

# Characterization of iron phosphate glasses prepared by microwave heating

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## Abstract

Phosphate glasses have been prepared by melting batch materials in electric furnaces, induction furnaces, and in microwave ovens. In the present work mixtures of  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$  were exposed to microwave energy, heated to 1200 °C, and cast to produce iron phosphate glasses. Glasses were also produced in electric furnaces for comparison. The material was analyzed by X-ray diffraction, Mössbauer spectroscopy, and differential thermal analysis. For magnetite-based glasses produced in an electric furnace, the  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio is compatible with the value in the batch material. The  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio is higher for glasses produced in a microwave oven. Glasses with nominal composition  $55\text{Fe}_3\text{O}_4\text{-}45\text{P}_2\text{O}_5$  (mol%) produced in an electric furnace present an arranged magnetic phase with hyperfine field that could be associated to hematite (estimated to be 21%). All the glasses submitted to heat treatments for crystallization present the following crystalline phases:  $\text{FePO}_4$ ,  $\text{Fe}_3(\text{PO}_4)_2$ ,  $\text{Fe}(\text{PO}_3)_3$ ,  $\text{Fe}(\text{PO}_3)_2$  and  $\text{Fe}_7(\text{PO}_4)_6$ . The amount of these phases depends on the glass composition, and glass preparation procedure. Microwave heating allows to reach melting temperatures at high heating rates, making the procedure easy and economical, but care should be taken concerning the final  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio.

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## 1. Introduction

Phosphate glasses have been investigated since the 40s because they require relatively low melting temperatures (1100–1200 °C), and also show low glass transition temperatures [1]. However, they are susceptible to humidity and are not chemically durable [2].

Iron phosphate glasses have been prepared by melting inorganic compounds in electric furnaces, and induction furnaces [3–6]. It has been shown that after pre-heating, inorganic bath materials couple very well with the electromagnetic radiation in the rf range. It has also been demonstrated that the addition of iron improves the chemical

durability of phosphate glasses making them a potential material to be used in the immobilization of nuclear wastes [7,8]. The use of microwave in the materials processing has been intensively investigated because it provides a fast and homogeneous way to heat materials [9–12], and reduces the amount of  $\text{OH}^-$  species in the structure of the final product [13]. The microwave radiation interacts with ions and dipoles in the structure of the material increasing the temperature of the bulk [9,14].

The preparation of alkaline silicate glasses by microwave heating was previously reported [15]; however, the raw material had to be previously heated at 500 °C to allow the energy coupling. Ionic conductor glasses [16] and niobium phosphate glasses were also prepared by microwave heating [9]. A preliminary experience to produce an iron phosphate glass by microwave heating was conducted in

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the Energy and Nuclear Research Institute with the collaboration of the University of Missouri-Rolla (USA) [17]; however, no conclusive results were succeeded at that time.

In the present work, iron phosphate glasses were prepared by melting mixtures of magnetite or ferrite with a phosphate precursor in a microwave oven and some properties were compared with glasses of same nominal composition produced in an electric furnace. Mössbauer spectroscopy, X-ray diffraction, and differential thermal analysis were used to characterize these materials.

## 2. Experimental procedure

### 2.1. Microwave heating

Iron phosphate glasses ( $X$ )Fe<sub>3</sub>O<sub>4</sub> – (100 –  $X$ )P<sub>2</sub>O<sub>5</sub> ( $40 \leq X \leq 55$  mol%) and ( $X$ )Fe<sub>2</sub>O<sub>3</sub> – (100 –  $X$ )P<sub>2</sub>O<sub>5</sub> ( $40 \leq X \leq 50$  mol%) were prepared by mixing magnetite (Fe<sub>3</sub>O<sub>4</sub>) and ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>), or ferrite (Fe<sub>2</sub>O<sub>3</sub>) and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, respectively.

A kitchen type microwave oven (Panasonic, model NH-S69BH) with 1100 W nominal power was used for this purpose. The batch materials were mixed, manually homogenized with a pestle and a mortar, and pressed at 4 T/cm<sup>2</sup> in a stainless steel die, to produce 2.5 cm in diameter and 3 cm in thickness pellets, and finally melted in a microwave oven or in an electric furnace.

Each pellet was placed into an alumina crucible wrapped by a ceramic blanket (fiberfax) to guarantee the thermal isolation inside the microwave oven. An alumina lid was used to cover the crucible to reduce thermal losses.

To avoid fast heating rates when the oven is turned on, two glass beakers containing 100 ml of distilled water were placed inside the resonant cavity to absorb part of the microwave energy. As the water evaporates, the remaining energy is absorbed by the material. The system was allowed to rotate inside the oven to homogenize the radiation exposure. The oven was turned on at maximum nominal power for 30–40 min, until the liquid is formed. An optical pyrometer (Minolta model Ciclops 52) was used to monitor the liquid temperature inside the microwave oven. A hole of 1 cm in diameter was drilled on the top of the cavity to allow this measurement. The temperature of the liquid before casting was 1200 °C. The liquid was cast in a copper die previously cooled at 5 °C.

Glasses were prepared by melting similar batch compositions in an electric furnace (Lindenberg, model Blue M) by heating the material from room temperature to 1200–1400 °C at 10 °C/min, and keeping at this temperature during 1 h for homogenization. The temperature was selected for each composition according to the maximum temperature measured on the liquid melted in the microwave oven to maintain similar experimental conditions. No ceramic lid was placed on the top of the crucible at this time; however, to check any influence concerning the local atmosphere in the iron redox equilibrium, an alumina cover was used on the top of the crucible during the melt of some

glasses, as it was used in the microwave heating process. After melting, the liquid was cast in a copper mold previously cooled at 5 °C, pressed on the top by a metal pole to guarantee a homogeneous cooling rate. The material was then removed and manually ground.

Room temperature X-ray powder diffraction (XRD) data (Rigaku, model DMAX 100) were collected in the  $2\theta$  range of 10–80° with rate of 4 °/min using a Cu  $k_{\alpha}$  radiation. Some samples were crystallized by heating at the maximum crystallization temperature determined by the differential thermal analysis (DTA) during 24 h, and the crystalline phases were identified by the XRD patterns and the JCPDS files.

DTA (Setaram) were performed in the range of 20–900 °C, with heating rate of 10 °C/min, by using a dynamic synthetic air flow.

