



# Mössbauer spectroscopy study of 60P<sub>2</sub>O<sub>5</sub>-40Fe<sub>2</sub>O<sub>3</sub> glass crystallization

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**Abstract.** 60P<sub>2</sub>O<sub>5</sub>-40Fe<sub>2</sub>O<sub>3</sub> glass was synthesized and <sup>57</sup>Fe Mössbauer spectroscopy study was presented. The main goal of the research was to investigate structural changes of local environment of iron ions during gradual crystallization of the glass. It was observed that some changes were evidenced at temperature of heat treatment higher than 400°C, above which content of tetrahedrally coordinated Fe<sup>3+</sup> was increased in cost of octahedral sites. This led to formation of areas of nucleation of α-FePO<sub>4</sub>. Crystallization of α-Fe<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> and Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> was also observed.

**Key words:** crystallization • iron phosphate glass • Mössbauer spectroscopy • nuclear waste • waste glass

## Introduction

Iron phosphate glasses are of special interest because of practical and scientific reasons. Phosphate glasses, in general, are characterized by a low-chemical durability and are used as matrix for encapsulation of microelements, which could be leached off in a controlled way to fertilize the soil [1]. On the other hand, iron can significantly increase its water resistance and glasses of composition 60P<sub>2</sub>O<sub>5</sub>-40Fe<sub>2</sub>O<sub>3</sub> have a superior chemical durability, which is even higher than commonly used borosilicate glasses for vitrification of radioactive waste [2, 3]. In waste vitrification technology, one of the very important parameters is homogeneity of the obtained melt without any inclusions of crystal phases, which could lead to segregation of radionuclides, creation of internal stresses and cracks in a vitrified product [2, 3]. Poor effect of crystallization of 60P<sub>2</sub>O<sub>5</sub>-40Fe<sub>2</sub>O<sub>3</sub> glass is observed above 700°C and leads to formation of a glass-ceramic material in which, beside amorphous-phase formation of α-FePO<sub>4</sub> and Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, crystal phases is present [4]. The FePO<sub>4</sub> is, in the case of iron phosphate glasses, the structural analogue of SiO<sub>2</sub> (a main building block of silicate glasses), which is characteristic of similar phase transition from α-quartz to β-quartz at 700°C with alternate corner sharing of both [FeO<sub>4</sub>]<sup>-</sup> and [PO<sub>4</sub>]<sup>+</sup> tetrahedra [5].

Therefore, the aim of the paper was to observe changes of local iron environment during gradual crystallization of the 60P<sub>2</sub>O<sub>5</sub>-40Fe<sub>2</sub>O<sub>3</sub> glass.

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## Experiment

Glass was prepared from chemical pure  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{Fe}_2\text{O}_3$ . Batches to produce 100 g of the  $60\text{P}_2\text{O}_5\text{-}40\text{Fe}_2\text{O}_3$  glass were melted for 2 h at  $1350^\circ\text{C}$  in  $\text{Al}_2\text{O}_3$  crucible in an electric furnace with the furnace atmosphere as close to natural as possible. The melt was vitrified by casting onto steel plate. The obtained sample was crushed and the pieces were heat treated at temperatures from  $350^\circ\text{C}$  to  $700^\circ\text{C}$  with step of  $50^\circ\text{C}$  degrees by 24 h.

For Mössbauer analysis, the heat-treated samples were powdered in an agate mortar. Spectrum was collected at room temperature using a 25 mCi  $^{57}\text{Co}$  source embedded in Rh matrix. A velocity range  $\pm 4$  mm/s was used and spectrometer was calibrated using  $\alpha\text{-Fe}$  foil.

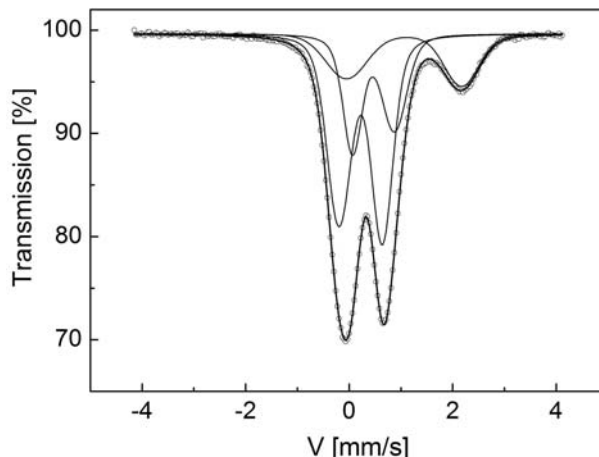
In the case of amorphous materials like glasses, the interpretation of a Mössbauer spectrum is not so unambiguous like for crystalline compounds. In crystalline compounds, every crystallographic iron site can be observed as one component of the spectrum. In disordered amorphous materials, however, there are many different local iron environments and every one of them is described by a different set of hyperfine interaction parameters. As a consequence, the collected spectrum is a composition of many individual components. In oxide glasses, every iron cation has only oxygen anions in the first neighborhood, but deviations in coordination or iron–oxygen distance, etc. should reflect the observed effect and the hyperfine interaction parameters. In the case of amorphous materials, one method for processing the spectra is an Extended Voigtian Based analysis (xVBF), which has been described in detail elsewhere [6, 7]. In this method, every iron atom site is given by a Gaussian distribution of an independent isomer shift and quadrupole splitting due to some randomness in the local environment of iron. Effectiveness of the method in fitting of Mössbauer spectra of iron phosphate glasses was previously proved [8, 9].

