Structural, Optical, and Magnetic Studies of the Metallic Lead Effect on MnO$_2$-Pb-PbO$_2$ Vitroceramics

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Abstract: MnO$_2$-lead materials have attracted attention in their applications as electrodes. This work reports a detailed spectroscopic study of the compositional variation of MnO$_2$-xLead vitroceramic materials with varied Pb contents. The concentration variation of lead and manganese ions is systematically characterized through the analysis of X-ray diffraction (XRD), Fourier transform infrared (FTIR), ultraviolet–visible (UV–Vis), and electron paramagnetic resonance (EPR) spectroscopy. The MnO$_2$-xLead samples consist of a vitroceramic structure with Pb, PbO, PbO$_2$, and Mn$_3$O$_4$ crystalline phases. The introduction of higher Pb content in the host vitroceramic reveals the [PbO$_6$] $\rightarrow$ [PbO$_n$], where $n = 3, 4$, and the formation of distorted [MnO$_6$] octahedral units. The UV–Vis data of the samples possess the intense bands between 300 and 500 nm, which are due to the presence of divalent lead ions (320 nm) and divalent and trivalent manganese ions (420 and 490 nm, respectively) in the structure of glass ceramics. The EPR data show resonance lines located around $g \approx 8$ and $4.3$, and a sextet hyperfine structure at $g \approx 2$, which is ascribed to the Mn$^{+3}$ and Mn$^{+2}$ ions.

Keywords: MnO$_2$-Pb-PbO$_2$; XRD; IR; UV–Vis; EPR

1. Introduction

Lead-containing glass and vitroceramics can be produced via the melt-quenching method at a low temperature [1–3]. Nowadays, lead glass and vitroceramics containing different transition metal ions can be used in optoelectronics and adacousto-optics for the production of devices and electrodes in batteries [4–8].

The manganese ions may enhance the chemical resistance of the lead network due to its unique chemistry. Different manganese ions, such as Mn$^{+2}$ and Mn$^{+3}$ ions, are known as paramagnetic ions. In glass and vitroceramics, the amount of these species depends on the mobility of the cations, field strength, condition of melting, concentration of manganese in the host matrix, glassy modifiers, and formers [9].

Manganese oxide materials, namely MnO$_2$ and Mn$_3$O$_4$, are considered some of the most promising electrode materials because they are inexpensive, eco-friendly, and have a highly specific capacitance and cycling stability [10].

Oxide glass and vitroceramics doped with transition metal ions, such as MnO$_2$, are technologically important because they contain semiconductor and photo-conduction properties, switching behavior, and good optical absorption [11]. The tetrahedral or octahedral geometries of the manganese ions incorporated into the host network by varying the composition of glass or vitroceramic can be performed in the EPR and UV–Vis spectra.

In order to better understand manganese-lead glass and vitroceramics from an application point of view, the study of structure is necessary. The MnO$_2$-Pb-PbO$_2$ vitroceramics can be used as electrodes for lead acid battery [8]. The present paper evidences structural information on the MnO$_2$-xLead vitroceramic materials with $x = 0$–100 mol% Pb. The molar percentage of manganese dioxide was constantly 15 mol% MnO$_2$. The effect of the substitution of lead dioxide by metallic lead on the host matrix was investigated through the
analysis of XRD, IR, and UV–Vis spectroscopy. In this context, the variation of manganese ions’ valence states as a function of Pb concentration was also studied using EPR spectroscopy. The role of the lead level on the structural aspects of MnO$_2$-xLead vitroceramics materials using a systematic study on spectroscopic characteristics was also investigated.

2. Experimental Procedure

The MnO$_2$-xLead samples with x = 0–100 mol% Pb were prepared from MnO$_2$, PbO$_2$, and metallic Pb powders. The fine mixtures of substances were melted in a sintered alumina crucible using an electric furnace set to 850 °C for 10 min. The melt was rapidly cooled on a steel plate.

The flow diagram of the synthesis and the Fujiﬁlm images of the obtained samples are shown in Figure 1. The samples have a metallic appearance and are black in color. The composition of the MnO$_2$-xLead prepared samples is listed in Table 1.

