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Acetylene adsorption on the iron-lead-borate glassy and vitroceramic surface

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ABSTRACT

A novel iron-lead-borate glassy and vitroceramic system for applications in solar cells technology and adsorption of small molecules (such as acetylene) on surfaces was obtained and studied in this work. In this sense, glasses and glass ceramics of the $xFe_2O_3\cdot(100 - x)[3B_2O_3\cdot PbO_2]$ system with $x = 5$–50 mol% Fe_2O_3 were synthesized by melt quenching method and characterized in order to obtain information about their structural and behavioral properties. The reciprocal effects of the iron ions addition to the host matrix together with the matrix effect on the paramagnetic behavior of the inserted iron ions were investigated by using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible (UV–Vis) spectroscopy and electron paramagnetic resonance (EPR) spectroscopy.

The XRD pattern for the prepared samples shows their vitreous nature only for $x \leq 30$ mol% Fe_2O_3. For samples containing 40 mol% Fe_2O_3, the presence of α-Fe_2O_3 crystalline phase embedded in an amorphous matrix was detected.

IR data suggest that addition of high iron (III) oxide content in the host matrix leads to the gradual conversion of $[PbO_4]$ to $[PbO_3]$ and $[BO_4]$ to $[BO_3]$ structural units and the formation of $[FeO_n]$ structural units by modifications of Pb—O—B and Pb—O—Pb linkages.

The UV–Vis data show that addition of higher Fe_2O_3 concentration produces a gradual shift of the absorption towards the higher wavelength side indicating the absorption of light from 295 to 1050 nm and a decrease of the energy gap.

EPR spectra exhibit resonance signals at $g \sim 4.3$ and $g \sim 2$ showing the presence of Fe^{+3} ions in sites of distorted octahedral symmetry as well as in clusters containing both Fe^{+3} and Fe^{+2} ionic species.

FTIR spectroscopy was employed to study the adsorption of acetylene on the obtained glasses and vitroceramics surface. The nature of the different molecular species is also discussed.

1. Introduction

Transition metal oxide nanoparticles are of scientific and technological importance because of their size-dependent physico-chemical properties and their potential applications in the fields of catalysis, electronics, energy storage, gas detection and magnetic resonance imaging [1–5].

Among the various polymorphic forms of iron (III) oxides: amorphous Fe_2O_3 and four polymorphs (alpha, beta, gamma and epsilon), the most frequent polymorph structure, hematite, α-Fe_2O_3 and maghemite, γ-Fe_2O_3 are of great importance in technological and industrial applications [6]. Maghemite with cubic spinel structure has numerous applications like in fields such as recording and memory devices, magnetic resonance imaging, drug delivery or cell targeting [7,8]. Epsilon Fe_2O_3 with orthorhombic structure is a transition phase between hematite and maghemite. Beta Fe_2O_3 has body-centered cubic bixbyite structure and is a paramagnetic material.

Maghemite has the same crystalline structure as Fe_3O_4 (magnetite). In maghemite all iron cations are in trivalent state where in Fe_3O_4 these cations appear as both Fe^{+2} and Fe^{+3} species. Magnetite is a metastable phase that, in time, turns into the hematite crystalline structure at room-temperature and will convert to maghemite under exposure to temperatures typically around 200 °C. Further heating to above 400 °C will produce α-Fe_2O_3.

Hematite has the corundum structure and exhibits high resistance to corrosion. Therefore, it has been extensively used in many fields which

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include photo-anode for photo assisted electrolysis of water. Hematite has applications in the manufacturing of gas sensors, catalyst and photocatalysts, lithium ion battery, magnetism, electrochemical capacitor and pigments [9–12].

Hematite has strong antiferromagnetic properties. Gamma and epsilon type Fe_2O_3 are ferromagnetic and differ from the inverse spinel structure through vacancies on the cation sublattice.

In amorphous Fe_2O_3, Fe^{+3} ions are surrounded by oxygen octahedra with the respective symmetry axes randomly orientated in a nonperiodic lattice. Amorphous iron oxide shows substantial industrial potential in magnetic memory storage, surface sorption, catalysis and in thin film solar cells technology. It absorbs light from 295 to 565 nm, which accounts for 38% of the photons at air mass (AM) 1.5 [13].

Iron (III) oxides (hematite in particular) with different particle sizes and morphologies were obtained by a variety of physical and chemical approaches which require expensive equipment, extra purification steps and long reaction times [6].

The aim of this study is to improve our understanding of the local environment and the dominant role of iron (III) oxide in lead-borate glasses and vitroceramics obtained by melt-quenching method. From the point of view of the basic research, iron (III) oxide is a convenient compound for the general study of polymorphism and the magnetic and structural phase transitions of nanoparticles. We interpret the origin of the most important optical transitions of iron ions by comparing EPR spectroscopy data with optical absorption spectroscopy data of glasses and crystalline references. Up to our best knowledge, the present paper reports for the first time the adsorption of acetylene on glassy and vitroceramic surfaces by using FTIR spectroscopy.

2. Experimental procedure

A series of glasses in the $xFe_2O_3 \cdot (100 - x)[3B_2O_3 \cdot PbO_2]$ system where x = 5–50 mol% Fe_2O_3 was prepared by melt quenching method. Amounts in suitable proportion of reagent grade purity of H_3BO_3, Fe_2O_3 and PbO_2, were mixed and melted in sintered corundum crucibles using an electric furnace at a temperature of 1150 °C. After 10 min, the molten material was quenched at room temperature by pouring onto a stainless-steel plate.