The Mössbauer spectra were obtained at room temperature with a conventional constant-acceleration spectrometer in a 10 mC Rh(<sup>57</sup>Co) source. The absorber unit was prepared by pressing the powder sample (0.2 g) between two Lucite plates 1.5 cm in diameter added to materials that are transparent to the radiation. The velocity of the source was calibrated using a pure iron foil that was also used as a reference for the isomer shift.

## 3. Results

### 3.1. XRD and DTA

All as-prepared materials show a broad diffraction halo in the X-ray diffraction patterns which are typical of amorphous structures, and no evidence of crystalline phase formation. However, after heat treatments at temperatures where exothermic peaks are depicted in the DTA curves, the diffraction patterns show diffraction peaks related to crystalline phases, which depend on the composition, and the heat treatment temperature.

The following results were obtained for glasses produced from a mixture of magnetite and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>. Fig. 1 shows the DTA curve for the 40Fe<sub>3</sub>O<sub>4</sub>–60P<sub>2</sub>O<sub>5</sub> glass prepared in an electric furnace. The glass transition temperature ( $T_g$ ) and the maximum crystallization temperatures ( $T_c$ 's) are depicted.

Figs. 2 and 3 show the XRD patterns after a heat treatment at 608 °C and 645 °C, respectively. The inset legends show the corresponding crystalline phases.

Fig. 4 shows the DTA curve for the 40Fe<sub>3</sub>O<sub>4</sub>–60P<sub>2</sub>O<sub>5</sub> glass produced in a microwave oven.

Figs. 5 and 6 show the XRD patterns after heat treatment at 644 °C and 683 °C, respectively.

Similar results have been obtained for the (45Fe<sub>3</sub>O<sub>4</sub>–55P<sub>2</sub>O<sub>5</sub>), (50Fe<sub>3</sub>O<sub>4</sub>–50P<sub>2</sub>O<sub>5</sub>), and (55Fe<sub>3</sub>O<sub>4</sub>–45P<sub>2</sub>O<sub>5</sub>) glasses produced in an electric furnace and in a microwave oven; however,  $T_g$ 's,  $T_c$ 's, and the crystalline phases vary depending on the glass composition.

Table 1 presents the values of  $T_g$ 's and  $T_c$ 's determined from the DTA curves for all magnetite-based glasses.

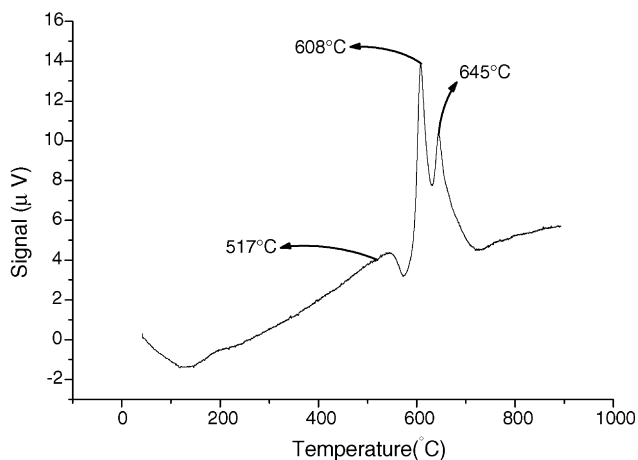


Fig. 1. DTA curve for the 40Fe<sub>3</sub>O<sub>4</sub>-60P<sub>2</sub>O<sub>5</sub> glass produced in an electric furnace.

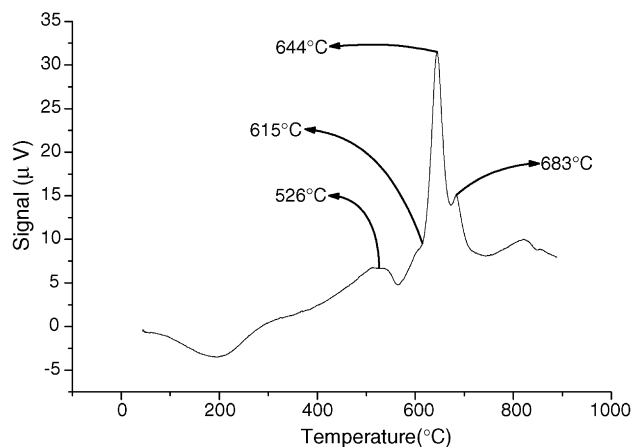


Fig. 4. DTA curve for the 40Fe<sub>3</sub>O<sub>4</sub>-60P<sub>2</sub>O<sub>5</sub> glass produced in a microwave oven.

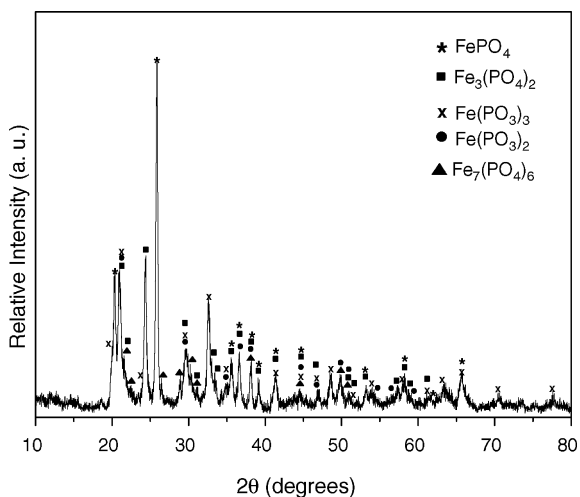


Fig. 2. XRD pattern of the 40Fe<sub>3</sub>O<sub>4</sub>-60P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 608 °C.

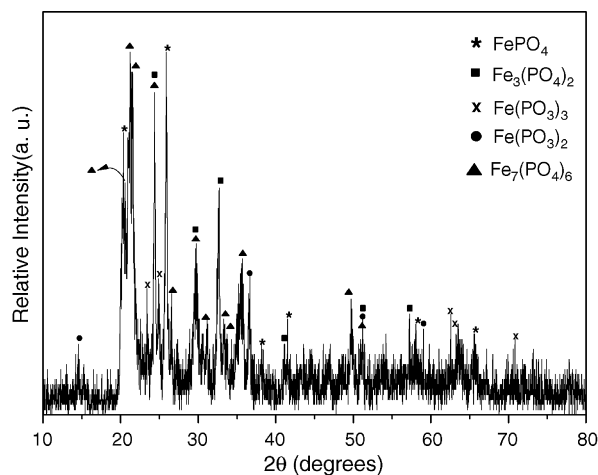


Fig. 5. XRD pattern of the 40Fe<sub>3</sub>O<sub>4</sub>-60P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 644 °C.

