ions in bismuth phosphate glasses makes them to be useful for potential applications in high-density memories, light modulation, large area display devices like smart windows and other electro-chromic devices [10–12].

The objective of the present investigation is to prepare ZnF_2–Bi_2O_3–P_2O_5 glass ceramics with MoO_3 as nucleating agent and to study the effect of compositional change of MoO_3 on the crystallization behavior and microstructural aspects of glass ceramics products. The prepared samples were characterized by XRD, SEM and DTA techniques and their spectroscopic (IR, Raman, optical absorption and ESR), magnetic and dielectric properties have been investigated and the results were analyzed in the light of variations in the concentration of different crystal phases embedded in the samples.

2. Experimental

In the present investigation, a particular composition $20ZnF_2$–$(20-x)$ Bi_2O_3–$60P_2O_5$: $xMoO_3$ (x — ranging from 0 to 10 mol%) was chosen. The detailed compositions (all in mol%) are as follows.

M_0:$20ZnF_2$–$20Bi_2O_3$–$60P_2O_5$
M_2:$20ZnF_2$–$18Bi_2O_3$–$60P_2O_5$:$2MoO_3$
M_4:$20ZnF_2$–$16Bi_2O_3$–$60P_2O_5$:$4MoO_3$
M_6:$20ZnF_2$–$14Bi_2O_3$–$60P_2O_5$:$6MoO_3$
M_8:$20ZnF_2$–$12Bi_2O_3$–$60P_2O_5$:$8MoO_3$
M_{10}:$20ZnF_2$–$10Bi_2O_3$–$60P_2O_5$:$10MoO_3$

Analytical grade reagents of grade ZnF_2 (Sigma Aldrich 99.99%), Bi_2O_3, P_2O_5,MoO_3 (LOBA, AR grade) reagents in the batches of 15 g were thoroughly mixed in an agate mortar and melted for 20 minutes in a thick walled platinum crucible at 970 ± 10 °C in PID controlled furnace until a bubble free liquid is formed. The melt was then poured on a brass mould at room temperature and subsequently annealed at 175 °C. The dopant free specimen (M_0) appeared to be a transparent

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brown color, later the color of the glass specimens (from M_2 to M_{10}) was observed to change gradually from light greenish blue to thick blue. All the glass specimens with various concentrations of MoO_3 were heat treated in a furnace at their crystalline temperature about 450 °C identified from the DTA of the glass samples for 6 h. Automatic controlling furnace was used to keep the temperature at a required level. After the heat treatment in a furnace at specified temperature, the samples were quenched in air to room temperature.

The crystalline phases in the glass ceramic samples were identified from the X-ray diffraction patterns of powdered glass samples recorded with Philips Xpert system using the step scan method with Cu-Kα radiation (λ = 1.5406 Å) operated at 40 kV, 25 mA. The surface morphology of prepared samples was carried out using Carl Zeiss, OXFORD INSTRUMENTS, Inca Penta FET x3 Scanning Electron Microscope to observe the crystallinity. Differential thermal analysis (DTA) of the samples was carried out using METTLER STAR SW 8.10 instrument (to an accuracy of ±0.1 °C) with a heating rate of 10 °C/min in the temperature range of 30–1000 °C. A programmable VIBRA HT density measurement kit was used to determine the densities and molar volumes of bulk samples automatically (with readability 0.0001 g/cm^3) by means of Archimedes' principle with O-Xylene (99.99% pure) as buoyant liquid. The FTIR spectra were recorded by dispersing the glass powders in KBr with a Perkin-ELMER FTIR spectrometer in the range of 400–1300 cm^{-1}. Micro Raman spectra were recorded using a Horiba Jobin-Yuon-UV800 Lab Ram HR spectrometer with a 17 mW internal He-Ne laser source of excitation wavelength of 514 nm with a spectral resolution of about ±0.33 cm^{-1}. The EPR spectra were recorded on JEOL-FE-IX ESR spectrometer operating at X-band frequency (9.125 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the micro wave power used was 10 mW. Glass sample in powdered form of 100 mg is taken in a quartz tube for EPR measurements. Magnetic susceptibility measurements were also carried out on these samples by Guoy's method using fine powders.

The optical absorption spectra of the samples (thickness 1 mm) were recorded in the wavelength range of 200–1200 nm up to a resolution of 0.1 nm using JASCO V-670 UV-Vis-NIR spectrophotometer. For dielectric studies, the glasses were grounded and polished to get 1 cm × 1 cm × 0.2 cm dimensions. A thin coating of silver paint was applied on either side of the samples to serve as electrode for electrical measurements. The dielectric measurements were taken on LF-impedance analyzer (Hewlett-Packard model 4192A) in the frequency range of 10^3–10^6 Hz and in the temperature range of 30–300 °C. The accuracy in the measurement of dielectric constant ε′ is ±0.01 and that in dielectric loss (tanδ) is ±0.001. The dielectric breakdown strength of all these glasses was determined at room temperature in air medium using a high a.c. voltage breakdown tester (ITL Model BOV-7, Hyderabad) operated with an input voltage of 230 V at a frequency of 50 Hz.