![Flow diagram of the synthesis and Fujiﬁlm images of prepared MnO$_2$-xLead materials](image)

**Figure 1.** (a) Flow diagram of the synthesis; (b) Photographic images of prepared MnO$_2$-xLead materials. Fujiﬁlm photographic images of prepared MnO$_2$-xLead materials.

X-ray diffractograms were obtained at room temperature with a Shimadzu XRD-6000 diffractometer using the fine powder sample and an increment of 0.02°·s$^{-1}$.

IR absorption spectra were recorded using the JASCO 6200 FTIR spectrometer. The FTIR measurements were carried out at a resolution of 4 cm$^{-1}$.

UV–Visible spectra of the samples were recorded using a Perkin-Elmer Lambda 45 UV/VIS spectrometer with an integrated sphere and a resolution of 2 nm. The sample-to-KBr ratio was 1:150.
Electron paramagnetic resonance (EPR) spectroscopy measurements were performed using a Bruker ELEXSYS 500 spectrometer in X-band. The samples were introduced in the glass tube using equal amounts of samples.

Table 1. Description of prepared MnO$_2$-xLead materials.

| Notation of MnO$_2$-xLead Vitroceramic Materials | Composition of MnO$_2$-xLead Vitroceramic Materials |
|-------------------------------------------------|-------------------------------------------------|
| 0.15MnO$_2$·0.85(1−x)PbO$_2$·xPb | 0.15MnO$_2$·0.85PbO$_2$ |
| x = 0 mol% Pb | 0.15MnO$_2$·0.85PbO$_2$ |
| x = 10 mol% Pb | 0.15MnO$_2$·0.85[0.9PbO$_2$·0.1Pb] |
| x = 20 mol% Pb | 0.15MnO$_2$·0.85[0.8PbO$_2$·0.2Pb] |
| x = 30 mol% Pb | 0.15MnO$_2$·0.85[0.7PbO$_2$·0.3Pb] |
| x = 40 mol% Pb | 0.15MnO$_2$·0.85[0.6PbO$_2$·0.4Pb] |
| x = 50 mol% Pb | 0.15MnO$_2$·0.85[0.5PbO$_2$·0.5Pb] |
| x = 60 mol% Pb | 0.15MnO$_2$·0.85[0.4PbO$_2$·0.6Pb] |
| x = 70 mol% Pb | 0.15MnO$_2$·0.85[0.3PbO$_2$·0.7Pb] |
| x = 80 mol% Pb | 0.15MnO$_2$·0.85[0.2PbO$_2$·0.8Pb] |
| x = 90 mol% Pb | 0.15MnO$_2$·0.85[0.1PbO$_2$·0.9Pb] |
| x = 100 mol% Pb | 0.15MnO$_2$·0.85Pb |

3. Results and Discussion

3.1. Structural Investigation by X-ray Diffraction (XRD)

X-ray patterns of the MnO$_2$-xLead samples are shown in Figure 2. The XRD data confirm the vitroceramic structure of all prepared samples. The diffraction peaks correspond to the Pb crystalline phase (pdf. no. 00-004-0686) as the main phase and small amounts of PbO$_2$ (00-052-0752), PbO (01-072-0093), and Mn$_3$O$_4$ (pdf. no. 00-018-803) crystalline phases.

![Figure 2](https://example.com/figure2.png)

Figure 2. X-ray diffractograms for the prepared MnO$_2$-xLead materials, where x = 0–100 mol% Pb.
3.2. **Structural Investigations by IR Spectroscopy**

The MnO$_2$-xLead vitroceramic materials, where $x = 0$–100 mol% Pb, were investigated by IR spectroscopy in order to obtain information concerning the compositional evolution of the structural units with the addition of the Pb content in the vitroceramic matrix. The obtained IR spectra are shown in Figure 3. Wavenumbers and the assignment of the IR bands characteristic of different structural units of the vitroceramic matrix are listed in Table 2.

