



Structure, electrochemical characterization and the role of copper oxide in lead-lead dioxide glasses and vitroceramics

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ARTICLE INFO

Keywords:

Copper oxide-lead-lead dioxide glasses and vitroceramics
XRD
SEM
FTIR
UV–Vis
PL and RES spectroscopy
Cyclic voltammetry

ABSTRACT

Glasses and vitroceramics in the $x\text{CuO}\cdot(100-x)[4\text{PbO}_2\cdot\text{Pb}]$ composition, where $x = 0\text{--}70\%$ CuO were prepared by melt quenching method and were investigated by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), InfraRed (IR), UltraViolet-Visible (UV–Vis), Photoluminescence (PL) and Electron Paramagnetic Resonance (EPR) spectroscopies and measurements of Cyclic Voltammetry (CV). XRD and SEM data show that the samples with $x \leq 60\text{ mol}\%$ CuO have vitreous structure. Increasing CuO content of these samples up to 70 mol% produces the formation of CuO nanoparticles with spherical morphology on the vitroceramic surface. IR data suggest that the accommodation of dopant in the host matrix will be realized considering the conversion of some $[\text{PbO}_6]$ and $[\text{PbO}_4]$ structural units into $[\text{PbO}_3]$ structural units and the intercalation of $[\text{CuO}_n]$ structural units. The EPR spectra offer information concerning the presence of the isolated Cu^{2+} ions located at sites with an axially distorted octahedral symmetry, coupled and/or clustered Cu^{+2} species. UV–Vis data reveal the presence of copper ions in the two valence states: Cu^{+1} and Cu^{2+} ions. As results, the gap energy value decreases and the effect of luminescence was quenched by increasing of CuO dopant levels.

1. Introduction

Lead dioxide (PbO_2) was extensively investigated since its first discovery as an electrode in lead-acid rechargeable battery > 150 years ago [1]. The glassy materials, which consist of heaviest metal oxides, such as lead, are more promising for photonics and optoelectronics [2].

Metallic lead is a heavy element also used for radioprotection against high energy radiations, and its radioprotection quality works also when lead is incorporated in glass [3]. Lead glasses were intensively used as ornaments, cups, or jewelry in historical and middle age for their beautiful colors and transparency [4].

Lead glasses doped with different transition metal ions were studied for the transport properties and the electrical conduction [5–7]. Glasses containing high concentration of transition metal oxide have usually semiconductor behavior. The general condition for electronic conduction is that the transition metal ion should be capable of existing in more than one valence state. Copper exists in glass in three stable oxidation states (Cu^0 , Cu^{+1} , Cu^{+2}) each giving the glass unique properties and special applications [8,9]. The oxidation state of copper depends on the method used for the doping of copper into the glass and on the composition of the particular glass. The conduction can take place by the electron transfer from ions in a lower valence state to those in a

higher valence state.

Glasses containing copper have beautiful colors and they have become a promising candidate for photonics applications [8]. Metallic copper, Cu^0 , introduces a ruby red coloration of the glass due to the absorption between 550 and 570 nm. Cu^{+1} and Cu^{+2} ions are present in the glass simultaneously. The glasses containing Cu^{+2} ions impart a blue color to the glass due to the absorption between 550 and 570 nm. The glasses containing Cu^{+1} ions are colorless and show a photoluminescence peak with a maximum in the visible region from 390 to 570 nm [10–13].

In this work lead-lead dioxide-copper oxide glasses and vitroceramics containing copper (II) oxide were synthesized and investigated through XRD and SEM analysis, InfraRed, UltraViolet-Visible, Photoluminescence and Electron Paramagnetic Resonance spectroscopies. The electrochemical performances of the samples used as working electrodes in the measurements of Cyclic Voltammetry were discussed.

2. Experimental procedure

Glasses and vitroceramics in the $x\text{CuO}\cdot(100-x)[4\text{PbO}_2\cdot\text{Pb}]$ composition, where $x = 0\text{--}70\%$ CuO were prepared by melt quenching

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methods using as starting materials CuO, PbO₂ and metallic Pb powders mixed in suitable proportions. The mixtures were melted in sintered corundum crucibles at 800 °C, in an electric furnace. After 10 min the molten material was quenched at room temperature by pouring it onto a stainless-steel plate.

X-ray diffraction (XRD) data were collected from the obtained samples using a Smart Lab Rigaku diffractometer with a graphite monochromator for the Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) at room temperature.

The samples were examined in an electronic microscope with JEOL JSM 5510LV scan, equipped with an elemental analysis system from Oxford Instruments Inca 300.

The FT-IR spectra of the glasses were obtained in the 350–1200 cm⁻¹ spectral range with a JASCO FTIR 6200 spectrometer. The spectra were carried out with a standard resolution of 2 cm⁻¹.

UV-Visible absorption spectra of the samples were recorded at room temperature in the 250–1700 nm range using a JASCO V-550UV/VIS spectrometer equipped with an integrating sphere. The validity of the band position is ± 2 nm. The photoluminescence (PL) measurements were carried out using an ABL&Jasco V 6500 spectrofluorometer with xenon lamp of 150 W.

EPR measurements of the powder samples were performed with a Bruker ELEXSYS 500 spectrometer in X-band (9.86 GHz).

The electrochemical properties were characterized by cyclic voltammetry measurements using an AUTOLAB 302 N potentiostat/galvanostat (EcoChemie, Netherlands) and the NOVA 1.11 software. Discs of obtained samples were used as working electrode, platinum as counter electrode, calomel as reference electrode and sulfate acid solution as liquid electrolyte. All experiments were conducted in a solution of H₂SO₄ with the concentration of 38%.

