



Photoluminescence and spectral performance of manganese ions in zinc phosphate and barium phosphate host glasses



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ABSTRACT

Zinc and barium metaphosphate glasses containing dopants of MnO₂ (2, 4, 8%) were prepared. Collective studies were carried out through optical, photoluminescence and Fourier transform infrared (FTIR) spectral measurements for the prepared glasses before and after gamma irradiation. Electron spin resonance (ESR), thermal expansion and crystallization studies were also investigated. Optical spectra for undoped and MnO₂-glasses reveal strong ultraviolet (UV) absorption due to trace iron impurity in the materials used for preparation of glasses and Mn²⁺ ions are not identified due to spin-forbidden nature of their spectra. Upon gamma irradiation, the MnO₂-doped glasses reveal extension of the UV absorption exhibiting two peaks together with the generation of an induced broad visible band centered at 570–580 nm. Extra two glasses doped with 8% MnO₂ were melted under reducing condition and they showed characteristic band at 410 nm related to Mn²⁺ ions absorption. Photoluminescence (PL) spectra reveal two excitation peaks in MnO₂-doped zinc phosphate glasses at 348 and a sharp peak at 410 nm while the MnO₂-doped barium phosphate glasses exhibit a sharp peak at 410 nm and a curvature at 348 nm. The emission spectra show a broad band centered at 620 nm in both glasses but with a curvature at 605–610 nm in zinc phosphate glasses which are correlated with the transition ⁴T_{1g} → ⁶A_{1g}. The efficiency of the photoluminescence increases with the MnO₂ content and the heat treatment. The values of the optical band gap (E_{opt}) and Urbach energy (ΔE) were calculated. FTIR spectra reveal vibrational bands due to phosphate network mainly of metaphosphate groups but in zinc phosphate glasses, the mid spectra show compact network because of the ability of Zn²⁺ ions to participate partly as ZnO₄ or P–O–Zn linkages. Thermal expansion data show different responses. Zinc phosphate glasses show anomalous behavior related to the change in the coordination of zinc cations while barium phosphate glasses exhibit normal expansion because Ba²⁺ ions exist only as modifiers. The crystallization behavior reflects also anomalous behavior. The zinc phosphate glass crystallizes in two crystalline species, mainly zinc metaphosphate phase and another zinc phosphate (3ZnO·P₂O₅) phase while the barium phosphate glass crystallizes only in barium metaphosphate phase.

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1. Introduction

It has been established that the introduction of any divalent, trivalent or tetravalent oxides to phosphate glasses increases their chemical durability while generally keeping their relatively lower preparation temperatures and their excellent and unique optical, thermal and electrical properties [1–3]. The addition of divalent oxides to P₂O₅ causes the breaking of the tetrahedral building PO₄ blocks and the conversion of the phosphate network to a system of entangled linear chains of phosphorus–oxygen tetrahedral cross linked by divalent ions [4]. Some of the alkaline earth oxides (CaO, SrO, BaO) when added to P₂O₅ result in the creation of non-bridging oxygens at the expense of bridging oxygens and the mentioned alkaline earth cations are solely acting as

modifiers [3]. Other divalent oxides (e.g. ZnO, MgO) combine with P₂O₅ – and the two binary systems of ZnO–P₂O₅ and MgO–P₂O₅ have been classified as anomalous because of discontinuities in composition–property trends near the metaphosphate (50 mol% P₂O₅) composition [5,6]. Such anomalous behavior can be related to several reasons including the change in the coordination number of Zn²⁺ or Mg²⁺ or the ability of their oxides to form partly structural building units (ZnO₄, MgO₄) or to other factors such as relatively high field strength of those divalent cations or to the change in the polarizability of the neighboring oxygen ions [5,6].

Manganese as one of 3d transition metals can exist in glasses in two valences, the divalent and trivalent states and the ratio of each depends on the glass type and composition and condition of melting [7]. The trivalent manganese ions exhibit a broad nearly symmetrical visible band at 450–540 nm which is related to a spin-allowed ⁵E_g → ⁵T_{2g} transition of octahedral symmetry [8,9]. The divalent manganese ions are known

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to exhibit four weak spin–forbidden peaks which vary in their positions with their symmetry of either octahedral or tetrahedral coordination. Both Mn^{3+} and Mn^{2+} ions are well-known paramagnetic ions, Mn^{3+} ion has a large anisotropy due to its spin–orbit interaction of the 3d orbital whereas such anisotropy energy of Mn^{2+} ion is small because its orbital angular momentum is zero [7,10].

When glasses are subjected to ionizing gamma irradiation (such as γ -rays, UV radiation), some of the glasses suffer darkening or the formation of induced color centers which can be identified by optical and/or E.S.R measurements [11,12]. It is accepted that the glasses containing some transition metal ions (e.g. Cu^{2+} , V^{5+}) exhibit some shielding effects and their optical spectral curves remain unchanged and closely parallel upon successive gamma irradiation [13,14]. Also, some glasses containing heavy metal oxides (e.g. PbO , Bi_2O_3 , BaO) show the same shielding behavior upon gamma irradiation because of the heavy masses of their cations which retard the free motion of excited electrons or positive holes during the irradiation process [15,16].