![Figure 3. FTIR spectra of the MnO$_2$-xLead vitroceramic materials, where (a) $x = 0$–50 mol% Pb and (b) $x = 50$–100 mol% Pb. (c) Deconvoluted IR spectrum for the sample with $x = 30$ mol% Pb.](image-url)
Figure 3. FTIR spectra of the MnO$_2$ - xLead vitroceramic materials, where (a) $x = 0$–50 mol% Pb and (b) $x = 50$–100 mol% Pb. (c) Deconvoluted IR spectrum for the sample with $x = 30$ mol% Pb.

Table 2. Wave numbers and IR band assignments for the MnO$_2$-xLead vitroceramic materials.

| Wave Number [cm$^{-1}$] | IR Band Assignment |
|-------------------------|---------------------|
| 370–400                 | Stretching (elongation) vibrations of the Mn$^{3+}$-O bond |
| 470                     | Deformation (bending) vibrations of Pb-O-Pb and O-Pb-O angles in [PbO$_4$] structural units |
| 480                     | Deformation vibrations of O-Mn-O angles in octahedral [MnO$_6$] structural units |
| 520                     | Specific vibrations of different types of Mn-O bonds in distorted octahedra |
| 580–600                 | Vibrations specific to Mn-O-Mn type bonds |
| 650–850                 | Elongation vibrations of the Pb-O bond in [PbO$_{n}$] structural units where $n = 3$ and 4 |
| 875                     | Elongation vibrations of the Pb-O bond in [PbO$_{n}$] structural units |
| 900–1100                | Elongation vibrations of the Pb-O bond in [PbO$_{n}$] structural units |

The IR band situated at $\sim$470 cm$^{-1}$ came from two contributions, namely, the deformation vibrations of the Pb-O-Pb and O-Pb-O angles in the [PbO$_4$] units [12] superimposed with the bending vibrations of the O-Mn-O angles from [MnO$_6$] octahedral units [13]. The intensity of this IR band increased up to a maximum value for the sample with 50 mol% Pb. The IR band centered at 880 cm$^{-1}$ corresponded to the stretching vibrations of the Pb-O bonds in the [PbO$_{n}$] units.

The IR band located at 520 cm$^{-1}$ corresponded to the stretching vibrations of the Mn-O bonds from distorted octahedral units. After introducing the dopant level up to $x \leq 90$ mol% Pb, this IR band became well-formed, and its intensity was enriched slightly.

The IR band located at 580 cm$^{-1}$ corresponded to the deformation vibrations of the Mn-O-Mn angles. This IR band appeared well-formed for samples with $x \leq 40$ mol% Pb. The PbO$_2$-MnO$_2$ consisted of [PbO$_{n}$] structural units with $n = 3, 4,$ and 6, as well as distorted octahedral [MnO$_6$] units between them, connected by Pb-O-Pb and Mn-O-Mn bridges.
Through the addition of lower Pb contents up to $x \leq 40$ mol%, the amount of these structural units increased due to the excess of non-bonding oxygen. By increasing the dopant level above $x \geq 50$ mol% Pb, the Mn-O-Mn linkages were broken and the affinity of lead atoms towards unbounded oxygen atoms from distorted [MnO$_6$] octahedral units produced an increase in the fractions of [PbO$_n$] structural units with $n = 3, 4,$ and 6 reaching maximum values for the sample with $x = 70$ and 80 mol% Pb.

The second region of intense IR bands, situated between 750 and 1100 cm$^{-1}$, corresponded to the stretching vibrations of the Pb-O bond in the [PbO$_n$] units ($n = 3$ and 4). Through the gradual addition of metallic lead in the host matrix up to $x \leq 40$ mol%, the intensity of the bands located in this region increased and showed a tendency to move towards higher wave numbers. The excess oxygen can be accommodated in the host matrix by the formation of [PbO$_n$] structural units with $n = 3, 4,$ and 6. For samples with $x \geq 50$ mol% Pb, a tendency of displacement of the IR bands towards higher wave numbers was evidenced, indicating the increase of [PbO$_n$] structural units with $n = 3$ and 4.

