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Optical, structural and thermal properties of sodium metaphosphate glasses containing Bi_2O_3 with interactions of gamma rays

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ABSTRACT

Sodium metaphosphate glasses with successive increasing added Bi_2O_3 contents (5–40%) were prepared to improve their chemical stability and increase their optical and thermal properties through the additional building BiO_6 and BiO_3 units. The optical spectrum of the base metaphosphate glass reveals strong UV absorption due to the presence of trace iron (Fe^{3+}) ions present as impurities. Glasses containing additional 5, 7.5 and 10% Bi_2O_3 show further band around 406 nm which can be related to absorption of Bi^{3+} ions. With increasing the Bi_2O_3 content, this near visible band is observed to disappear indicating peculiar behavior needing further work. Gamma irradiation causes only minor changes in the position of the strong UV peaks but an obvious induced visible broad band centered at 452–460 nm in the base and Bi_2O_3 containing glasses. This induced band is related to the generation of phosphorus oxygen hole center or non bridging oxygen hole center as revealed by various authors. FTIR results reveal characteristic vibrational bands due to phosphate groups and with the addition of Bi_2O_3, some interference of Bi—O vibrational units are expected. Gamma irradiation causes limited changes in the IR spectra due to suggested shielding effect of the heavy metal oxide Bi_2O_3.

1. Introduction

Phosphate glasses are interesting vitreous system that has gained great attention in the past and in recent applications. In the 1950s, interest in amorphous alkali phosphates was stimulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing pigment manufacturing [1].

Owing to the outstanding optical properties of phosphate glasses including higher transparency for ultraviolet light especially when additional multivalent oxides are formulated in their compositions, they are introduced and recommended as laser glasses [2]. Also, the high thermal expansion coefficients, and low softening temperatures of phosphate glasses make them suitable for hermetic seals [3]. Biocompatible phosphate glasses and glass-ceramics have been recommended for medical applications [4] and lithium phosphate glasses [5] have fast ion conductivity that makes them useful as solid state electrolytes. The application extends to explore lead iron phosphate glass to be a host matrix for radioactive wastes because of possessing promising chemical durability, radiation shielding beside lower melting temperature [6].

Glasses containing heavy metal Bi_2O_3 have wide and potential applications in the field of optical glasses with high refractive indices, low melting temperature, semiconducting glasses and also as a shielding candidate for gamma irradiation [7–9]. The ability of Bi_2O_3 like PbO to share or behave partly as glass forming oxide comes from the high polarizability of Bi^{3+} and Pb^{2+} cations and their constitutional asymmetric polyhedra which inhibit crystallization and thus possess wide range of glass formation beside being less toxic than PbO [10].

The aim of the present work is to study by combined optical and FT infrared absorption spectroscopic measurements detailed spectral properties of sodium metaphosphate glasses containing increasing Bi_2O_3 contents before and after gamma irradiation. It is expected that these collective spectral studies will throw some insight on the effect of Bi_2O_3 on the phosphate network with the introduction of additional Bi—O units and to deduce the induced defects generated during the irradiation process through the addition of heavy metal oxide (Bi_2O_3) expected to cause shielding behavior. A further aim includes the study of the thermal expansion properties of the studied glasses to find out their possible suitability to serve as sealing glass candidate.

2. Experimental and methods

2.1. Preparation of the glasses

Glasses of the basic sodium metaphosphate composition (50 mol% Na_2O-50 mol% P_2O_5) to which successive added Bi_2O_3 contents (5% → 40%) were prepared. Laboratory chemicals of NaH_2PO_4 and Bi_2O_3 were used to prepare the glasses. All weighed batches were melted in alumina crucibles at 1100 °C and melting time was extended to 1 h with stirring of the melts at intervals to promote complete mixing and homogeneity. The melts were cast into warmed stainless steel

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molds of the required dimensions. The prepared glassy samples were immediately transferred to a muffle furnace regulated at 250 °C for annealing to remove any stresses or strain formed during the rapid cooling of the melts. The annealing muffle was left to cool to room temperature after 1 h with the samples inside with a cooling rate of 20 °C/h.

2.2. Optical absorption spectral measurements

The optical (UV–visible) absorption spectra of polished glass samples (2 mm + 0.1 mm) were recorded at room temperature before and after gamma irradiation by a recording spectrophotometer (type T80 PG Instruments, England) in the range 190–1000 nm.

2.3. FT infrared absorption measurements

FTIR absorption spectra of the glasses were measured at room temperature in the range 400–4000 cm^{-1} by a Fourier transform infrared spectrometer (type Nicolet is 10, USA) using the KBr disc technique. The IR measurements were immediately done after preparing the discs to avoid moisture attack. The same measurements were repeated after subjecting the glass powder to a gamma dose of 8 M rad (8×10^4 Gy).

2.4. Gamma irradiation facility

An Indian ^{60}Co gamma cell (2000Ci) was used as a gamma ray source with a dose rate of 1.5 Gy/S (150 rad/s) at a temperature of 30 °C. The glasses were subjected to a total dose of 8 M rad (8×10^4 Gy). This specific amount of radiation dose was chosen based on previous studies on irradiation of glasses which revealed that distinct optical spectral variations were observed until the gamma dose reached 6 M rad after which saturation effect was reached stopping the creation of more induced defects [11,12].

