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Manganese oxide – antimony oxide – lead – lead dioxide vitroceramics

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Abstract

The number of spent batteries was increased significantly in recent years along with the use of mobile phones, vehicles, and other high-tech products. In this work the vitroceramics in the $5MnO_2·xSb_2O_3·(95\text{-}x)[9Pb·PbO_2]$ composition where x = 0 – 40 mole% Sb_2O_3 were synthesized by melt – quenching method using as raw materials the spent plates of a car battery (the anode as Pb source and cathode as PbO_2 source), MnO_2 and Sb_2O_3 powders. The prepared samples were characterized by XRD, IR and UV-Vis data. The electrochemical performances of the antimony – manganese - lead materials used as working electrode at a car battery were demonstrated by measurements of cyclic voltammetry. The combined results from varied techniques show that antimony ions play the important role in the conductive and electrochemical properties.

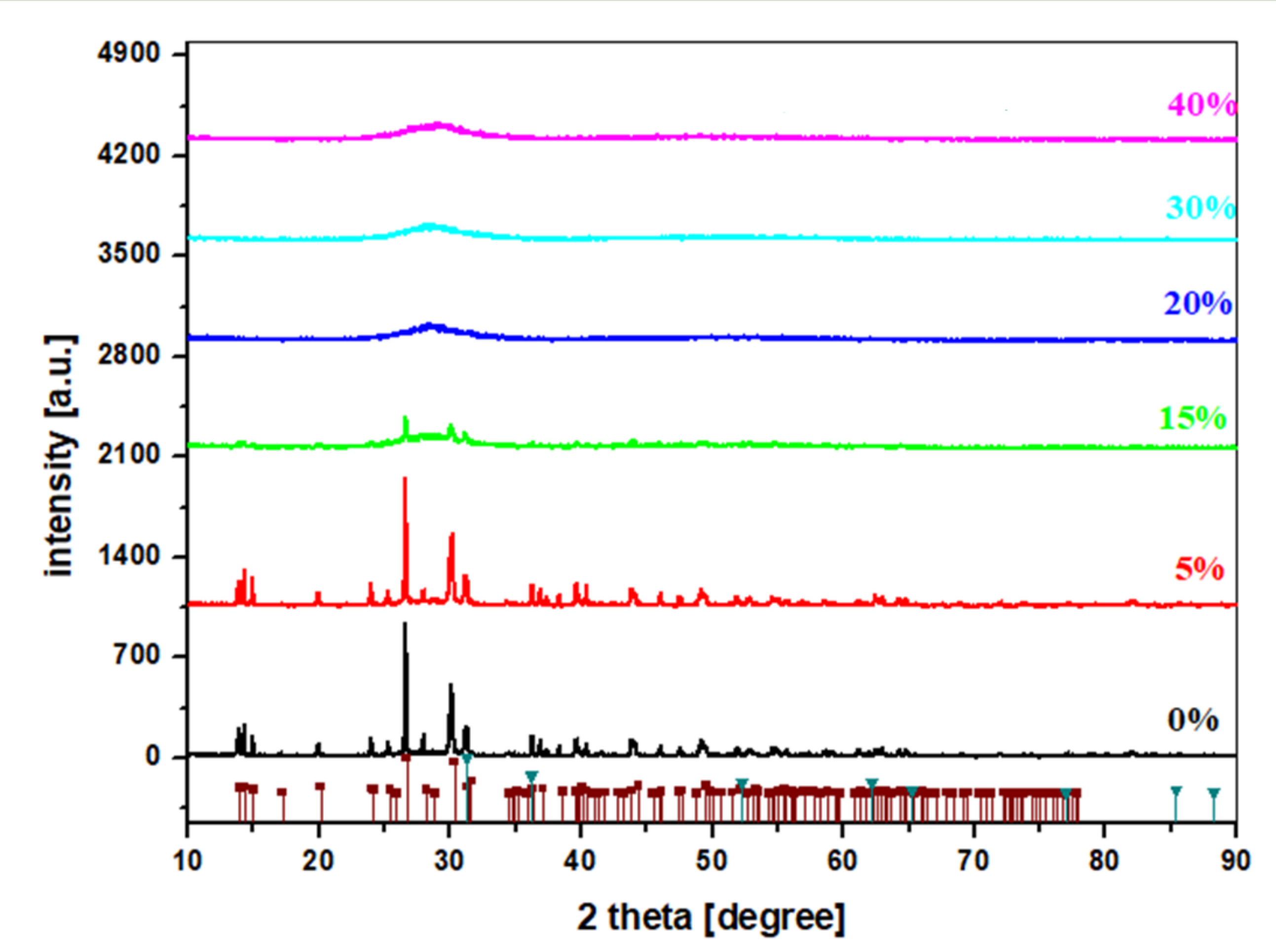
Motivation

An approach to improve the performance of the recycled electrodes provided from spent car battery using MnO_2 and Sb_2O_3 as additive in view of new applications in the renewable batteries.

Experimental procedure

Samples were prepared by melt quenching method using as starting materials spent electrodes from a disassembled car battery as sources of PbO_2 and Pb (in 9 : 1 molar ratio) mixed in suitable proportions with 5 mol% MnO_2 and *x* mol % Sb_2O_3 powders. The mixtures were melted in sintered corundum crucibles at 1300 °C, in an electric furnace. After 10 minutes the molten material was quenched at room temperature by pouring it onto a stainless-steel plate. The recycled and manganese-antimony doped samples were characterized by the analysis of X-ray diffraction (XRD). The FT-IR spectra of the samples were obtained in the 350-1500 cm^{-1} spectral range with a JASCO FTIR 6200 spectrometer using the standard KBr pellet disc technique. UV-VIS and cyclic voltammetry (VC) measurements. A potentiostat / galvanostat tip AUTOLAB PGSTAT 302N (EcoChemie, Netherlands) and the NOVA 1.11 software were used to test the cyclic voltammograms of the electrode material. Discs of obtained samples were used as working electrode, platinum as counter electrode, saturated calomel electrode as reference electrode and sulfate acid solution as liquid electrolyte. All experiments were conducted in a solution of H_2SO_4 with the concentration of 38%, in agreement with the electrolyte solution used in the lead acid batteries.