The IR band from 875 cm$^{-1}$ was assigned to the [PbO$_6$] structural units. The intensity of this IR band increased up to $x \leq 70$ mol% Pb, and then decreased and reached a maximum value for the sample with $x = 70$ mol% Pb.

For the sample with 100 mol% Pb containing the 0.15MnO$_2$·0.85Pb composition, the formation of a glass–ceramic structure was identified due to the ability of lead atoms to form [PbO$_n$] units (some structural units [PbO$_6$]-band IR from 875 cm$^{-1}$ decreased in intensity) and manganese to form distorted [MnO$_6$] structural units interspersed between Pb-O-Pb linkages.

For the validation of the results, a deconvolution procedure of IR spectra was applied using a Gaussian-type function with fit multi-peaks of the Origin software. The deconvoluted IR spectrum of the sample with 30 mol% Pb is shown in the Figure 3c. The parameters of deconvolution, such as location of the center, C and integral intensity, A of detected IR peaks of deconvolution, are summarized in Table 3. Information concerning the compositional evolution of [MnO$_4$], [PbO$_4$], and [PbO$_n$] structural units, as well as Pb-O-Pb and Mn-O-Mn bridges with increasing Pb content, can be obtained from their integral intensity. Our results show that the integral intensities of these structural units depend on the Pb content.

The fractions of [PbO$_6$] structural units give the maximum values for the samples with $x = 20, 50,$ and 90 mol% Pb. The integral intensity of the [PbO$_3$] structural units decreased abruptly for the sample with $x = 50$ mol% Pb, and after that, its area increased up to 100 mol% Pb. The areas of the Pb-O-Pb and Mn-O-Mn bridges were enriched for the vitroceramics with $x = 60$ and 80 mol% Pb, respectively. A trend of formation of the Mn-O-Mn bridges can be evidenced up to 60 mol% Pb when the enrichment of the integral intensity of [MnO$_6$] structural units was reached by adding a Pb level up to 80 and 90 mol% Pb.

The IR data indicate the following structural modifications through the introduction of varied dopant levels: (i) For low Pb contents up to $x \leq 40$ mol%, the host vitroceramic adapts with the excess lead by involving it in the formation of [PbO$_n$] polygons ($n = 3$ and 4) and distorted [MnO$_6$] octahedral units. The polymerization degree of the lead–manganese vitroceramic increased and the number of Mn-O-Mn fractions attained a maximum value; (ii) By increasing the lead content from $50 \leq x \leq 70$ mol% Pb, the Mn-O-Mn bonds in the host vitroceramic were broken and the number of [PbO$_n$] structural units increased; (iii) At high dopant concentrations $70 < x \leq 90$ mol% Pb, the inadequacy of [PbO$_n$] octahedral units with the excess oxygen will produce their conversion into [PbO$_n$] structural units ($n = 3$ and 4). (iv) The Pb-MnO$_2$ matrix consists mainly of [PbO$_n$] structural units and some distorted [MnO$_6$] octahedral units.

The structural effect of Pb in MnO$_2$-Pb-PbO$_2$ vitroceramics is distinguished by the role as network former and modifier. At smaller Pb contents, the lead atoms prefer [PbO$_4$] tetrahedral units and distorted [PbO$_6$] structural units. This is accompanied by the simultaneous conversion of [MnO$_4$] into [MnO$_6$] structural units. At higher Pb levels, glass–ceramics are
characterized by the presence of a number of \([\text{PbO}_n]\) polyhedrons \(n = 3\) and \(4\), which act as a network modifier and remain in the structure as \(\text{Pb}^{2+}\) ions.