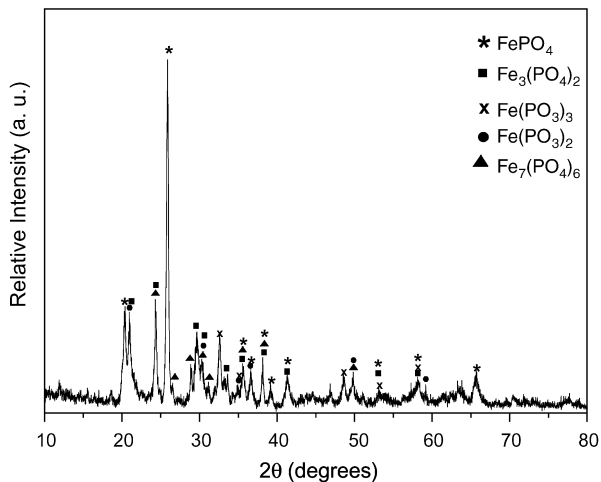


Fig. 3. XRD pattern of the 40Fe<sub>3</sub>O<sub>4</sub>-60P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 645 °C.

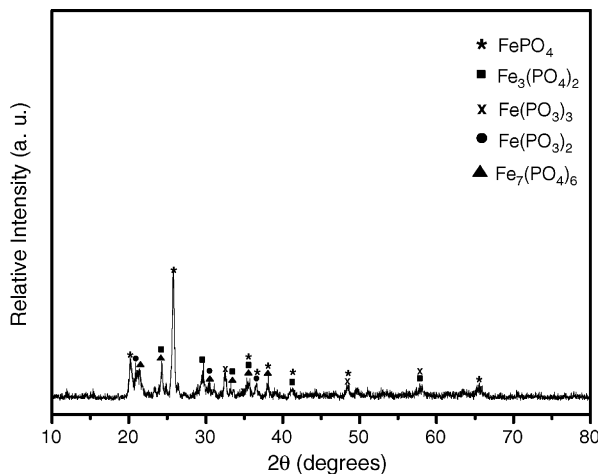


Fig. 6. XRD pattern of the 40Fe<sub>3</sub>O<sub>4</sub>-60P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 683 °C.

Table 1  
Values of  $T_g$ 's and  $T_c$ 's determined from the DTA curves for all magnetite-based glasses

Type of heating device	Nominal magnetite amount (mol%)	$T_g$ (°C)	$T_{c1}$ (°C)	$T_{c2}$ (°C)	$T_{c3}$ (°C)	$T_{c4}$ (°C)
Electric furnace	40	517 ± 5	608 ± 5	645 ± 5	–	–
	45	497 ± 5	605 ± 5	650 ± 5	715 ± 5	–
	50	497 ± 5	628 ± 5	675 ± 5	725 ± 5	–
	55	500 ± 5	630 ± 5	673 ± 5	723 ± 5	–
Microwave oven	40	526 ± 5	615 ± 5	644 ± 5	683 ± 5	–
	45	485 ± 5	622 ± 5	–	–	–
	50	503 ± 5	646 ± 5	673 ± 5	730 ± 5	–
	55	464 ± 5	609 ± 5	642 ± 5	698 ± 5	711 ± 5

The following results were obtained for glasses produced from ferrite. Fig. 7 shows the DTA curve for the 50Fe<sub>2</sub>O<sub>3</sub>–50P<sub>2</sub>O<sub>5</sub> glass produced in an electric furnace.

From the DTA curve in Fig. 7,  $T_g$  is determined to be 470 °C, and there are two exothermic peaks at 547 and 581 °C corresponding to three different processes of crystallization.

Figs. 8–10 show the XRD patterns for this glass after heat treating the material at 470, 547, and 581 °C, respectively.

Fig. 11 shows the DTA curve for the glass 50Fe<sub>2</sub>O<sub>3</sub>–50P<sub>2</sub>O<sub>5</sub> produced in a microwave oven.

From this curve the  $T_g$  was determined to be 445 °C, and three exothermic peaks corresponding to different crystallization processes are seen at 497, 548, and 578 °C.

Figs. 12–14 show the XRD patterns for the same glass after heat treating the material at 497, 548, and 578 °C, respectively.

Similar results have been obtained for the 45Fe<sub>2</sub>O<sub>3</sub>–55P<sub>2</sub>O<sub>5</sub> and 55Fe<sub>2</sub>O<sub>3</sub>–45P<sub>2</sub>O<sub>5</sub> glasses produced in an electric furnace and in a microwave oven; however,  $T_g$ 's,  $T_c$ 's, and the crystalline phases vary according to the glass

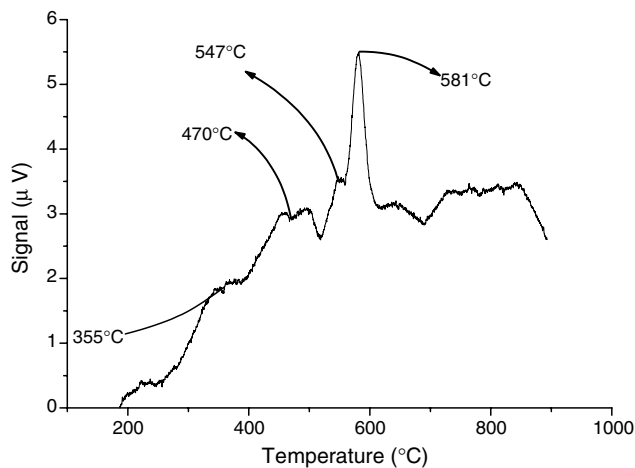


Fig. 7. DTA curve for the 50Fe<sub>2</sub>O<sub>3</sub>–50P<sub>2</sub>O<sub>5</sub> glass produced in an electric furnace.