3. Results

The density measurements indicate the gradual decrease in their value with increase in concentration of MoO_3. From the measured values of the density and average molecular weight $\overline{M}$ of the samples, various other physical parameters such as molybdenum ion concentration N_i, mean molybdenum ion separation R_i, polaron radius R_p of ZnF_2–Bi_2O_3–P_2O_5:MoO_3 glass-ceramics are evaluated and presented in Table 1.

3.1. XRD

Fig. 1 shows the X-ray diffraction patterns (XRD) of the MoO_3 free samples before and after crystallization and one of the glass ceramic samples doped with 2.0 mol% of MoO_3. The XRD analysis of the pre-heated glass samples indicates the amorphous in nature. After the samples are crystallized at 450 °C, the concerned diffraction patterns exhibit peaks due to $BiPO_4$(JCPDS No. 89-0287), α- $Zn_3(PO_4)_2$ (JCPDS No. 76-0518), $MoOPO_4$(JCPDS No. 73-2333), Bi_2MoO_6(JCPDS No. 84-0787), γ- Bi_2MoO_6(JCPDS No. 82-2067), $Bi_2Mo_2O_9$(JCPDS No. 84-0829), and α-$ZnMoO_4$(JCPDS No. 25-1023) [13]. These are kinetically and thermodynamically feasible crystalline products which are identified in all the present investigated samples. The patterns indicate that bismuth ions exist in Bi^{3+} oxidation state. Similarly, the crystalline phases of Mo^{5+} ions were also detected in addition to Mo^{6+} ion phases. We observed a diffraction peak with a maximum intensity due to $MoOPO_4$ crystal phase at about $2\theta = 28.77^o$. The presence of such phase suggests that more fraction of molybdenum ions do exist in Mo^{5+} state. As the concentration of MoO_3 increased, the considerable hike in the intensity of the peak is observed.

Table 1
Various physical properties of ZnF_2–Bi_2O_3–P_2O_5 glass ceramics doped with different concentrations of MoO_3.

Sample	M_0	M_2	M_4	M_6	M_8	M_{10}
Concentration of MoO_3 (mol%)	0	2	4	6	8	10
Average molecular weight, $\overline{M}$ (g/mol)	199.03	192.59	186.15	179.71	173.27	167.19
Density, ρ (g/cm^3) (±0.0001)	4.2891	4.1532	3.9891	3.8389	3.6808	3.5216
Molybdenum ion concentration, N_i (×10^{20} ions/cm^3) (±0.01)	–	2.60	5.11	7.74	10.23	12.69
Inter ionic separation, R_i (Å) (±0.01)	–	15.67	12.51	10.89	9.92	9.24
Polaron radius, R_p (Å) (±0.01)	–	6.32	5.04	4.39	4.00	3.72

3.2. SEM

Fig. 2 refers some of the SEM pictures of the samples M_0, M_2 and M_{10} and they show an increasing crystallinity with increasing concentration of the crystallizing agent MoO_3. The remaining glass phase is being acted as interconnecting zones among the crystallized areas of all the samples, avoiding voids and cracks. The electron

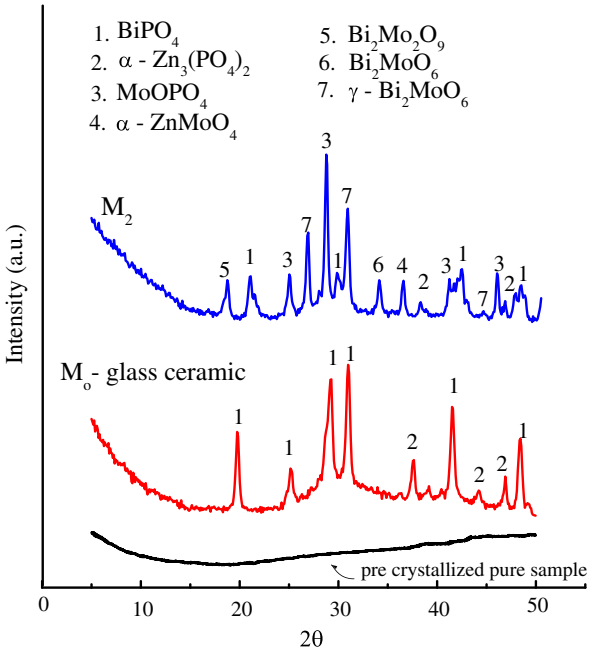

Fig. 1. XRD patterns of ZnF_2–Bi_2O_3–P_2O_5 glass ceramics doped with 0 and 2.0 mol% of MoO_3 showing different possible crystalline phases. XRD pattern of pre-crystallized dopant free sample is also included.