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Optical character enrichment of NdF_3 – doped lithium fluoroborate glasses

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ABSTRACT

Optical spectra in combination with Fourier transform infrared FTIR spectra of base undoped lithium fluoroborate glasses and samples that doped with NdF_3 were measured before and after subjecting to (8 Mrad) gamma irradiation. Base glass reveals strong absorption in the UV region attributed to unavoidable iron impurity (Fe^{3+} ions) while gamma irradiated sample shows extended additional peaks related to the photochemical reactions of some Fe^{2+} impurities transformed to Fe^{3+} ions by acquiescent positive holes while the induced visible band is related to (BOHC) boron oxygen hole center or (NBOHC) nonbridging oxygen hole center. The NdF_3-doped samples display the same strong UV spectra as the undoped sample beside additional characteristic visible absorption peaks due to the presence of Nd^{3+} ions. UV–Vis. absorption spectra were applied to assess their optical properties, comprising indirect and direct optical energy band gaps taking into account the effect of gamma irradiation. Infrared absorption spectra of the undoped lithium fluoroborate glass reveal characteristic IR bands due to both BO_3 and BO_4 borate groups as usually observed in various alkali–oxide B_2O_3 glasses. Suggested BO_3F tetrahedral units are advanced to interpret the close similarity of the IR spectra obtained from fluoroborate glass with alkali or alkaline earth oxide borate glasses. The increase of NdF_3 content causes minor changes in the IR spectra that can be attributed to the non-conventional loose OH, H_2O or similar vibrations while the structural building borate units remain unchanged as evidence from the deconvoluted FTIR data before and after the irradiation process.

1. Introduction

For many decades, properties and structure of borate containing glasses have attracted the awareness of various glass scientists and many international conferences have been held for this specific borate glasses, their melts and crystals because of their intriguing and interesting peculiarities [1–4]. Adding of alkali oxide or alkaline earth oxide such as Bi_2O_3 or PbO to B_2O_3 leads to transformation of some triangular building units to tetrahedral coordination until (20 − 33) percent after which nonbridging oxygens are formed such as that is happened in all compositions of silicate glasses. Some physical properties of alkali borate glass exhibit reverse direction with change of composition and this anomalous behavior is termed as "borate anomaly" [5,6]. However, Bray [7] has considered that borate anomaly result from the formation of large inadequate tetraborate groups and not due to the abrupt variation in the percent of four-coordinated borons.

Some glass scientists have studied borate glasses containing alkali or alkaline earth halides instead of the respective oxides [8–12] because of their interesting optical and anionic conduction. They proposed that the fluoroborate glasses contain mainly BO_3, BO_2F triangles and BOF_3 tetrahedral. However, the formation of BO_2F triangles is excluded. Doweidar et al. [12] have reached through IR spectral analysis that CaF_2 modifies B_2O_3 in binary CaF_2–B_2O_3 glasses and form BOF_3 tetrahedral units and are responsible for the vibrational bands in the region 800–1200 cm^{-1}.

It is recognized [13] that color variations result from 3d transition metal ions caused by the electronic transitions between degenerate energy levels of d-electrons. Similar arguments can be applied to rare earth ions, where absorption bands in the visible region originate from the splitting of the 4f levels. Less intense and more complex spectra of rare earth result from the variances between 3d and 4f and large number of possible configurations of the seven 4f levels in comparison with compared with five 3d levels of transition metals. It is also known that changes of anions character leads to changes in its corresponding ligand field strength and position of the absorption bands with no change in their numbers. The ligand field strength of the common anions decreases in the order $O^{2-} > F^- > Cl^- > Br^- > I^-$ [13].

Color results from rare earth or TM ions can be varied according to their content which is reflected in the absorption process and type of network former that influence the changes in the bond distances and bond strengths between dopants and surrounding matrices.

Glasses that are doped with Nd^{3+} ($4f^3$) have been extensively studied because of their interesting UV, Visible and infrared emissions which characterize these materials for luminescent centers [14,15].

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Recently, structural, optical properties of Nd^{3+} in Na_2O-NaF borate glasses [16], and in lithium fluoroborate glasses [17] have been investigated owing to their potential applications in optical amplifiers and high power laser.

In a previous publication [18] the authors have studied by combined optical and FTIR spectral investigations the behavior of Nd^{3+} ions in a borophosphate glass composition and investigated the effect of gamma irradiation on such collective properties. This study aims to investigate the role of Nd^{3+} in a new host fluoroborate glass together with evaluation of the effects of gamma irradiation on the optical and FTIR spectral properties of such fluoroborate glass. A further study includes the calculation of the optical energy gap for the studied glasses. It is expected that the collective properties will give new interesting data for the neodymium ions in this new fluoroborate host glass and the effect of gamma irradiation on the spectral properties. The importance of the study of the effect of gamma rays as one of the ionizing radiation on rare-earth Nd^{3+}-doped fluoroborate glass comes from the variety of photonic applications such as in optical amplifiers and solid state lasers and to wider or knowledge in the studied field.

2. Experimental details

Undoped glass with a composition ($15LiF \cdot 85B_2O_3$wt.%) together with five glasses of the same composition containing (0.5, 1, 1.5, 2, 3%) NdF_3 as dopant were prepared from reagent grade chemicals as described in Table 1.