Table 3. Parameters (location of the center, C and integral intensity, A of IR peak) of deconvolution of the FTIR spectra of the MnO\(_2\)-xLead vitroceramic materials, where \(x = 0–100\) mol\% Pb.

| Samples \(x = \%\) | Assignments of the Detected Peaks | \(\text{Pb-O-Pb}\) | \([\text{MnO}_6]\) | \(\text{Mn-O-Mn}\) | \([\text{PbO}_n]\) | \([\text{PbO}_3]\) | \([\text{PbO}_4]\) |
|-----------------|----------------------------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(x = 0\%\)    | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 476              | 550             | 554             | 688             | 870             | 892             |
|                 | \(A\hbox{ [a.u.]}\)               | 5.75             | 2.28            | 0.21            | 0.83            | 6.005           | 12.26           |
| \(x = 10\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 475              | 520             | 581             | 680             | 840             | 923             |
|                 | \(A\hbox{ [a.u.]}\)               | 6                | 3               | 3               | 3               | 2               | 15              |
| \(x = 20\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 462              | 520             | 580             | 700             | 832             | 913             |
|                 | \(A\hbox{ [a.u.]}\)               | 1.44             | 8               | 1               | 1               | 3               | 19.32           |
| \(x = 30\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 470              | 520             | 688             | 752             | 870             | 950             |
|                 | \(A\hbox{ [a.u.]}\)               | 6                | 4.1             | 4.5             | 2.22            | 12.01           | 16.03           |
| \(x = 40\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 470.2            | 520             | 689             | 752.3           | 870             | 950             |
|                 | \(A\hbox{ [a.u.]}\)               | 6.01             | 4.1             | 4.55            | 2.23            | 20.22           | 16.05           |
| \(x = 50\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 470              | 553             | 600             | 778             | 870             | 970             |
|                 | \(A\hbox{ [a.u.]}\)               | 7.11             | 4.56            | 1.01            | 5.15            | 25.55           | 2.02            |
| \(x = 60\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 476              | 520             | 590             | 700             | 870             | 950             |
|                 | \(A\hbox{ [a.u.]}\)               | 7.88             | 5.55            | 6.56            | 2.34            | 19.9            | 22.43           |
| \(x = 70\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 475              | 520             | 600             | 680             | 875             | 970             |
|                 | \(A\hbox{ [a.u.]}\)               | 8.88             | 4.55            | 1.54            | 10.66           | 16.78           | 23.45           |
| \(x = 80\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 470              | 550             | 600             | 785             | 870             | 950             |
|                 | \(A\hbox{ [a.u.]}\)               | 9.98             | 12.33           | 1.12            | 15.5            | 27.7            | 33.5            |
| \(x = 90\%\)   | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 486              | 520             | 600             | 720             | 877             | 950             |
|                 | \(A\hbox{ [a.u.]}\)               | 7.78             | 14.89           | 2.3             | 1.12            | 28.9            | 40.5            |
| \(x = 100\%\)  | \(C\hbox{ [cm}^{-1}\hbox{]}\)    | 475              | 520             | 585             | 750             | 875             | 950             |
|                 | \(A\hbox{ [a.u.]}\)               | 2.34             | 3.44            | 2.11            | 1.11            | 23.67           | 42.30           |

3.3. Structural Investigation by UV–Vis Spectroscopy

The UV–Vis spectra of the MnO\(_2\)-xLead samples are shown in Figure 4. The first region of UV–Vis bands located between 200 and 300 nm is due to \(\pi-\pi^*\) transitions of the \(\text{Pb = O}\) bond in the \([\text{PbO}_3]\) structural units. The second region of UV–Vis bands located between 300 and 500 nm is due to the presence of \(\text{Pb}^{2+}\) (320 nm), \(\text{Mn}^{2+}\) (420 nm) [13,14], and \(\text{Mn}^{3+}\) (490 nm) ions [15] in the structure of glass ceramics. The band situated at about 420 nm is attributed to the transition of \(6\hbox{A}_1(S)\) to \(4\hbox{A}_1\) of \(\text{Mn}^{2+}\) ions [16].

By increasing the Pb content over 70 mol\%, the intensity of UV–Vis bands located in the range between 300 and 440 nm was enriched. This indicates an increase in the fractions of \(\text{Pb}^{2+}\) and \(\text{Mn}^{2+}\) ions by increasing the dopant level.