Results and discussion



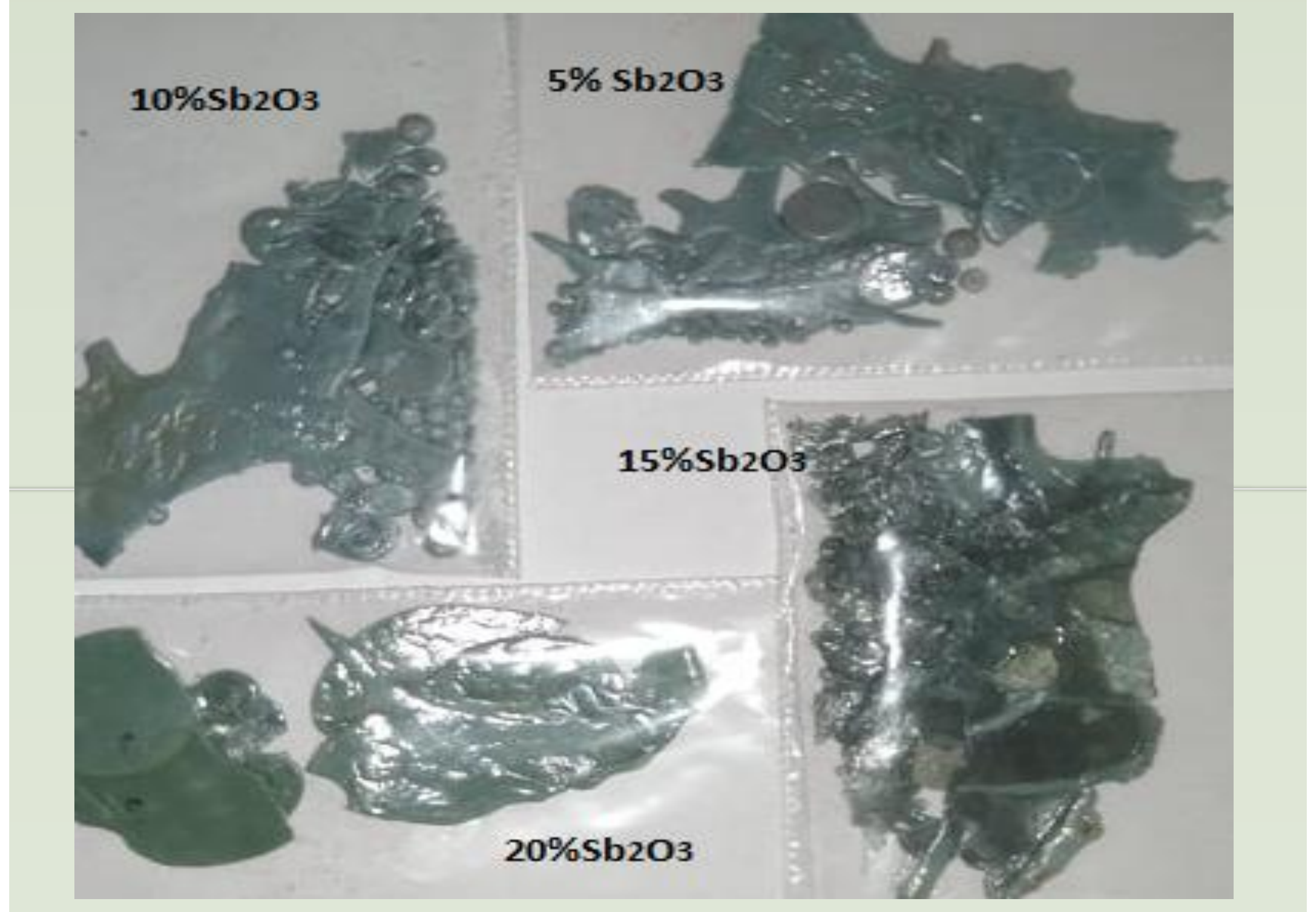


Figure 1: a) XRD difractograms and b) FujiFilm images of $xSb_2O_3·5MnO_2·[9Pb·PbO_2]$ samples where x = 0 - 40 mol% Sb_2O_3.

The **X - ray patterns** of studied samples (*Figure 1a)* indicate the presence of the $PbO·PbSO_4$ crystalline phase with monoclinic structure and metallic Pb with cubic structure for samples with x ≤ 15 mol% Sb_2O_3. By addition of lower Sb_2O_3 content up to 15 mol% in the vitroceramic network the amount of these crystalline phases were decreased. For the samples with x ≥ 20 mol% Sb_2O_3 an amorphous structure were evidenced. The compositional evolution of the IR spectra (Figure 2) shows the following structural modifications by doping: i) the decrease of intensity of the IR bands situated at 600, 1050 and 1150 cm^{-1} due to the sulfate units; ii) the appearance of new IR bands situated in the region between 750 and 950 cm^{-1} (corresponding to the $[PbO_n]$ structural units with n = 3,4 and 6) for samples with higher Sb_2O_3 contents over 15 mol%; iii) an increasing trend of the IR bands located between 950 and 1250cm^{-1} towards higher wavenumbers and enriched intensities at higher dopant level. By doping the excess of oxygen atoms can be accomodated in the host matrix by the formation of $[PbO_n]$ structural units (with n = 3, 4 and 6) and $SbO_3]$ structural units (IR band centered at about 600 cm-1).

UV-Vis data show an intense band centered at about 310 nm corresponding to the electronic transitions due to the Pb^{+2} ions (see *Figure 3*). By doping the intensity of this band was decreased. This evolution suggests that for higher dopant level, the modifications take place in the host matrix related mainly to the $[PbO_4]$ and $[PbO_6]$ structural units.

Cyclic voltammograms illustrated in *Figure 4* show much more formed the oxidation and reduction waves for the sample with 30 mol% Sb_2O_3 compatively with undoped sample.

