

Mössbauer spectroscopy study of 60P₂O₅-40Fe₂O₃ glass

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Abstract. A ⁵⁷Fe Mössbauer spectroscopy study is presented. The main goal of the research was to investigate the structural information of the glass-like the coordination numbers and redox ratio of the iron. Most of the iron, about 80%, is present in the glass as Fe³⁺, which is composed of tetrahedral (57%) and octahedral (23%) coordinated iron. The rest of the iron, about 20%, is in the oxidation state Fe²⁺. This iron could be mostly present as ^{VI}Fe²⁺, but five-fold coordinated iron is also possible. Finally, the structural model of the synthesized 60P₂O₅-40Fe₂O₃ glass was proposed.

Key words: iron-phosphate glass • Mössbauer spectroscopy • nuclear waste • waste glass

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Introduction

The Fe₂O₃-P₂O₅ glass system is of great interest for scientific reason and because it is being considered as a matrix for the storage of different types of radioactive waste. The worldwide used borosilicate glasses for nuclear waste vitrification are not suitable for immobilization of high content of molybdenum, sulfate, chromium or salts waste because of low solubility of these constituents in the glass. They form the so-called “yellow phase” at the surface of the melt which could be easily leached out [3, 6]. The new kind of nuclear reactors Gen-IV will probably generate new streams of the “problematic” waste which could not be vitrified in borosilicate waste glasses [2]. The iron-phosphate glasses could incorporate in their structure those “problematic” components. However, the P₂O₅ glasses have a low chemical durability. Addition of Fe₂O₃ leads to rapid increasing of durability of the glasses. The highest chemical durability is observed for the 60P₂O₅-40Fe₂O₃ glass, in which part of the weak P-O bonds is being replaced by much stronger Fe-O bonds. The iron in these glasses could act as a glass modifier or a glass network cation depending on its coordination number. If it is the network modifier, iron cations are located nearby non-bridging oxygen ions. They start to open weak P=O bonds and create much stronger P-O-Fe bonds. As the network modifier, Fe is present in octahedral coordination. If the iron is in tetrahedral coordination, it substitutes P⁵⁺ cations in phosphate chains acting as the network former. In both the cases iron could increase chemical durability of the glass.

Table 1. The hyperfine interaction parameters of the measured glass (A – area of the component, IS – mean isomer shift, QS – mean quadrupole splitting, σ_{IS} and σ_{QS} – Gaussian widths for the isomer shift and quadrupole splitting distribution, respectively, $r(IS, QS)$ – correlation parameter between IS and QS)

| No. | A (%) | IS (mm/s) | σ_{IS} (mm/s) | QS (mm/s) | σ_{QS} (mm/s) | $r(IS, QS)$ |
|-----------------------|---------|-----------|----------------------|-----------|----------------------|-------------|
| 1. (Fe^{3+} octa) | 23.0(2) | 0.421(5) | 0.087(5) | 0.540(14) | 0.163(10) | -0.021(8) |
| 2. (Fe^{3+} tetra) | 57.3(7) | 0.411(2) | 0.124(5) | 0.967(3) | 0.274(9) | 0.071(4) |
| 3. (Fe^{2+}) | 19.7(9) | 1.240(10) | 0.282(12) | 2.085(19) | 0.418(20) | -0.431(6) |

Structure of the Fe_2O_3 - P_2O_5 glass system is especially complicated because of the coexistence of the Fe^{3+} and Fe^{2+} ions whose content depends on the synthesis conditions, batch preparation, etc. The glass can crystallize in about 24 different crystallographic systems, in which the iron can be present in tetrahedral, octahedral and five-fold coordination. There is a wide discussion in the literature about structure of the Fe_2O_3 - P_2O_5 glasses and the role of the iron in them.

The first model of the Fe_2O_3 - P_2O_5 glass structure was proposed in [9] and according to these authors the glass is built of three different structural units FeO_4 , PO_4 tetrahedra sharing all four vertices, and $O=PO_3$ tetrahedra units with three corner sharing single bonded oxygen ions and one non-bridging double bonded oxygen ion. Any of the Fe^{2+} cations present could act as a network modifying in octahedral coordination. An alternative model was proposed in [5]. This model is based on the crystal structure of $Fe_3(P_2O_7)_2$ in which iron is present as $(Fe_3O_{12})^{16-}$ clusters built of Fe^{2+} in trigonal prismatic coordination and two Fe^{3+} ions in octahedral coordination. The model [5] is in opposition with detailed neutron diffraction studies [9] and the authors proposed another model in which, according to their experimental measurements, at least about 50% of Fe^{3+} must be present in tetrahedral coordination and playing the network forming role. The rest of the Fe^{3+} ions could be present as the modifiers in octahedral coordination. The existence of five-fold coordinated iron is also possible. The Fe^{2+} cations are present as the network modifying mostly in octahedral coordination, but $Fe^{2+}O_5$ polyhedral in the phosphate network is also possible. This model is in good agreement with later theoretical classical molecular dynamics simulations [2].