## Results and discussion

An exemplary Mössbauer spectrum of the glass sample heated at  $500^\circ\text{C}$  is presented in Fig. 1 and is typical for iron phosphate glass [8, 9]. The analogous spectra were obtained for all studied materials and were deconvoluted using three different iron sites, which represent tetrahedrally coordinated  $^{\text{IV}}\text{Fe}^{3+}$ , octahedrally coordinated  $^{\text{VI}}\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  that are assumed to exist in various coordination environments [9]. The fitted hyperfine interaction parameters for the sample heated at  $500^\circ\text{C}$  are presented in Table 1, namely: A – area of the site, IS – isomer shift,

**Table 1.** The hyperfine interaction parameters of  $60\text{P}_2\text{O}_5\text{-}40\text{Fe}_2\text{O}_3$  glass heated at  $500^\circ\text{C}$

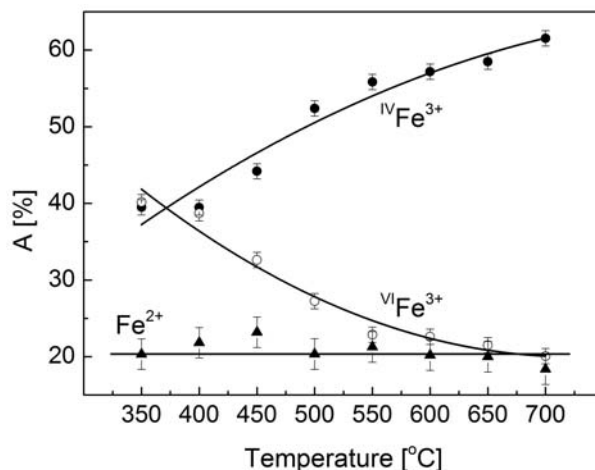
Site	A [%]	IS [mm/s]	QS [mm/s]	$\sigma_{\text{IS}}$ [mm/s]	$\sigma_{\text{QS}}$ [mm/s]	$\rho(\text{IS}, \text{QS})$
$^{\text{IV}}\text{Fe}^{3+}$	52.4	0.320(5)	0.84(6)	0.128	0.24	-0.140
$^{\text{VI}}\text{Fe}^{3+}$	27.3	0.580(5)	0.80(4)	0.129	0.21	0.336
$\text{Fe}^{2+}$	20.3	1.170(10)	2.17(1)	0.230	0.47	-0.193



**Fig. 1.**  $^{57}\text{Fe}$  Mössbauer spectra of the  $60\text{P}_2\text{O}_5\text{-}40\text{Fe}_2\text{O}_3$  glass heat treated at  $500^\circ\text{C}$ .

QS – quadrupole splitting,  $\sigma_{\text{IS}}$  and  $\sigma_{\text{QS}}$  – Gaussian widths of the distribution of isomer shift and quadrupole splitting, respectively, and  $\rho(\text{IS}, \text{QS})$  – correlation parameter between IS and QS.

Share percentages of the components independent of sample heating temperature are presented in Fig. 2. The  $\text{Fe}^{2+}$  concentration was approximately 20% and was almost constant. The rest of iron ions were present as  $\text{Fe}^{3+}$  with almost equal population between 4 and 6 coordinated sites for samples heated at the lowest temperature. This gave mean coordination number of  $\text{Fe}^{3+}$  equal 5, which was previously observed [5]. At temperature above  $400^\circ\text{C}$  is evidenced gradual increase of tetrahedrally coordinated  $\text{Fe}^{3+}$  in cost of  $^{\text{VI}}\text{Fe}^{3+}$ , which is probably due to increase of local order of the both sites and formation of regions, which are enriched in  $^{\text{IV}}\text{Fe}^{3+}$ . This effect could be related to nucleation of  $\alpha\text{-FePO}_4$  crystallization.