2.5. Thermal expansion investigations

Thermal expansion properties of base sodium metaphosphate glass together with samples containing varying Bi_2O_3 contents were measured using a computerized dilatometer (type NETZSCH DIL 402 PC 5, Germany). All the measurements were made within the temperature range from room temperature up to the dilatometeric softening temperature (Tg) with a heating rate of 5 °C/min. The cylindrical glass samples with the dimension (25 × 6 mm) were used and at least two measurements were made on each glass with reproducibility (±0.01%).

3. Results

3.1. Optical absorption spectra before and after gamma irradiation

Fig. 1 illustrates the optical spectrum of the base sodium metaphosphate glass together with the spectra of samples of the same composition and containing successive Bi_2O_3 additions (5–40% Bi_2O_3).

The base glass exhibits a strong and broad UV absorption band with two distinct peaks at 240 and 300 nm and with no further visible absorption to the end of measurement at 1100 nm. On introducing 5% Bi_2O_3, the UV spectrum remains strong revealing two peaks at 228 and 282 nm and with the appearance of a new visible peak at 403 nm. The spectrum of the glass containing 7.5% Bi_2O_3 reveals strong UV absorption with two bands at 306 nm and a lower band at 384 nm followed by a distinct visible band at 430 nm.

The sample containing 10% Bi_2O_3, reveals a strong UV absorption with two distinct peaks at 240 and 305 nm very similar to that of the base glass but with a small peak at 394 nm. The samples with 12.5% or 15% Bi_2O_3 show the same spectrum consisting of a strong UV absorption the same as the spectrum of the base glass but the positions of the two

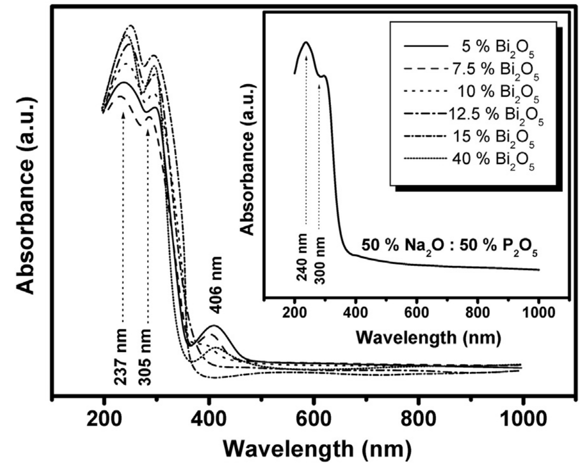

Fig. 1. UV–visible absorption spectra of undoped and Bi_2O_3 doped sodium phosphate glasses before gamma irradiation.

peaks are identified at 240 and 310 nm and with no further visible absorption.

The glass containing 40% Bi_2O_3 shows a strong UV absorption with two peaks at 240 and 298 nm and two small peaks 380 nm and 420 nm and with no further bands in the rest of the visible region.

Fig. 2 illustrates the optical spectra of the studied glasses after gamma irradiation with a dose of 8 M rad. The base glass containing no Bi_2O_3 reveals strong UV absorption with two peaks at 240 and 296 nm and with a distinct induced visible band at 452 nm. All the Bi_2O_3-containing glasses exhibit the same UV absorption with two distinct peaks at about 240 and 296 nm and together with a further broad visible band centered at about 460 nm.

3.2. FT infrared absorption spectra of the glasses

Fig. 3 illustrates the FTIR spectra of all the studied glasses before irradiation. The IR spectral features of the base sodium metaphosphate glass can be summarized as follows:

(a) The far-IR absorption reveals distinct and sharp connected five peaks at about 430, 457, 485, 518 and 550 cm^{-1}.
(b) The appearance of a medium broad band with two peaks at 732 and 769 cm^{-1}.
(c) A very broad and strong absorption extending from about 800 to 1600 cm^{-1} is observed with seven peaks at about 873, 968, 998, 1014, 1089, 1205 and 1275 cm^{-1}.

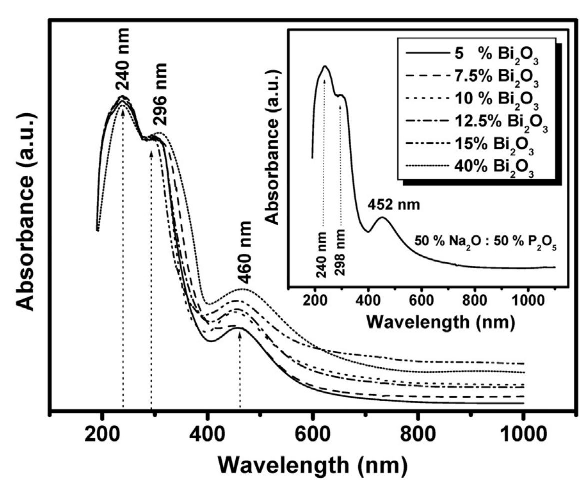

Fig. 2. UV–visible absorption spectra of undoped and Bi_2O_3 doped sodium phosphate glasses after 8 MR gamma irradiation.