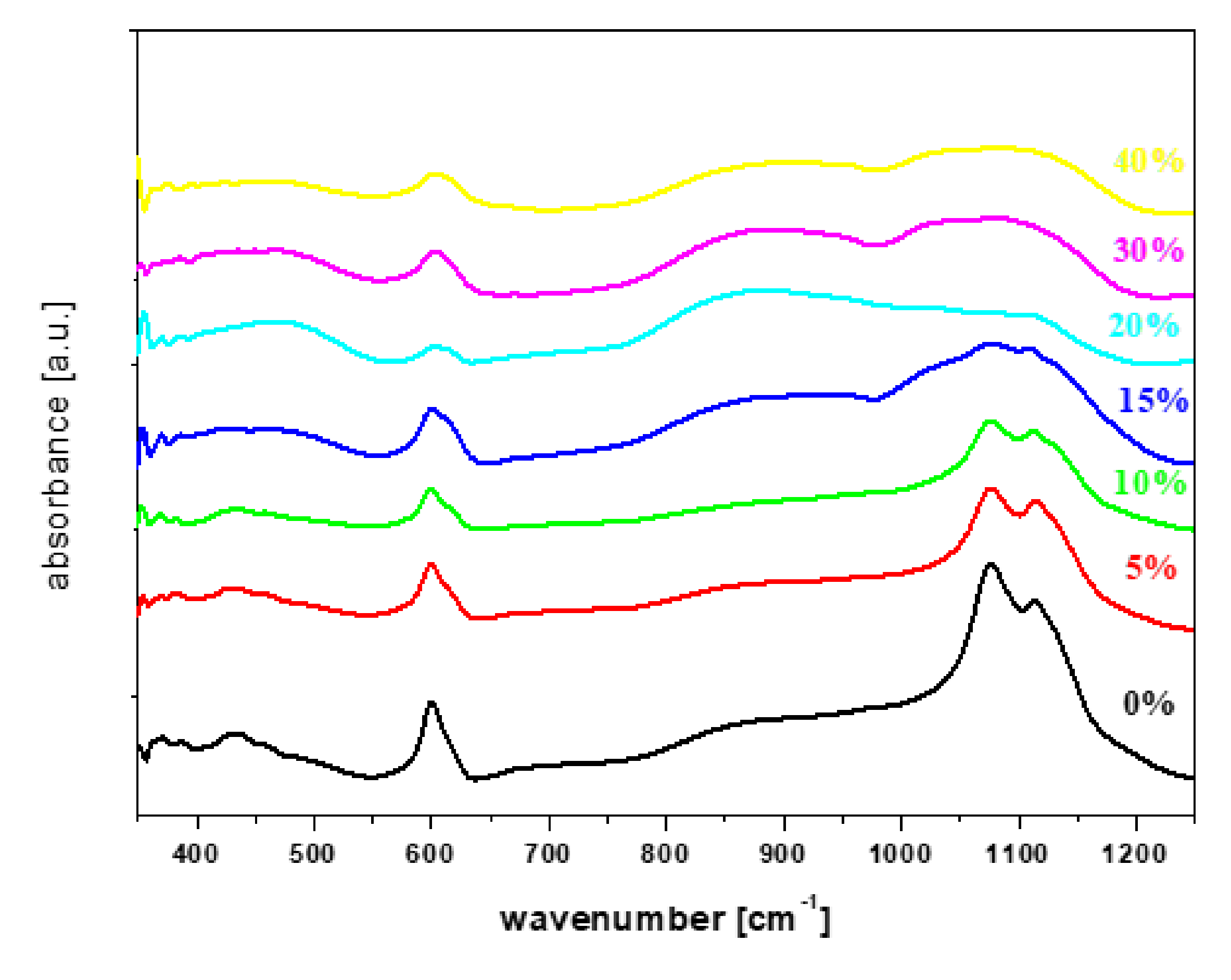


Figure 2: FTIR spectra of $xSb_2O_3·5MnO_2·[9Pb·PbO_2]$ samples where x = 0 - 40 mol% Sb_2O_3.