3.4. Optical Band Gap Energy

The variation of \((\alpha h\nu)^{1/2}\) and \((\alpha h\nu)^2\) as functions of photon energy, \(h\nu\), and the dependence of the \(x\) mol\% Pb on the optical band gap energy, \(E_g\), for the MnO\(_2\)-xLead samples are plotted in Figures 5 and 6. The value of \(E_g\) was determined by extrapolating the linear domain of the \((\alpha h\nu)^{1/2}\) and \((\alpha h\nu)^2\) graphs as a function of \(h\nu\) at \(\alpha h\nu \rightarrow 0\) [17]. The \(E_g\) values are situated between 2.47 and 2.65 eV for indirect transitions (with \(n = 2\)) and between 2.2–2.49 eV for direct transitions (with \(n = 1/2\)). This indicates a semiconductor behavior (gap energy, \(E_g < 3\) eV) for all samples.
3.3. Structural Investigation by UV–Vis Spectroscopy

The UV–Vis spectra of the MnO$_2$-xLead samples are shown in Figure 4. The first region of UV–Vis bands located between 200 and 300 nm is due to n-$\pi^*$ transitions of the Pb=O bond in the [PbO$_3$] structural units. The second region of UV–Vis bands located between 300 and 500 nm is due to the presence of Pb$^{+2}$ (320 nm), Mn$^{+2}$ (420 nm) [13,14], and Mn$^{+3}$ (490 nm) ions [15] in the structure of glass ceramics. The band situated at about 420 nm is attributed to the transition of $^6A_1$(S) to $^4A_1$ of Mn$^{+2}$ ions [16].

By increasing the Pb content over 70 mol%, the intensity of UV–Vis bands located in the range between 300 and 440 nm was enriched. This indicates an increase in the fractions of Pb$^{+2}$ and Mn$^{+2}$ ions by increasing the dopant level.

![Figure 4](image-url)

**Figure 4.** UV–Vis spectra of the MnO$_2$-xLead vitroceramic materials (a) x = 0–50 mol% Pb (b) x = 50–100 mol% Pb.

3.5. Structural Investigation by EPR Spectroscopy

The local geometry of the two manganese paramagnetic ions Mn$^{+2}$ and Mn$^{+3}$ was characterized by EPR spectroscopy. The EPR spectra of the MnO$_2$-xLead vitroceramic materials are shown in Figure 7. Our EPR data indicate that the local geometry around the paramagnetic ions depends on the Pb content of the host vitroceramic. The EPR spectra show three resonance lines: two absorption signals centered at $g \sim 2$ and $g \sim 4.3$ corresponding to the Mn$^{+2}$ ions [18–20], and the resonance line located at $g \sim 8$ is attributed to Mn$^{+3}$ ions.

The resonance line centered at $g \sim 2$ was assigned to isolated Mn$^{+2}$ ions located in sites with distorted octahedral geometry, as well as to those involved in dipole and/or superexchange magnetic interactions. Through the addition of metallic Pb up to $x \leq 60$ mol% in vitroceramics, this resonance line consisted of a poorly hyperfine structure superposed over a wider resonance line corresponding to the clustered Mn$^{+2}$ ions. For $x \geq 70$ mol% Pb,
this line became broader and more intense, becoming predominant in the EPR spectrum. This fact highlights the clustered nature of the main fraction of Mn$^{+2}$ ions.

The Mn$^{+2}$ ions at low manganese concentration had a hyperfine structure consisting of six resonance lines, which result from the dipole–dipole interaction between the magnetic moment of the $^{55}$Mn nucleus and the electronic moment of the paramagnetic Mn$^{+2}$ ion [16].

For the samples with $x \leq 60$ mol%, the gradual disappearance of the hyperfine structure in the vitroceramics by doping with Pb content suggested the improvement of dipole–dipole interactions. The addition of higher Pb concentrations ($x \geq 70$ mol% Pb) indicates an increase in magnetic exchange interaction.