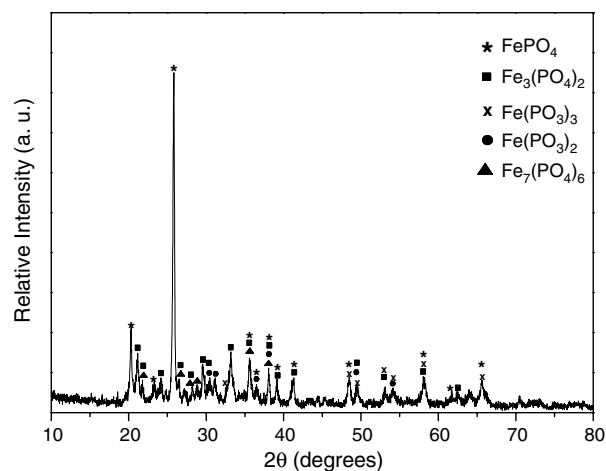


Fig. 8. XRD pattern of the 50Fe<sub>2</sub>O<sub>3</sub>–50P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 470 °C.

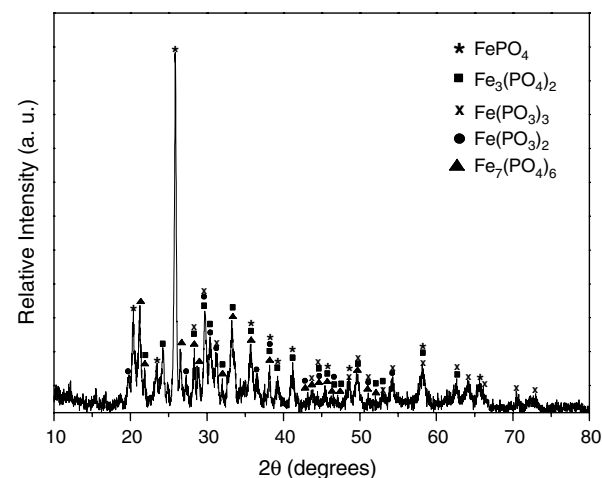


Fig. 9. XRD pattern of the 50Fe<sub>2</sub>O<sub>3</sub>–50P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 547 °C.

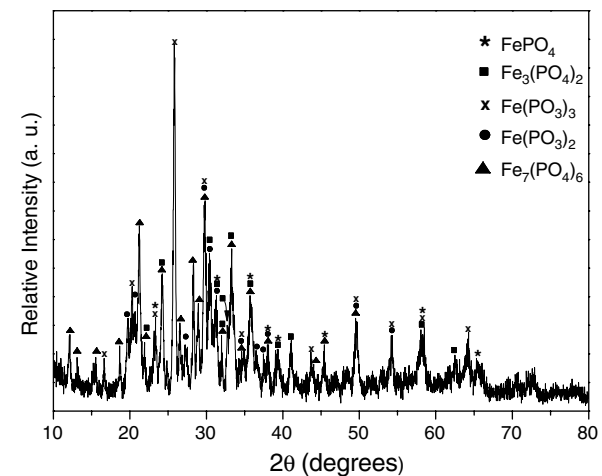


Fig. 10. XRD pattern of the 50Fe<sub>2</sub>O<sub>3</sub>–50P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 581 °C.

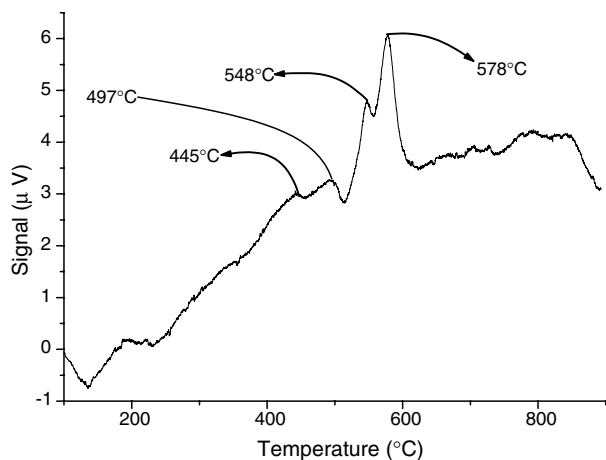


Fig. 11. DTA curve for the 50Fe<sub>2</sub>O<sub>3</sub>-50P<sub>2</sub>O<sub>5</sub> glass produced in a microwave oven.

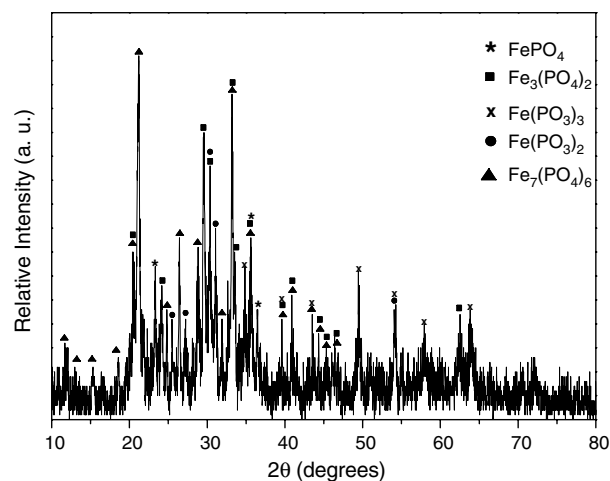


Fig. 14. XRD pattern of the 50Fe<sub>2</sub>O<sub>3</sub>-50P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 578 °C

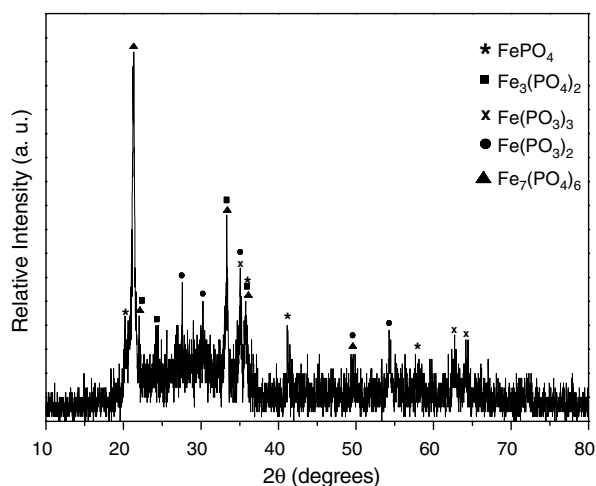


Fig. 12. XRD pattern of the 50Fe<sub>2</sub>O<sub>3</sub>-50P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 497 °C.