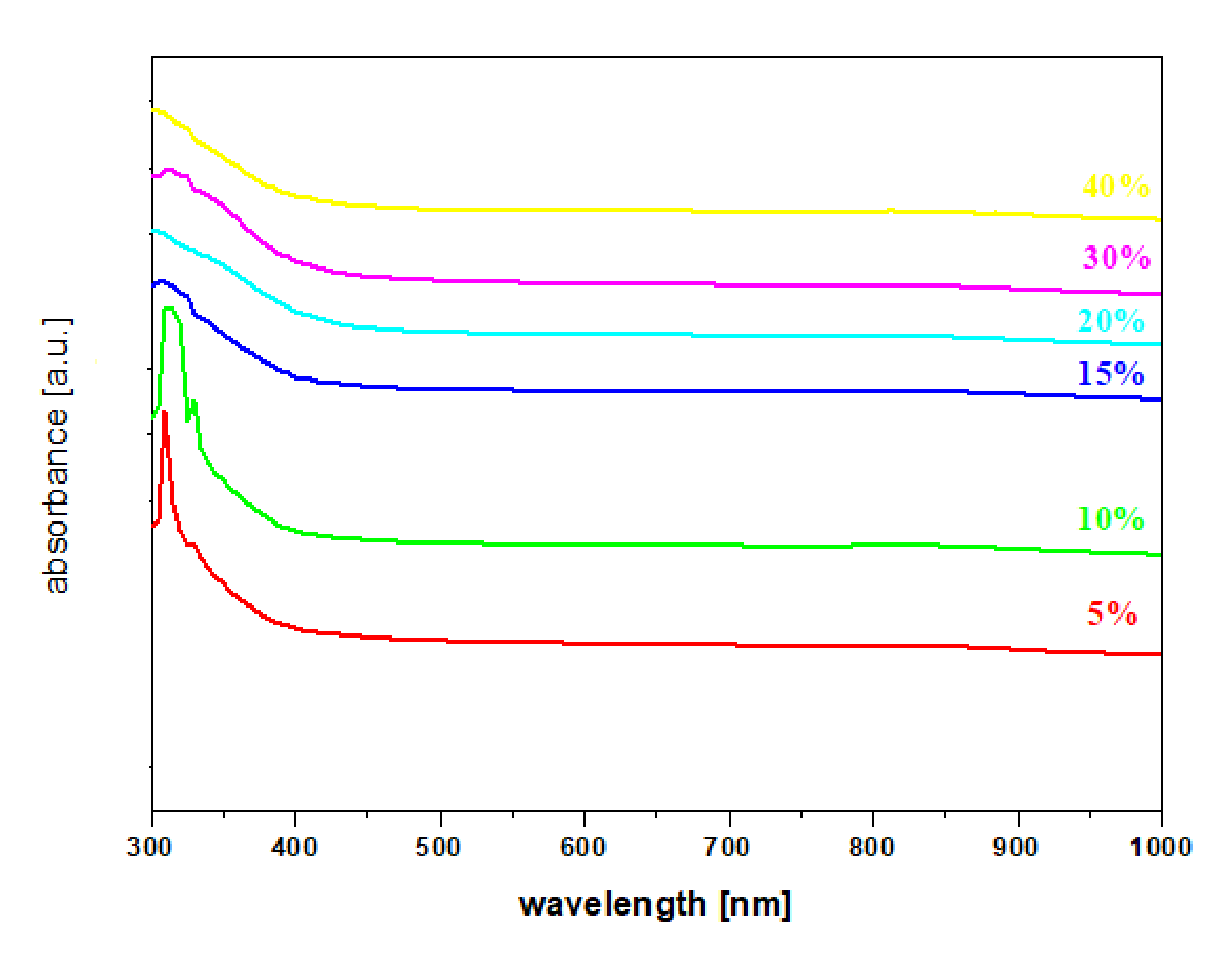


Figure 3: UV-VIS spectra of the $xSb_2O_3·5MnO_2·[9Pb·PbO_2]$ samples where x = 0 - 40 mol% Sb_2O_3.