In this paper Mössbauer spectroscopy was used to investigate the coordination of Fe^{3+} and Fe^{2+} ions in the $60P_2O_5$ - $40Fe_2O_3$ glass.

Experimental

The glass was prepared from chemically pure $NH_4H_2PO_4$ and Fe_2O_3 . Batches to produce 100 g of the $60P_2O_5$ - $40Fe_2O_3$ glass were melted for 2 h at $1150^\circ C$ in an Al_2O_3 crucible in an electric furnace with the furnace atmosphere as close to natural as possible. The melt was vitrified by casting onto a steel plate.

For Mössbauer analysis, the glass was crushed and powdered in an agate mortar. The spectrum was collected at room temperature using a 25 mCi ^{57}Co source embedded in a Rh matrix. A velocity range ± 4 mm/s was used and a spectrometer was calibrated using an ARMCO foil. A Mössbauer spectrum was deconvoluted with the application of three Voigt line shapes.

Extended Voigt based fits (xVBF) were used because the Gaussian component of the line shape is suitable for modelling the distribution of sites in the amorphous glass [1].

In the xVBF method each site is represented by the Gaussian distributed centre shift and quadrupole splitting and is characterized by an amplitude, mean isomer shift, quadrupole splitting, Gaussian widths for the isomer shift and quadrupole splitting distributions and correlation between the isomer shift and quadrupole splitting distribution. The method allows for independent fitting of isomer shift and quadrupole splitting distributions. The xVBF analysis provides more detailed information that allows for the visualization of the relationship between the hyperfine parameters of differently coordinated Fe environments and quantitative information such as redox ration of iron or Mössbauer parameter of ferrous and ferric ions can be extracted as well as the widths of ferrous and ferric iron distributions [8].

Results

Mössbauer spectroscopy measurement was performed on the sample that was X-ray amorphous (Fig. 1). The obtained spectrum was deconvoluted using three Gaussian components which represents tetrahedrally coordinated Fe^{3+} , octahedrally coordinated Fe^{3+} and Fe^{2+} which is assumed to exist in various coordination environments. The obtained hyperfine interaction parameters like: A – area of the component, IS – mean isomer shift, QS – mean quadrupole splitting, σ_{IS} and σ_{QS} – Gaussian widths for the isomer shift and quadrupole splitting distribution, respectively, $r(IS, QS)$ – correlation parameter between IS and QS are presented in Table 1. The fitted spectrum is shown in Fig. 2 and the contour plots of Fe^{3+} and Fe^{2+} of the probability

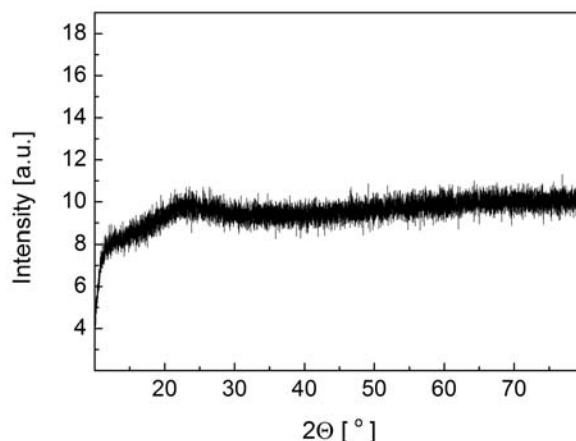


Fig. 1. X-ray pattern of the $60P_2O_5$ - $40Fe_2O_3$ glass.

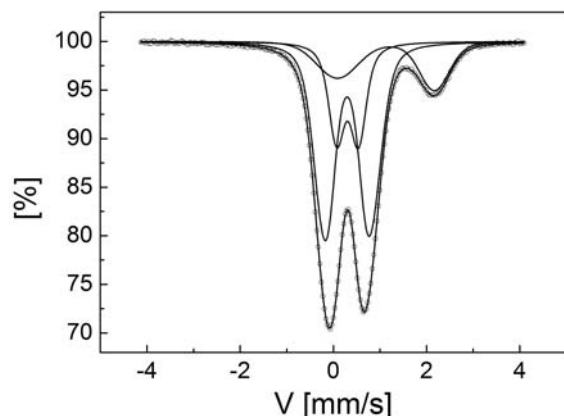


Fig. 2. Fitted ⁵⁷Fe Mössbauer spectrum of the 60P₂O₅-40Fe₂O₃ glass at room temperature.