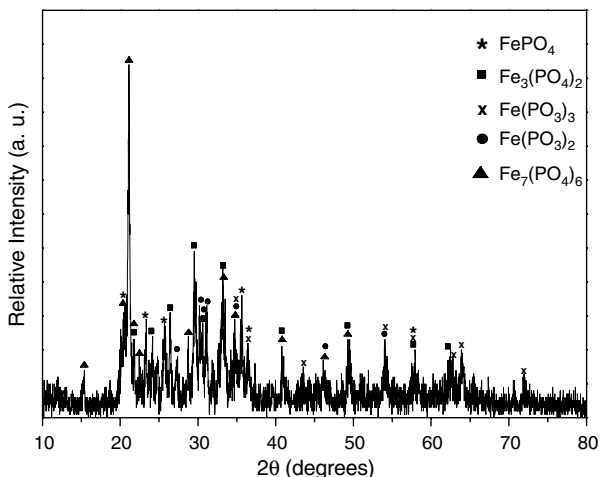


Fig. 13. XRD pattern of the 50Fe<sub>2</sub>O<sub>3</sub>-50P<sub>2</sub>O<sub>5</sub> glass after heat treatment at 548 °C.

Table 2

Values of  $T_g$ 's and  $T_c$ 's determined from the DTA curves for all ferrite-based glasses

Type of heating device	Nominal ferrite amount (mol%)	$T_g$ (°C)	$T_{c1}$ (°C)	$T_{c2}$ (°C)	$T_{c3}$ (°C)
Electric furnace	40	396 ± 5	487 ± 5	585 ± 5	715 ± 5
	50	470 ± 5	547 ± 5	581 ± 5	–
Microwave oven	40	400 ± 5	497 ± 5	578 ± 5	673 ± 5
	50	497 ± 5	548 ± 5	578 ± 5	–

composition. Table 2 presents the values of  $T_g$ 's and  $T_c$ 's determined from the DTA curves for two ferrite-based glasses.

### 3.2. Mössbauer spectroscopy

In the following discussion consider the index 1 related to the hyperfine parameters for the Fe<sup>2+</sup> sites, such as quadrupole splitting ( $\Delta_1$ ), isomer shift ( $\delta_1$ ), relative subspectral area (AR<sub>1</sub>) and the index 2 for the Fe<sup>3+</sup> sites, such as  $\Delta_2$ ,  $\delta_2$ , and AR<sub>2</sub>.

Fig. 15 shows the Mössbauer spectrum for the 40Fe<sub>3</sub>O<sub>4</sub>-60P<sub>2</sub>O<sub>5</sub> glass prepared in the microwave oven.

Similar spectra have been obtained for the 45Fe<sub>3</sub>O<sub>4</sub>-55P<sub>2</sub>O<sub>5</sub>, and the 50Fe<sub>3</sub>O<sub>4</sub>-50P<sub>2</sub>O<sub>5</sub> glasses produced in a microwave oven.

Fig. 16 shows the Mössbauer spectrum for the 55Fe<sub>3</sub>O<sub>4</sub>-45P<sub>2</sub>O<sub>5</sub> glass prepared in a microwave oven.

Table 3 presents the Mössbauer hyperfine parameters and relative subspectral area.

For the magnetite-based glasses produced in an electric furnace the Mössbauer spectra are similar and Table 4 presents the Mössbauer hyperfine parameters and relative subspectral area.

Ferrite-based phosphate glasses produced in a microwave oven show similar Mössbauer spectra. Fig. 17 shows

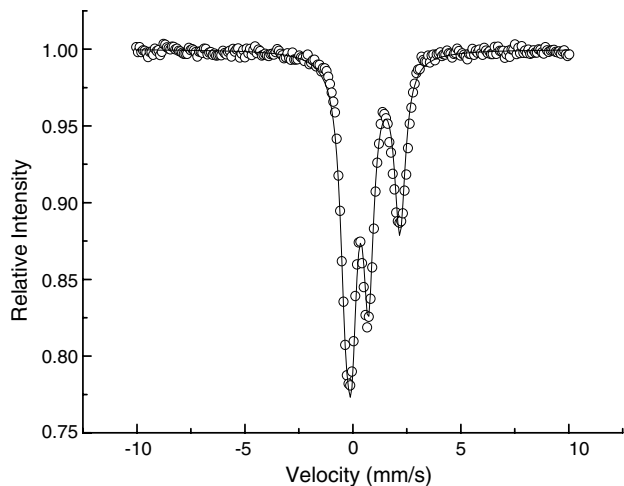


Fig. 15. Mössbauer Spectrum for the 40Fe<sub>3</sub>O<sub>4</sub>–60P<sub>2</sub>O<sub>5</sub> glass prepared in a microwave oven.

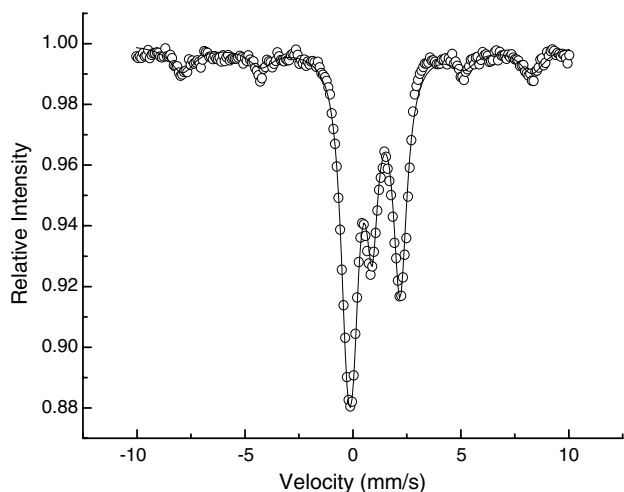


Fig. 16. Mössbauer spectrum for the 55Fe<sub>3</sub>O<sub>4</sub>–45P<sub>2</sub>O<sub>5</sub> glass prepared in a microwave oven.

Table 3

Mössbauer spectra parameters for glasses produced in a microwave oven: quadrupole splitting ( $\Delta$ ), isomer shift with respect to metallic iron ( $\delta$ ) and relative subspectral area (AR)

Nominal amount of magnetite in the batch material (mol%)	$\Delta_1$ (mm/s)	$\delta_1$ (mm/s)	AR <sub>1</sub> (%)	$\Delta_2$ (mm/s)	$\delta_2$ (mm/s)	AR <sub>2</sub> (%)
40	2.52	1.05	44	0.78	0.47	56
45	2.50	1.16	44	0.74	0.52	56
50	2.54	1.17	49	0.84	0.60	51
55	2.45	1.08	54	0.87	0.59	46

The standard deviation in  $\Delta$  and  $\delta$  is  $\pm 0.01$ .

the Mössbauer spectrum for the 55Fe<sub>3</sub>O<sub>4</sub>–45P<sub>2</sub>O<sub>5</sub> glass prepared in an electric furnace. Table 5 presents the Mössbauer hyperfine parameters and relative subspectral area.