The resonance signal located at $g \sim 4.3$ corresponded to a rhombic distorted geometry of isolated Mn$^{+2}$ ions. The intensity of this line decreased slightly with the addition of metallic Pb up to $x \leq 70$ mol%, after which it disappeared. For higher dopant concentrations above 70 mol% Pb, the Mn$^{+2}$ ions situated in isolated rhombic or distorted octahedral positions became clustered manganese ions. At higher metallic lead contents, $x \geq 80$ mol%, the structural disorder around the Mn$^{+2}$ ions increased, and these ions were present only as clustered Mn$^{+2}$ species.

The resonance line located at $g \sim 8$ was given by the Mn$^{+3}$ ions (at ~800G in the X band) [20]. Its intensity decreased with the introduction of Pb levels up to $x \leq 70$ mol%, and for higher concentrations, the resonance line was not detected. This structural evolution is explained through the Mn$^{+3} \rightarrow$Mn$^{+2}$ conversion (according to the UV–Vis data) by increasing the Pb content over $x \geq 70$ mol%.

Figure 4. UV–Vis spectra of the MnO$_2$-xLead vitroceramic materials...
Figure 5. Dependence of $(\alpha h\nu)^{1/2}$ as function of $h\nu$ and the dependence of $x$ mol% Pb on gap energy values for the $\text{MnO}_2$-xLeadvitroceramic materials (a) $x = 0$–50 mol% Pb (b) $x = 50$–100 mol% Pb.
Figure 6. Cont.
Figure 6. Dependence of $(\alpha h \nu)^2$ as function of $h \nu$ and the dependence of x mol% Pb on gap energy values for the MnO$_2$-xPb vitroceramic materials (a) $x = 0$–50 mol% Pb (b) $x = 60$–100 mol% Pb.
spectra show three resonance lines: two absorption signals centered at \( g \approx 2 \) and \( g \approx 4.3 \) corresponding to the Mn\(^{+2} \) ions \([18–20]\), and the resonance line located at \( g \approx 8 \) is attributed to Mn\(^{+3} \) ions. 

**Figure 7.** EPR spectra of the MnO\(_2\)-xLead vitroceramic materials. (a) \( x = 0–60 \text{ mol}\% \) Pb (b) \( x = 70–100 \text{ mol}\% \) Pb.

In conclusion, the effect of the Pb content on the host vitroceramic can be presented by two mechanisms: (i) For the vitroceramics with \( x \leq 70 \text{ mol}\% \) Pb, manganese ions are present in two valence states, Mn\(^{+2} \) and Mn\(^{+3} \). Mn\(^{+3} \) ions are obtained during synthesis, upon sudden cooling of the melt. There is a local ordering process of the oxygen atoms around the Mn\(^{+2} \) ion; (ii) For the vitroceramics with \( x \geq 80 \text{ mol}\% \) Pb, only clustered Mn\(^{+2} \) ions predominated in the studied vitroceramics.
4. Conclusions

In this paper, the structural properties of the $\text{MnO}_2$-$x\text{PbO}$ vitroceramic materials were investigated in order to find the role of lead content in the host matrix. The structural investigations of the prepared samples were realized by XRD, FTIR, UV–Vis, and EPR spectroscopy. The structure of the vitroceramic materials containing the $0.15\text{MnO}_2$-$0.85\text{Pb}_2\text{O}_5$, $0.15\text{MnO}_2$-$0.85\text{PbO}_2$, and $0.15\text{MnO}_2$-$0.85\%(1-x)\text{Pb}_2\text{O}_5$-$x\text{Pb}$ compositions depends on the lead content.

XRD data indicated vitroceramic structures for $\text{MnO}_2$-$x\text{PbO}$ samples. The analysis of IR data evidenced that the structures are mainly composed of [$\text{PbO}_n$] and [$\text{MnO}_n$] structural units. The presence of the lead and manganese ions were evidenced in the UV–Vis spectra.

The EPR data indicated three resonance lines. The resonance lines located at $g \approx 2$ and $4.3$ are due to $\text{Mn}^{2+}$ ions, while the last resonance signal corresponds to the $\text{Mn}^{3+}$ ions.

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