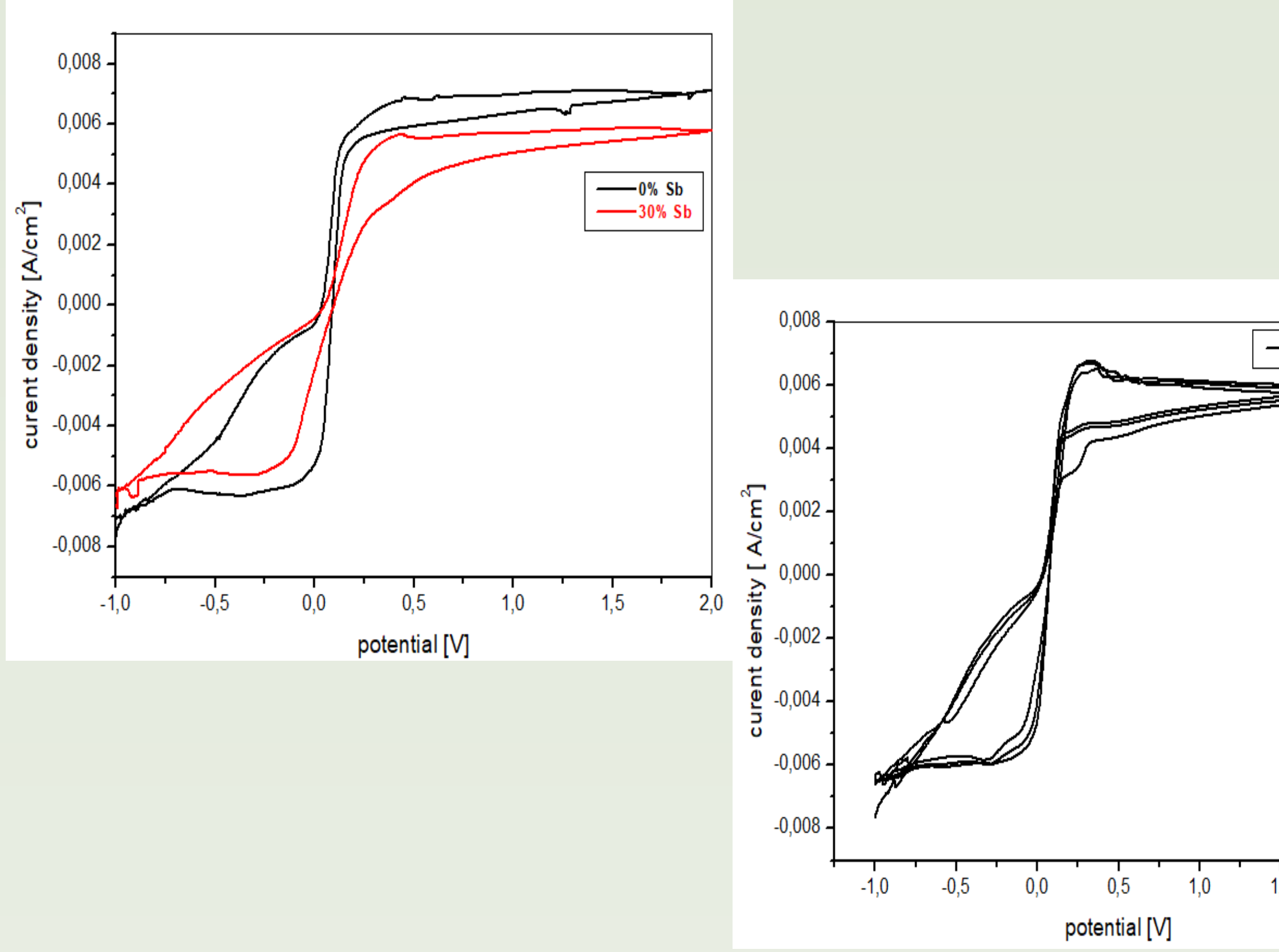


Figure 4: Cyclic voltammograms of studied samples in the $xSb_2O_3·5MnO_2·(9Pb\text{-}PbO_2)$ composition where x=0-30 mol% Sb_2O_3 as working electrod performed between -1.0 V and -0.50 V with a scan rate of 0.1mV/s in 38% H_2SO_4 aqueous solution.

Conclusions

In this study, a series of new $xSb_2O_3·5MnO_2·[9Pb·PbO_2]$ glasses and glass ceramics with x = 0 - 40mol% Sb_2O_3 were prepared by melt-quenching method using as raw materials the spent plates of a car battery. Their structure, optical and electrochemical properties were investigated by XRD, FTIR and UV-VIS spectroscopies and cyclic voltammetry measurements. XRD data reveal the presence of $PbOPbSO_4$ crystalline phase with monoclinic structure in the vitroceramics with x ≤ 15 mol% Sb_2O_3. By increasing of the dopant level up to 20 mol% Sb_2O_3 an amorphous structure can be evidenced. IR data show the decrease of sulphate units and the formation of $[PbO_n]$ structural units with n = 3, 4 and 6 by adding of Sb_2O_3 contents in the host matrix. The intensity of the UV-Vis band centered at about 310 nm due to the free Pb^{+2} ions were decreased by doping, in agreement with IR data (the high-coordinated lead atoms were increased). Recycled and manganese-antimony samples show electrochemical performances.

References : S. Rada, et. all, J. Electroanalytical Chemistry 780 (2016) 187.

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