Phosphate glasses produced from ferrite in an electric furnace show similar Mössbauer spectra. Table 6 presents

the Mössbauer hyperfine parameters and relative subspectral area.

#### 4. Discussion

From Table 1 it is observed that  $T_g$  values depend on the glass composition and the production procedure (including device used for heating, heating rate, soaking time, etc.). Some compositions show three to four crystallization peaks. The value of  $T_g$  varies from 464 to 526 °C.

From the XRD patterns shown in Fig. 2, it is possible to determine the crystalline phase formed after the heat treatment. The following crystalline phases were identified: FePO<sub>4</sub>, Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Fe(PO<sub>3</sub>)<sub>3</sub>, Fe(PO<sub>3</sub>)<sub>2</sub>, and Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>.

Base on the peak intensity of the XRD patterns shown in Fig. 2, it is inferred that the predominant crystalline phases of a crystallized 40Fe<sub>3</sub>O<sub>4</sub>–60P<sub>2</sub>O<sub>5</sub> glass are FePO<sub>4</sub> and Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Although Fig. 3 presents a similar XRD pattern, the peak intensities corresponding to the crystalline phase Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub> are approximately the same when compared to the ones of the phase Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, suggesting that the increase of the heat treatment temperature increases the amount of Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>.

For the 40Fe<sub>3</sub>O<sub>4</sub>–60P<sub>2</sub>O<sub>5</sub> glass produced in a microwave oven followed by a heat treatment at 644 °C, the predominant crystalline phases are FePO<sub>4</sub>, Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, and Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>. After heat treating the material at 683 °C the predominant phase is Fe(PO<sub>3</sub>)<sub>2</sub>.

There are no relevant differences in the XRD patterns for the 45Fe<sub>3</sub>O<sub>4</sub>–55P<sub>2</sub>O<sub>5</sub> glass produced in an electric furnace and heat treated at 605 and 650 °C, but the increase of the amount of the FePO<sub>4</sub> crystalline phase. However, for glasses heat treated at 715 °C, the amount of Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> increases.

For the crystallized 45Fe<sub>3</sub>O<sub>4</sub>–55P<sub>2</sub>O<sub>5</sub> glass produced in a microwave oven, the predominant crystalline phases are Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>, and Fe(PO<sub>3</sub>)<sub>2</sub>, however, the relative amount of the FePO<sub>4</sub> and Fe(PO<sub>3</sub>)<sub>3</sub> crystalline phases is small. According to the XRD relative peak intensities, the amount of these phases differs from the ones determined for the glasses prepared in an electric furnace.

For the 50Fe<sub>3</sub>O<sub>4</sub>–50P<sub>2</sub>O<sub>5</sub> glass produced in an electric furnace and heat treated at 628 °C, the predominant crystalline phases are FePO<sub>4</sub> and Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. When the temperature of crystallization is raised to 675 °C, the predominant phases are Fe(PO<sub>3</sub>)<sub>3</sub> and Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>. However, the relative amount of these crystalline phases is similar.

For the 50Fe<sub>3</sub>O<sub>4</sub>–50P<sub>2</sub>O<sub>5</sub> glass produced in a microwave oven,  $T_g$  is 503 °C and three maximum crystallization temperatures are observed at 646 °C, 673 °C, and 730 °C. Opposing to the glasses produced in an electric furnace, glasses produced in a microwave oven and later crystallized show that the predominant crystalline phases are Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub> and Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

For the 55Fe<sub>3</sub>O<sub>4</sub>–45P<sub>2</sub>O<sub>5</sub> glass produced in an electric furnace, the predominant crystalline phases are Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and FePO<sub>4</sub> when the glass is heat treated at 630 °C. It

Table 4

Mössbauer spectra parameters for glasses produced in an electric furnace: quadrupole splitting ( $\Delta$ ), isomer shift with respect to metallic iron ( $\delta$ ), hyperfine field ( $B_{\text{hf}3}$ ), and relative subspectral area (AR)

Nominal amount of magnetite in the batch material (mol%)	$\Delta_1$ (mm/s)	$\delta_1$ (mm/s)	AR <sub>1</sub> (%)	$\Delta_2$ (mm/s)	$\delta_2$ (mm/s)	AR <sub>2</sub> (%)	$B_{\text{hf}3}$ (T)	$\Delta_3$ (mm/s)	$\delta_3$ (mm/s)	AR <sub>3</sub> (%)
40	2.47	1.04	29	0.81	0.47	71	0	0	0	0
45	2.47	1.05	32	0.83	0.43	68	0	0	0	0
50	2.55	1.01	30	0.93	0.46	70	0	0	0	0
55	2.55	1.05	26	0.97	0.53	53	$51.2 \pm 0.1$	-0.26	0.45	21

The standard deviation in  $\Delta$  and  $\delta$  is  $\pm 0.01$ .

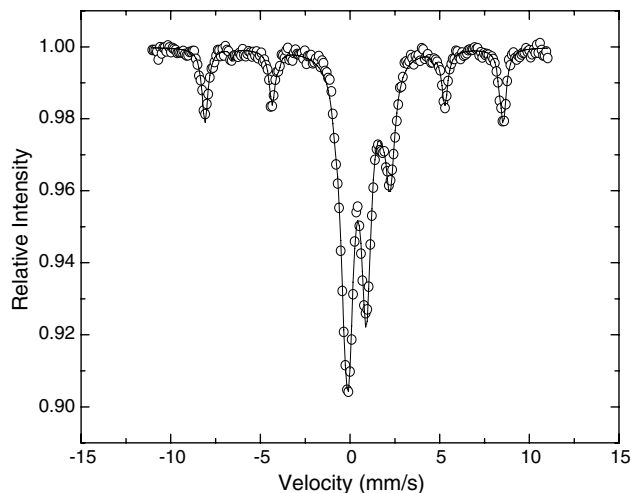


Fig. 17. Mössbauer spectrum for the  $55\text{Fe}_3\text{O}_4$ - $45\text{P}_2\text{O}_5$  glass prepared in an electric furnace.