3. Results

X-ray diffractograms of the vitreous system in the xCuO·(100-x)[4PbO₂·Pb] composition, where x = 0–70% CuO are shown in Fig. 1.

The Scanning Electron Microscopic (SEM) images of the obtained samples with the xCuO·(100-x)[4PbO₂·Pb] composition, where x = 15, 40–70% CuO are shown in Fig. 2.

FTIR absorption spectra of the vitreous system in the xCuO·(100-x)[4PbO₂·Pb] composition, where x = 0–70% CuO are shown in Fig. 3. A simple inspection of the IR data indicates three broad regions

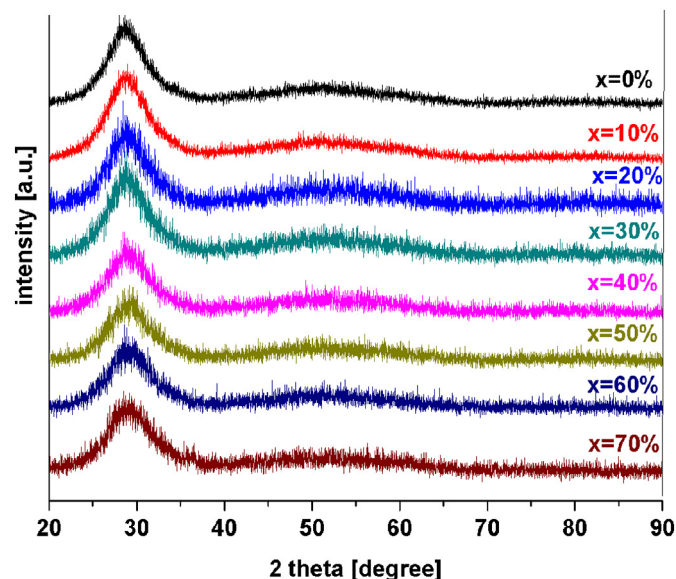


Fig. 1. XRD diffractograms of xCuO·(100-x)[4PbO₂·Pb] samples where x = 0–70 mol% CuO.

characteristic of the [PbO_n]_n and [CuO]_n structural units of the network.

UV-Vis absorption spectra of the samples in the xCuO·(100-x)[4PbO₂·Pb] composition where x = 0–70 mol% CuO are shown in Fig. 4a. An examination of the UV-Vis spectra reveals that with progressive CuO addition a shift of the absorption edge towards longer wavelength side and an increase in intensity in both of the UV and visible regions were identified. Accordingly, the absorption edge and Cu⁺² absorption band show different dependences on the CuO concentration. These compositional evolutions suggest that other species than Cu⁺² ions alone such as Cu⁺¹ ions contribute to the overall absorption spectra.

The Cu⁺¹ ions with its fully occupied d-orbitals (having the 3d¹⁰ electronic configuration) does not show any d-d electronic transitions, and a glass containing only the monovalent Cu⁺¹ species will appear colorless.

The direct and indirect band gap values are obtained by the extrapolating of linear portions of the plots $h\nu$ versus $(\alpha h\nu)^{1/2}$ and $h\nu$ versus $(\alpha h\nu)^2$ to the energy axis as shown in Fig. 5. The values of optical band gap, E_g for indirect and direct allowed transitions dependence on the copper (II) oxide content of prepared samples obtained from fitting in accordance with calculations developed of Tauc plots are also presented in Fig. 5 (see also Table 1).

The room temperature photoluminescence (PL) spectra of lead-lead dioxide vitreous system doped with different contents of CuO up to 70 mol% are shown in Fig. 6 after excitation at 250 nm.

Electron spin resonance (ESR) spectra at room temperature of the vitreous system having the xCuO·(100-x)[4PbO₂·Pb] composition where x = 5–70 mol% CuO are shown in Fig. 7.

The presence of Cu⁺² ions with 3d⁹ electronic configuration in the lead-lead dioxide glasses having electron spin S = 1/2 and nuclear spin I = 3/2 gives rise to good electron spin resonance (ESR) spectra.

In order to investigate the electrochemical properties of the samples used as working electrode, cyclic voltammograms were recorded in a 38% H₂SO₄ solution in the potential range from -1 to 2 V vs. calomel reference electrode and at a scan rate of 0.005 V/s. Cyclic voltammograms with the samples in the xCuO·(100-x)[4PbO₂·Pb] composition where x = 60 and 70 mol% CuO synthesized at 800 °C and 900 °C, respectively are shown in Fig. 8.

4. Discussion

4.1. XRD and SEM analysis

All diffractograms indicate the presence of two large halos characteristic structure of amorphous samples. For sample with x = 70 mol % CuO a small diffraction peak centered at about 35.4° assigned to the monoclinic CuO crystalline phase was observed. In the monoclinic CuO crystalline phase, the copper atom is coordinated by 4 oxygen atoms in an approximately square planar configuration.

By introduction of higher CuO content (x \geq 40 mol% CuO) in the host matrix, the SEM micrographs evidenced inhomogeneous regions with some crystalline grains with the spherical morphology formed on the surface. At higher CuO concentration, copper oxide are unable to accommodate in the glass network and accumulate in form of grains, which induces glass structure deformation for sample with x = 70 mol % CuO. Copper ions did not penetrate deep inside the matrix network and diffuse out, which leaves traces in the structure of the sample.

4.2. FTIR spectroscopy

The first region of IR bands of intermediate intensity located in the region between 360 and 560 cm⁻¹ is derived from the overlaps of deformation vibrations of the O–Pb–O and Pb–O–Pb angles from [PbO₄] structural units [14,15] and stretching vibrations of the Cu–O bond [16,17]. By doping with copper (II) oxide, the IR bands in this region become intensely and some modifications of the IR band centered at

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