The main objective of this present work is to characterize and compare collective optical, photoluminescence, FTIR spectral analysis together with ESR and thermal properties of manganese-doped within both zinc meta-phosphate and barium meta-phosphate glasses. The present study also includes the investigation of the effects of gamma irradiation on the combined optical, photoluminescence and FTIR spectral properties of the two glass systems containing varying added dopants (2, 4, 8 wt%) of manganese. Two further selected glasses (8% MnO_2) were prepared at reducing condition and their main spectral properties were measured and characterized. A final study in this work is focused on the crystallization behavior of some selected zinc phosphate and barium phosphate glasses upon controlled thermal two step heat treatment regime.

2. Materials and methods

2.1. Preparation of the glasses

The glasses were prepared from pure laboratory chemicals. The materials include ammonium dihydrogen ortho phosphate ($NH_4H_2PO_4$), 99% Winlab Ltd., Harborough, Leicestershire, UK) was the source of P_2O_5 , zinc oxide was introduced as ZnO (BDH, Laboratory reagent, England) and anhydrous heavy barium carbonate ($BaCO_3$) (MERCK G. Darmstadt, Germany, Fe 0.001%) for BaO and MnO_2 (Fluka, Buchs, LUKA – Switzerland, Fe 0.3%) was added as such. The accurately weighed batches in Table 1 were melted under atmospheric condition in alumina crucibles at 1100 °C for 90 min in SiC heated furnace (Vecstar, Chesterfield, UK). The melts were rotated at intervals to reach complete mixing and homogeneity. The homogenized melts were poured into preheated stainless steel molds of the required dimensions. The prepared glassy samples were immediately transferred to an annealing muffle regulated at 300 °C to obtain glasses free from stresses or strains. The muffle was switched after 1 h with the samples inside and left to cool to room temperature at a rate of 30 °C/h. Table 1 depicts the chemical compositions of the prepared glasses.

Table 1
Chemical composition in mol% and optical parameters of the prepared glasses.

Sample no.	P_2O_5	ZnO	BaO	MnO_2	E_{opt} (eV)		ΔE (eV)		n	
					Added in wt%	0 MR (± 0.05)	10 MR (± 0.031)	0 MR (± 0.035)	10 MR (± 0.052)	0 MR (± 0.011)
(1)	50	50	–	–	4.149	3.199	0.405	0.743	2.141	2.345
(2)	50	50	–	2	4.100	3.160	0.570	0.621	2.150	2.355
(3)	50	50	–	4	4.048	3.137	0.625	0.567	2.160	2.361
(4)	50	50	–	8	4.018	3.088	0.675	0.547	2.166	2.373
(5)	50	–	50	–	3.920	3.385	0.346	0.960	2.185	2.300
(6)	50	–	50	2	3.849	3.250	0.485	0.683	2.199	2.332
(7)	50	–	50	4	3.797	3.190	0.496	0.547	2.210	2.347
(8)	50	–	50	8	3.614	3.103	0.519	0.436	2.248	2.369

2.2. Preparation of the corresponding glass–ceramic derivatives

The heat treatment temperatures are based on differential thermal analysis (DTA) measurements (Fig. 1) using SDTQ600 under N_2 gas. Glass samples were subjected to controlled thermal heat-treatment through a two-step regime (Table 2). The glasses were first heat treated slowly at a rate of 5 °C/min to reach 450 °C and kept at this temperature for 12 h which was sufficient to provide sufficient nucleation sites. The muffle was then raised to reach 600 °C and kept at this second hold temperature for 6 h. The muffle furnace with the heat-treated samples inside was switched off and then left to cool to room temperature at a rate of 30 °C/h.

2.3. X-ray diffraction analysis

Identification of the crystalline phases formed during controlled heat-treatment was performed by X-ray diffraction analysis using a Bruker AXS diffractometer (CD8-ADVANCE) with Cu-Ka radiation, operating at 40 kV and 10 mA. The diffraction data were recorded for 2θ values between 4° and 70° and the scanning rate was 10°/min.

2.4. Thermal expansion measurements

The thermal expansion characteristics of the glasses were measured through specified samples using a recording dilatometer (type NETZCH – 1–402 PC Geräebau GmbH, Selb Germany) with a heating rate of 10 °C/min up to the dilatometric softening temperature. The thermal data for the transformation and softening temperatures were collected to be used for controlled thermal heat treatment of the glasses to their corresponding glass–ceramic derivatives.

2.5. Optical absorption measurements

Optical (UV–visible) absorption measurements were carried out on polished samples ($2\text{ mm} \pm 0.1\text{ mm}$) using a recording spectrophotometer (type JASCO V-570, Japan) covering the range from 200 to 1100 nm.

2.6. Photoluminescence measurements

Photoluminescence measurements were recorded at room temperature under the excitation wavelength of 410 nm in the spectral range 500–750 nm using a fluorescence spectrophotometer (type JASCO, FP-6500, Japan) equipped with a xenon flash lamp as the excitation light source. The scan speed is 0.15 step – 1 with a step length of 0.25 nm and slit width 0.2 nm.

2.7. Calculations of optical band gap (E_{opt}), Urbach energy (ΔE) and refractive index

Mott and Davis [17] model has been applied to determine the optical band gap energies (E_{opt}) of the prepared glasses using Eq. (1), by

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