Table 5

Mössbauer spectra parameters for glasses produced in a microwave oven: quadrupole splitting ( $\Delta$ ), isomer shift with respect to metallic iron ( $\delta$ ) and relative subspectral area (AR)

Nominal amount of ferrite in the batch material (mol%)	$\Delta_1$ (mm/s)	$\delta_1$ (mm/s)	AR <sub>1</sub> (%)	$\Delta_2$ (mm/s)	$\delta_2$ (mm/s)	AR <sub>2</sub> (%)
40	2.45	1.15	29	0.77	0.48	71
45	2.44	1.12	33	0.79	0.46	67
50	2.41	1.17	39	0.76	0.47	61

The standard deviation in  $\Delta$  and  $\delta$  is  $\pm 0.01$ .

Table 6

Mössbauer spectra parameters for glasses produced in an electric furnace: quadrupole splitting ( $\Delta$ ), isomer shift with respect to metallic iron ( $\delta$ ) and relative subspectral area (AR)

Nominal amount of ferrite in the batch material (mol%)	$\Delta_1$ (mm/s)	$\delta_1$ (mm/s)	AR <sub>1</sub> (%)	$\Delta_2$ (mm/s)	$\delta_2$ (mm/s)	AR <sub>2</sub> (%)
40	2.53	1.05	11	0.83	0.40	89
45	2.49	1.05	13	0.84	0.39	87
50	2.45	1.06	16	0.66	0.39	84

The standard deviation in  $\Delta$  and  $\delta$  is  $\pm 0.01$ .

seems that when the crystallization temperature is raised to  $673^\circ\text{C}$  the relative amount of  $\text{Fe}_7(\text{PO}_4)_6$  is similar to the  $\text{Fe}_3(\text{PO}_4)_2$  and  $\text{FePO}_4$ . However, when the crystallization

temperature is raised to  $723^\circ\text{C}$ ,  $\text{Fe}_3(\text{PO}_4)_2$  becomes the predominant crystalline phase again.

For  $55\text{Fe}_3\text{O}_4$ - $45\text{P}_2\text{O}_5$  glass produced in a microwave oven, four maximum crystallization peaks can be seen in the DTA curve at  $609^\circ\text{C}$ ,  $642^\circ\text{C}$ ,  $698^\circ\text{C}$ , and  $711^\circ\text{C}$ . The crystalline phase  $\text{Fe}_7(\text{PO}_4)_6$  is present in all crystallized materials, whereas the  $\text{Fe}_3(\text{PO}_4)_2$  crystalline phase predominates in crystallized glasses produced in an electric furnace. Therefore, the predominance of the phase  $\text{Fe}_7(\text{PO}_4)_6$  in the crystallized materials originated from glasses produced in microwave oven might be related to the presence of iron in the  $2+$  valence state, as shown by the Mössbauer spectroscopy.

For the crystallized  $40\text{Fe}_2\text{O}_3$ - $60\text{P}_2\text{O}_5$  glass, as for the  $50\text{Fe}_2\text{O}_3$ - $50\text{P}_2\text{O}_5$  glass produced in the microwave oven, the predominant crystalline phases is  $\text{Fe}_7(\text{PO}_4)_6$ , followed by  $\text{Fe}_3(\text{PO}_4)_2$ . As seen before, the presence of the  $\text{Fe}_7(\text{PO}_4)_6$  and  $\text{Fe}_3(\text{PO}_4)_2$  could be related to the predominance of  $\text{Fe}^{2+}$  in the precursor glass produced in the microwave oven, as the very low amount of  $\text{FePO}_4$  could be related to the lower amount of  $\text{Fe}^{3+}$  in the glass.

Among all the crystallized glasses produced in the electric furnace, the only one that shows a predominance of the crystalline phase  $\text{Fe}(\text{PO}_3)_3$  is the  $50\text{Fe}_2\text{O}_3$ - $50\text{P}_2\text{O}_5$  glass after heat treated at  $581^\circ\text{C}$ . All the other crystallized glasses show relatively high amount of  $\text{FePO}_4$  and  $\text{Fe}_3(\text{PO}_4)_2$  that might be related to the amount of  $\text{Fe}^{3+}$  in the precursor glass.

The crystalline phases  $\text{Fe}_3(\text{PO}_4)_2$ ,  $\text{Fe}(\text{PO}_3)_3$ ,  $\text{Fe}(\text{PO}_3)_2$ , and  $\text{Fe}_7(\text{PO}_4)_6$  are present in all crystallized glasses, however the relative amount depends on the original glass composition, and the temperature of the heat treatment for crystallization. To quantify the amount of the crystalline phases the Rietveld method should be applied, however, this is not within the scope of the present work.

Concerning the Mössbauer spectroscopy, it is noticed that in magnetite-based glasses produced in the microwave oven, there is a large change of the valence state of Fe ions compared to the state in the magnetite, since the magnetite presents about 33% of  $\text{Fe}^{2+}$  and 67% of  $\text{Fe}^{3+}$ .

As the amount of magnetite is increased in the nominal glass composition, it is noticed an increase of the relative amount of  $\text{Fe}^{2+}$  in the glass final composition, in other words, a valence reduction from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  around 15%.

The increase of the relative amount of  $\text{Fe}^{2+}$  could be due to the time interval during the melting or the local atmo-

sphere, since a ceramic lid is used to cover the crucible inside the microwave oven to improve the thermal isolation.

In magnetite-based glasses produced in the electric furnace, the relative amount of  $\text{Fe}^{3+}$  is lightly greater than the one in the original  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  ratio of magnetite, opposed to what was found for the glasses produced in the microwave oven, where the relative amount of  $\text{Fe}^{2+}$  has increased. Even a slightly reduction of the amount of  $\text{Fe}^{2+}$  when compared to the original  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  ratio of the magnetite is observed when the electric furnace is used for melting glasses.

As seen in Fig. 17 and Table 4, for the magnetite-based glass (containing 55 mol%) the Mössbauer spectrum show the presence of an arranged magnetic phase with hyperfine field that could be associated to hematite (estimated to be 21%). Even having the magnetite as the raw material for the glass preparation, hematite was formed, indicating that all the magnetite was dissolved in the melting process and hematite was further precipitated.

The fact that in glasses produced by melting raw materials in an electric furnace the  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  ratio does not deviate from the original ones can be related to the time for melting (1 h), or the local atmosphere, in this case, no ceramic lid was covering the crucible. Variation of the  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  ratio has been observed previously for iron phosphate glasses produced in different conditions [3].