Boric acid (H_3BO_3) from Winlab, Leicestershire, UK, Assy 99.5% and LiF Fluka, Germany (Fe 0.01%) and NdF_3 Sigma Aldrich 99.99% trace metals basis were used as sources for the corresponding glasses constituents. The melting of the batches were carried out under atmospheric condition in platinum 2%Rh crucibles in an SiC electric furnace (Vecstar, UK) at 1100 °C for 1 h. To get homogeneous glasses, the platinum crucibles were rotated from time to time. The homogeneous melts were poured into preheated stainless steel molds of the required dimensions and the samples were immediately transferred to a muffle furnace regulated at 400 °C for annealing to remove any stresses or strains found during rapid cooling. The annealing muffle was switched off after one hour and left to cool to room temperature at a rate of 30 °C/h. UV–visible absorption spectra were measured for perfectly polished glass samples of equal thickness (2 ± 0.1 mm) using a double beam spectrophotometer (type JASCO Corp., V-570, Rel-80, Japan) covering the range from 200 to 900 nm. The same measurements were repeated after gamma irradiation with a dose of 8 Mrad (8×10^4 Gy).

FT infrared absorption spectra were recorded at room temperature using the KBr disc technique. A Fourier transform computerized IR spectrometer type (JASCO, FT/IR 4600, Japan) in the wavenumber range 4000–400 cm^{-1}. 2 mg of powdered samples were added to 198 mg spectroscopic KBr and well mixed. The final mixtures were subjected to a load of 5 $tons/cm^2$ to produce clear homogenous discs of diameter 1 cm. At least two spectra measurements for each sample were recorded. Infrared spectra were corrected for the dark current noises and back ground using the two-point baseline correction. The FTIR measurements were carried out immediately after preparing the discs and the same measurements were repeated directly after gamma irradiation.

Table 1
Composition of glass samples.

Sample	B_2O_3	LiF	NdF_3
	wt.%		gm/batch
0Nd	85	15	0.0
0.5Nd	85	15	0.5
1Nd	85	15	1.0
1.5Nd	85	15	1.5
2Nd	85	15	2.0
3Nd	85	15	3.0

A ^{60}Co gamma cell (2000 Ci) was used as a gamma ray source with a dose rate of 1.5 Gy/s (150 rad/s) at room temperature (30 °C). Each glass was subjected to a gamma dose of 8×10^4 Gy (8 Mrad).

3. Results

3.1. (UV–visible) optical absorption spectra of base glass

Fig. 1 reveals optical absorption spectrum of base undoped lithium fluoroborate glass. The optical spectrum of this sample shows strong charge transfer ultraviolet absorption with two distinct peaks at 240 and 295 nm with no absorption in the visible region. The optical absorption intensity of the UV increases after being subjected to gamma irradiation. The peaks at 237 and 298 are clearly related to those at 240 and 295 nm followed by a curvature of a small broad visible band centered at about 540 nm.

3.2. Optical absorption spectra of NdF_3-doped glasses

Fig. 2 shows the optical absorption spectra for samples containing increasing NdF_3 contents before and after irradiation. The spectral curves show stretched absorption spectra including visible bands characteristic for Nd^{3+} ions in addition to the UV absorption peaks previously mentioned for the undoped glass. The observed visible bands are labeled in Fig. 2.

The irradiated NdF_3-doped glasses reveal the following spectral characteristics (Fig. 2):

(a) The 0.5% NdF_3-doped glass shows the increase of the optical absorption within the UV–visible region together with the extension of the UV spectrum revealing four peaks at 237, 304, 355, 370 nm. The rest of the visible absorption bands characteristics for Nd^{3+} ions are observed to be almost persistent in their number and position as before irradiation.

(b) The 1% NdF_3-doped glass reveals the increase of the whole UV–visible spectrum including also the extension of the UV absorption showing four peaks at 242, 294, 354 and 371 nm. The visible bands observed before irradiation are persistent and remain in almost their number and position after radiation.

(c) The rest 1.5, 2 and 3% NdF_3-doped glasses reveal almost the same spectral changes observed with the spectrum of the glass containing 1%NdF_3. The spectral visible bands are observed to be

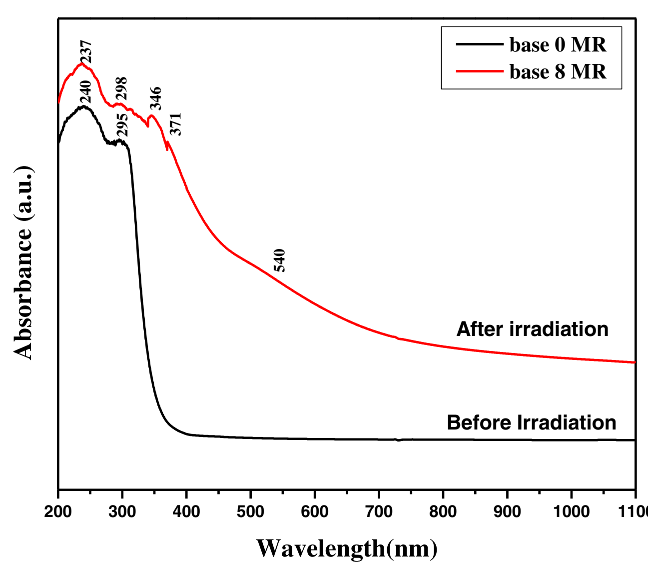

Fig. 1. UV–visible absorption spectra of base undoped LiF-B_2O_3 before and after gamma irradiation.