The obtained materials were characterized by X-ray diffraction using a XRD-6000 Shimadzu diffractometer, with a monochromator of graphite for the Cu-Kα radiation ($\lambda = 1.54$ Å) at room temperature

The FTIR spectra of the glasses were obtained in the 350–2000 cm^{-1} spectral range with a JASCO FTIR 6200 spectrometer using the standard KBr pellet disc technique. The spectra were carried out with a standard resolution of 2 cm^{-1}.

UV–Visible absorption spectra of the powdered glass samples were recorded at room temperature in the 250–1050 nm range using a Perkin-Elmer Lambda 45 UV/VIS spectrometer equipped with an integrating sphere. These measurements were made on glass powder dispersed in KBr pellets. The validity of the band position is ±2 nm.

EPR measurements were performed at room temperature using an ADANI portable EPR PS 8400-type spectrometer, in the X frequency band and a field modulation of 100 kHz. The microwave power was 5 mW.

3. Results and discussion

3.1. XRD diffraction

XRD diffraction patterns of the synthesized $xFe_2O_3 \cdot (100 - x)[3B_2O_3 \cdot PbO_2]$ samples with x ≤ 30 mol% Fe_2O_3 (presented in Fig. 1) display no distinct diffracting peaks confirming the amorphous nature of these samples. In sample with x = 40% Fe_2O_3, the XRD patterns reveal two large halos with the characteristic peaks attributed to the standard data of rhombohedral α-Fe_2O_3 crystalline phase (PDF 330664).

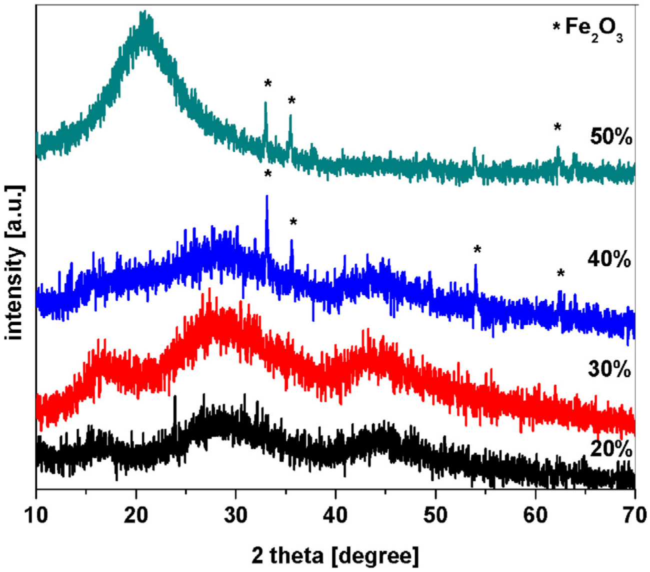

Fig. 1. XRD diffractograms of the $xFe_2O_3 \cdot (100 - x)[3B_2O_3 \cdot PbO_2]$ system where x = 20–50 mol% Fe_2O_3.

The sample with x = 50 mol% Fe_2O_3 shows a broad peak centered at around $2\theta = 21°$ overlapped with the characteristic peaks corresponding to α-Fe_2O_3 crystalline phase. The presence of the diffraction halos in the low angle range shows that diffraction peak intensities characteristic to α-Fe_2O_3 crystalline phase are low suggesting either a low crystallinity or a low crystallite size or the presence of amorphous Fe_2O_3. Accordingly, small sized α-Fe_2O_3 nanoparticles in the host matrix were successfully synthesized using melt quenching method in the absence of any heat treatment.

The α-Fe_2O_3 crystalline phase, hematite, is the most stable iron oxide under ambient conditions. It has a rhombohedral-hexagonal unit cell with prototype corundum structure in which two-thirds of the octahedral sites are occupied by Fe^{+3} ions [13]. Hematite is an n-type semiconductor with the gap energy of 2.1 eV and an interesting anode material. It was extensively investigated for a wide range of applications because it has unique electrical and catalytic properties, is non-toxic, readily available and shows high resistance to oxidative change [6].

3.2. FTIR spectroscopy

Fig. 2 illustrates the FTIR spectra of the iron-doped lead-borate glasses and vitroceramics in the $xFe_2O_3 \cdot (100 - x)[3B_2O_3 \cdot PbO_2]$ system with x = 5–50 mol% Fe_2O_3. In the FTIR spectrum of Fe_2O_3, the bands situated at about 470 and 510 cm^{-1} are attributed to Fe—O vibrations. The IR band situated at about 580 cm^{-1} is associated to Fe—O vibrations from $[FeO_4]$ structural units.

By increasing of Fe_2O_3 content in the host matrix, the IR data reveal three features:

i. The intensity of the broader IR bands situated in the region between 360 and 740 cm^{-1} increase gradually up to 30 mol% Fe_2O_3. After that, the characteristic features of the IR bands increase abruptly in strength and intensity with adding higher Fe_2O_3 concentrations up to 50 mol%. In this sense, the broadening of the band centered at about 450 cm^{-1} becomes more defined and intense for the sample with x = 40 mol% Fe_2O_3. The features of this IR band can be due to the stretching vibrations of Fe—O bonds overlapped with the bending vibrations of Pb—O—Pb modes in $[PbO_4]$ structural units [14]. For the sample with x = 50 mol% Fe_2O_3, IR band splits into some components centered at about 470, 530, 650 and 680 cm^{-1}. Introduction of higher Fe_2O_3 content in the host vitroceramic matrix