Physica B 408 (2013) 115–118

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Conversion of Ce^{3+} to Ce^{4+} ions after gamma ray irradiation on CeO_2–PbO–B_2O_3 glasses

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A R T I C L E I N F O

Article history:
Received 2 July 2012
Received in revised form
1 September 2012
Accepted 3 September 2012
Available online 26 September 2012

Keywords:
Gamma radiation
Cerium oxide
Borate glass

A B S T R A C T

The structural and optical parameters of gamma ray irradiated cerium doped lead borate glasses have been analyzed using FTIR, UV–visible absorption, transmittance and density measurement techniques. It has been observed that due to gamma ray exposure, the optical band gap decreases, density increases and molar volume decreases correspondingly. FTIR spectroscopy confirms the conversion of [BO_3] to [BO_4] and also shows the presence of [CeO_4] groups of cerium in glass samples. The transmittance of the glass samples decreases due to formation of hole centers.

1. Introduction

An excessive survey of scientific work is already devoted to the studies of gamma radiation interaction with different glasses [1–3]. The study of radiation-induced defect centers in glasses has been a fascinating subject of exploration in recent years [4], since such studies help in examining the suitability of glasses for radiation dosimetery applications. The gamma-ray irradiation on glasses creates secondary electrons from the sites where they are in a stable state and have an excess energy. When glass is exposed to high-energy radiation, a number of defects can be formed [5]. These defects are basically formed due to trapped electrons or holes in either the pre-existing sites or voids of glass created by bond breaking due to irradiation [6]. Three basic processes are proposed by El-Batal: (a) radiolytic processes, (b) atomic displacement and ionization and (c) charge trapping or electron rearrangements [7]. The properties of glasses are usually subjected to a variety of changes under the influence of gamma ray irradiation due to partial rupture of chemical bonds or destruction of the network as well as introduction of defects. It has been reported that defects in glasses are produced in pairs of positive hole centers (HC) and negative electron centers (EC) [8]. The electronic transitions of these defects regularly cause high absorbance in the UV and visible region. As these defects are in resemblance to absorbance in crystals which is historically called color-centers [9,10]. The generation rates of defects due to irradiation have been studied by optical spectroscopy [11–13].

In rare earth metal oxides, cerium oxide has great importance in the field of glasses due to many applications [14,15]. Cerium readily changes its oxidation state from Ce^{3+} to Ce^{4+} and vice versa. Cerium ion has been used earlier as a photosensitive or as defect-Scavenger in order to suppress the photo-ionization in glasses in the visible range [16,17].

This work is a continuation of our previous work [18]. The objective of the present work involves the study of gamma ray induced effects on structural and optical parameters of CeO_2–PbO–B_2O_3 glasses. For structural investigation density and FTIR spectroscopy have been employed and optical properties like transmittance and absorption are measured with help of UV–visible spectroscopy.

2. Experimental procedure

2.1. Sample preparation

The sample preparation and other experimental techniques are same as discussed in our previous work [18].

A ^{60}Co gamma cell (2000 Ci) has used as gamma-ray source with a dose rate 7.27 KGy/h at room temperature. Each investigated glass sample was subjected to a total final dose of 25 kGy.

3. Results and discussion

3.1. FTIR

The FTIR spectra of gamma irradiated CeO_2–PbO–B_2O_3 glasses have been illustrated in Fig. 1. It has been observed that gamma

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http://dx.doi.org/10.1016/j.physb.2012.09.005

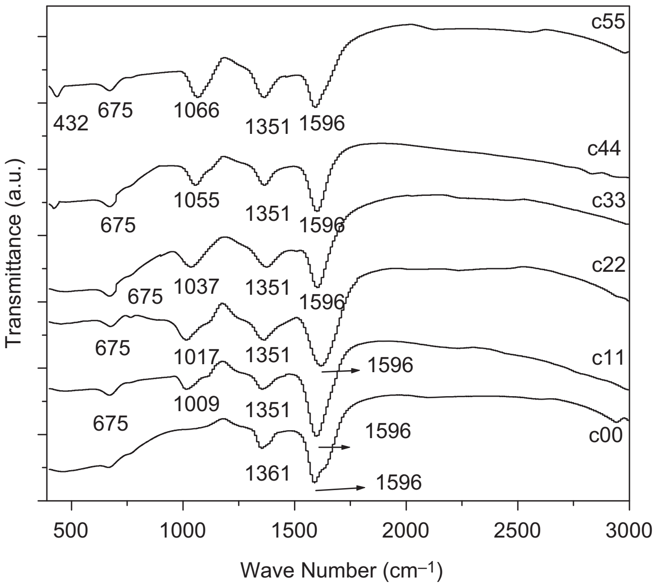

Fig. 1. FTIR spectra of CeO_2–PbO–B_2O_3 glasses.

rays affect the structure of the borate network in glasses which is summarized below.