Considering that  $\text{Fe}^{3+}$  is the predominant valence state in  $\text{Fe}_2\text{O}_3$ , the reduction to  $\text{Fe}^{2+}$  is observed for glasses produced in the microwave oven. The  $\text{Fe}^{2+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  ratio increases up to 0.35. As the amount of ferrite is increased, the  $\text{Fe}^{2+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  ratio increases in the final glass composition.

Once again it is observed a substantial increase of  $\text{Fe}^{2+}$  in glasses produced in a microwave oven. This fact could be related to the short time for melting (1 min) or by a change of the local atmosphere. Even when the raw material is ferrite (100%  $\text{Fe}^{3+}$ ), the final glass composition presents some  $\text{Fe}^{2+}$  when glasses are prepared in the microwave oven. This fact has also been previously reported for  $40\text{Fe}_2\text{O}_3\text{--}60\text{P}_2\text{O}_5$  glasses produced at 1200 °C in an electric furnace [3].

For glasses produce in the electric furnace, even observing a valence state reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , the relative amount of  $\text{Fe}^{2+}$  is well below the ones produced in microwave oven with the same composition.

Therefore, glasses produced in a microwave oven presents  $\text{Fe}^{2+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  ratios higher than the ones observed in glasses with the same nominal composition produced in the electric furnaces.

Assuming that the local atmosphere could vary for both processing methods because  $[(\text{NH}_4)_2\text{HPO}_4]$  decomposes to produce  $\text{P}_2\text{O}_5$  and  $\text{NH}_3$ , according to the following reaction



and a ceramic lid covers the crucible to improve the thermal isolation in the microwave heating process,  $\text{NH}_3$  could

Table 7

Mössbauer spectra parameters for glasses produced in an electric furnace with crucibles covered by a ceramic lid: quadrupole splitting ( $\Delta$ ), isomer shift with respect to metallic iron ( $\delta$ ) and relative subspectral area (AR)

Nominal amount in batch material (mol%)	$\Delta_1$ (mm/s)	$\delta_1$ (mm/s)	AR <sub>1</sub> (%)	$\Delta_2$ (mm/s)	$\delta_2$ (mm/s)	AR <sub>2</sub> (%)
50 $\text{Fe}_3\text{O}_4$	2.27	1.24	37	0.89	0.38	63
50 $\text{Fe}_2\text{O}_3$	2.19	1.20	14	2.49	0.38	86

The standard deviation in  $\Delta$  and  $\delta$  is  $\pm 0.01$ .

be responsible for the  $\text{Fe}^{3+}$  reduction. To prove this assumption, an experience was performed in an electric furnace by melting glasses with the same nominal composition, but keeping a ceramic lid on the top of the crucible to maintain the same experimental condition used in the microwave heating. Ferrite-based glasses as magnetite-based glasses were used for these experiences. According to the Mössbauer data of Table 7 for  $50\text{Fe}_3\text{O}_4\text{--}50\text{P}_2\text{O}_5$  and  $50\text{Fe}_2\text{O}_3\text{--}50\text{P}_2\text{O}_5$  glasses produced in an electric furnace with a crucible covered by a ceramic lid, and compared with the previous data for glasses produced in crucibles without any lid, there is only a slightly reduction of the relative amount of  $\text{Fe}^{3+}$  caused by the local atmosphere, which does not fully explain the results obtained in the microwave oven.

Another assumption to explain the  $\text{Fe}^{3+}$  reduction in the microwave process could be the different heating rate compared to the electric furnace process, and the time during the melting process (soaking time). In the electrical furnace the heating rate is 10 °C/min, keeping the liquid in the melting temperature for about 1 h. For the microwave processing, the heating rate is 50 °C/min, and the liquid is kept at the melting temperature for 1 min before cast. The question is, could this experimental differences be responsible for the equilibrium of the  $\text{Fe}^{3+}\text{--}\text{Fe}^{2+}$  redox couple, or another assumption should be evoked the effects of microwave radiation on the 3d levels of Fe. Since the 3d level is incomplete for the Fe element, although the energy is the same for all electrons in the  $3d^6$  level, a interaction of the microwave radiation with these electrons could disturb the energy distribution (as it has been observed for the crystal field effects related to color in glasses) and therefore affects the redox equilibrium in these materials.

Considering that the redox equilibrium is a matter of time, a short period at the melting temperature could displace the equilibrium to a more favorable direction, as the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . Further support for this assumption is necessary, and new experiences are been design with a more controlled energy transfer, to help the establishment of an equilibrium mechanism in the experimental conditions of the present work.

## 5. Conclusions

Iron phosphate glasses have been produced by microwave heating using mixtures of ferrite or magnetite and

(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> as batch material. The apparent density of those mixtures is an important matter to be considered to get the self-heating when the material is exposed to microwave radiation.

The Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio has been determined by the Mössbauer spectroscopy for glasses of same nominal composition produced in an electric furnace and in a microwave oven. The Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio is higher for glasses produced in a microwave oven compared to the ones for glasses produced in an electric furnace. For magnetite-based glasses produced in an electric furnace, the Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio is compatible with the one original founded in the batch material.

Glasses with nominal composition 55Fe<sub>3</sub>O<sub>4</sub>–45P<sub>2</sub>O<sub>5</sub> (mol%) produced in an electric furnace present an arranged magnetic phase with hyperfine field that could be associated to hematite (estimated to be 21%). Even having the magnetite as the raw material for the glass preparation, hematite was formed, indicating that all the magnetite was dissolved in the melting process and hematite was further precipitated.

All the glasses submitted to heat treatments for crystallization present the following crystalline phases: FePO<sub>4</sub>, Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Fe(PO<sub>3</sub>)<sub>3</sub>, Fe(PO<sub>3</sub>)<sub>2</sub>, and Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>. The amount of these phases depends on the glass composition, glass preparation procedure (if a microwave oven or an electric furnace was used), and the heat treatment temperature.

Glasses produced in a microwave oven and crystallized afterwards present the Fe<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub> and Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> crystalline phases as predominant ones, while glasses of the same nominal composition produced in an electric furnace present the FePO<sub>4</sub> and Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> as the predominant phases after crystallization. This fact might be related to the different Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio in the glasses.

Microwave heating allows to reach melting temperatures at high heating rates, making the procedure easy

and economical, but care should be taken concerning the final Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio.

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