**Fig. 2.** Share percentage of different iron sites independent of the sample heating temperature.

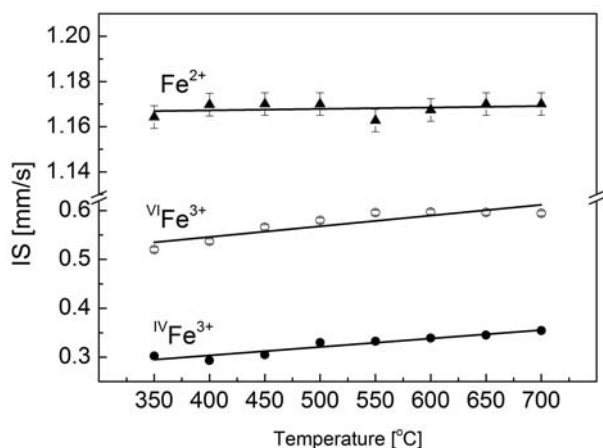


Fig. 3. The mean isomer shift of the iron sites independent of the sample heating temperature.

The mean isomer shift of the sites is presented in Fig. 3. The <sup>IV</sup>Fe<sup>3+</sup> isomer shift was slightly increased from 0.29 to 0.33 mm/s. Similar behavior was observed for <sup>VI</sup>Fe<sup>3+</sup> and, as would be expected, the IS values were higher and ranged between 0.5 and 0.6 mm/s. The IS value of Fe<sup>2+</sup> was almost constant and took approximately value of 1.17 mm/s.

The mean quadrupole splittings of the sites are presented in Fig. 4. The QS values of Fe<sup>2+</sup> were almost independent of the sample heating temperature. In case of the tetrahedrally coordinated Fe<sup>3+</sup> sites, the QS parameter was decreasing at low-heating temperatures up to 500°C, an opposite effect was observed for octahedral iron sites. Both parameters were almost constant for the higher heating temperatures.

According to the previous results of 60P<sub>2</sub>O<sub>5</sub>-40Fe<sub>2</sub>O<sub>3</sub> glass crystallization studies, it was observed that crystallization started above 700°C with a very poor effect of crystallization on DSC curve. It was found that the obtained material was glass-ceramic and the main crystal phases based on X-ray diffraction analysis were identified as α-FePO<sub>4</sub> and Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> [4]. In α-FePO<sub>4</sub> crystal structure, there is one tetrahedral Fe<sup>3+</sup> iron site and IS value of this site is in the range of 0.27–0.32 mm/s [10, 11], which is in accordance with the values obtained in the present studies. In case of Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase, there

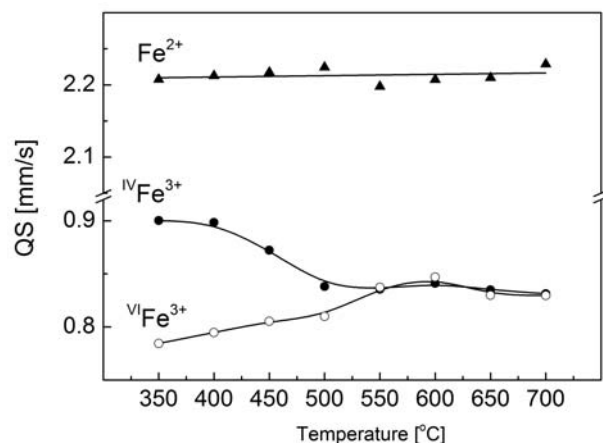


Fig. 4. The mean quadrupole splitting of the iron sites independent of the sample heating temperature.

are two Fe<sup>2+</sup> iron sites characterized by similar IS values approximately 1.2 mm/s and slightly different QS [12]. This IS value is close to the 1.17 mm/s, which was obtained in the present paper. On the other hand, the studied material part of Fe<sup>3+</sup> iron was situated in octahedral coordination with high IS values above 0.5 mm/s. These ions could not be assigned to α-FePO<sub>4</sub> or Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase. The IS values of approximately 0.5 mm/s were previously reported for six coordinated Fe<sup>3+</sup> iron in α-Fe<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> phase where beside two Fe<sup>3+</sup> cations existed one Fe<sup>2+</sup> per formulae characterized by IS about 1.2 mm/s [11]. Taking all into account, it could be concluded that approximately: 60% of iron was present in α-FePO<sub>4</sub>, 30% in α-Fe<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>, and 10% only in Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> crystal phase after crystallization process.

## Conclusions

The <sup>57</sup>Fe Mössbauer effect spectrum of 60P<sub>2</sub>O<sub>5</sub>-40Fe<sub>2</sub>O<sub>3</sub> sample was composed of three different iron environments. In the glass, approximately 20% of iron ions were present as Fe<sup>2+</sup> in octahedral environment in which they could be classified as glass network modifiers. The rest of iron ions were present as Fe<sup>3+</sup> in octa- and tetrahedral coordination in which they were glass network modifier and former, respectively. Heat treatment of the glass did not significantly change the local neighborhood of ferrous iron. Much bigger differences were observed in case of ferric iron. During heat treatment procedure, gradually part of octahedrally coordinated iron were transformed into tetrahedrally. This led to formation of areas enriched in four-fold coordinated Fe<sup>3+</sup> and nucleating crystallization of α-FePO<sub>4</sub>, which is the main crystal phase in crystallize sample beside which formation of α-Fe<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>, Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> was also observed.

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