1. The first medium weak band at 432 cm^{-1} has been raised in sample c44 due to the effect of gamma irradiation. It has also been noticed that the intensity of this band goes on increasing at higher concentration of cerium oxide in sample c55. This band is attributed to the presence of Ce–O stretching vibration of [CeO_4] groups of cerium [19]. This band is absent in our previous study of un-irradiated glasses [18].
2. The small band centered at 675 cm^{-1} confirms the B–O–B bending vibration of [BO_3] groups [20].
3. The third band exists at 1009 cm^{-1} in sample c11 which is due to the presence of stretching vibrations of different tetrahedral [BO_4] groups. This band is shifting towards the higher wave number (1009–1066 cm^{-1}) in the remaining samples and its intensity also increases with an increase of CeO_2 contents [21]. This band is also absent in our previous work of un-irradiated samples.
4. The intensity of the band due to [BO_3] groups present at 1351 cm^{-1} decreases under the influence of gamma ray exposure which reflects the decrease of trigonal boron groups in glass network [22].
5. The intensity of the band present at 1596 cm^{-1} also decreases under the influence of irradiation [23].
6. It has been assumed that the applied irradiation dose breaks up the trigonal [BO_3] connectivity of network and converts it into [BO_4] groups.

Above discussion shows that intensity of the bands between 800–1200 cm^{-1} increases and intensity of the band between 1200–1600 cm^{-1} decreases after the exposure to gamma radiation. This result reflects an increase in concentration of [BO_4] groups at the expense of [BO_3] units. It is also believed that the higher content of rare earth metal plays an important role to improve the glass strength as well as its structure under the influence of irradiation.

3.2. Density

The irradiation effects on density and molar volume have been listed in Table 1. It can be observed that gamma irradiation leads to an increase in density of CeO_2–PbO–B_2O_3 glasses and this decrease can be attributed to the change in the structure after irradiation. The density increases for all of the studied glasses when subjected to irradiation.

There are some expected causes of change in density observed by some authors after irradiation which is summarized below [24]:

(a) Density change depends on the composition or state of aggregation.
(b) The compact state is produced due to a decrease in bond angle.
(c) Induced damage is responsible for induced color centers.

At higher irradiation doses, the irradiated species can cause the compaction of B_2O_3 by breaking the bonds between trigonal groups thus allowing the formation of tetrahedral [BO_4].

Shelby suggested that the irradiation affected the boron–oxygen bond [25]. Displacement of atoms from their position in the glass network caused by irradiation can give rise to a number of structural changes which cause change in density.

3.3. UV–vis spectroscopy

Fig. 2 shows the optical absorption spectra of CeO_2–PbO–B_2O_3 glasses after gamma ray exposure. It is observed that band edge of the glasses has been progressively shifting towards the longer

Table 1
Nominal composition (mole fraction), density and energy band gap of the glass samples.

Glass	CeO_2 (%)	PbO (%)	B_2O_3 (%)	Density (D) (g/cm^3)	Optical band gap before irradiation, $E_{opt.}$ (eV)	After irradiation optical band gap, $E_{opt.}$ (eV)
c00	0	30	70	3.11	2.89	2.59
c11	2	28	70	3.34	2.60	2.37
c22	4	26	70	3.44	2.45	2.33
c33	6	24	70	3.51	2.43	2.28
c44	8	22	70	3.58	2.35	2.13
c55	10	20	70	3.99	2.30	1.99

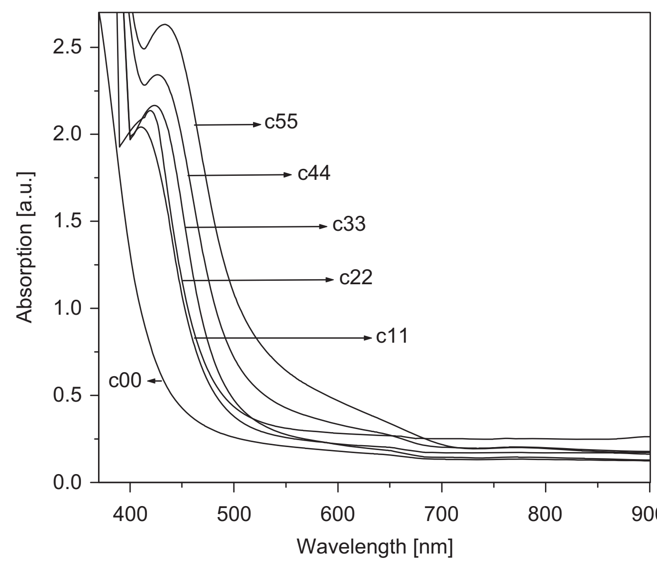

Fig. 2. Optical absorption of CeO_2–PbO–B_2O_3 glasses.