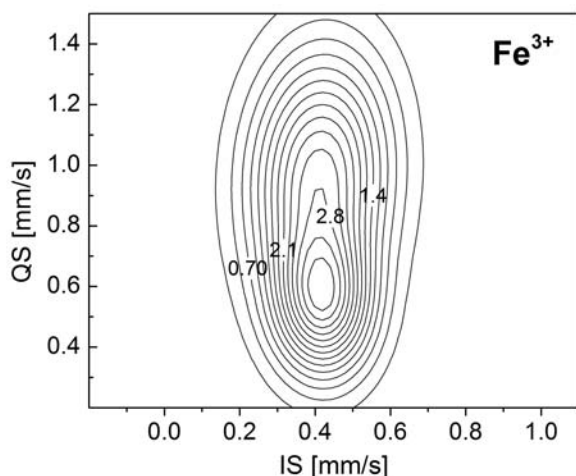


Fig. 3. Contour plot of the Fe³⁺ probability function projected on the IS/QS surface.

distribution, as a function of IS and QS, are presented in Figs. 3 and 4, respectively.

The iron was introduced in the melt as a Fe³⁺ only. In the glass about 20% of the iron is present as Fe²⁺ (component 3, Table 1). The Fe²⁺ probability distribution (Fig. 4) is a wide distribution with an IS mean value of 1.240 mm/s which suggests octahedral coordination of the Fe²⁺. On the other hand, the distribution is wide with a high negative value of the r (IS, QS) correlation

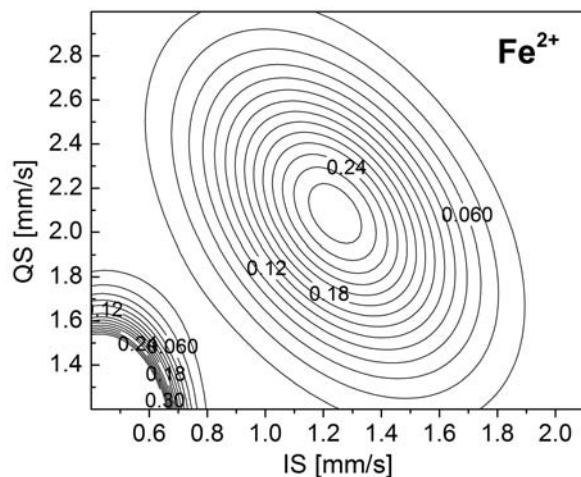


Fig. 4. Contour plot of the Fe²⁺ probability function projected on the IS/QS surface.

parameter, which rotates the distribution in direction of the higher values of the QS for lower values of the IS. This phenomenon suggests that the part of the iron Fe²⁺ could be in the five-fold coordination which could be highly distorted ^{VI}Fe²⁺ site. The existence of the Fe²⁺ in six- and five-fold coordination was confirmed previously by a neutron diffraction study [10].

The rest of the iron occurred as Fe³⁺ ions in the glass. In the highly distorted amorphous materials the IS values could be very close to each other for tetrahedral and octahedral coordinated iron. The difference is observed in the QS parameters only, and for iron in four-fold coordination QS is higher with the value of about 1 mm/s than for octahedrally coordinated for which QS is about 0.5 mm/s [4]. Therefore, lower values of the QS component 1 (Table 1) was assigned to ^{IV}Fe³⁺ and the higher QS component 2 was assigned to ^{VI}Fe³⁺. Most of the Fe³⁺ iron is present in tetrahedral coordination whose distribution is wider than in the case of octahedral coordination. This suggests much bigger distortion of the tetrahedral site in which also could be present iron in five-fold coordination.

Discussion and conclusions

Despite the oxidation state of the substrate iron in the glass of about 20% of the total iron is present as Fe²⁺ and 80% as Fe³⁺.

The obtained results show that the iron Fe²⁺ is probably in the octahedral environment, but this site could be highly distorted and five-fold coordinated Fe²⁺ is also possible. Most of the Fe³⁺ is in tetrahedral coordination which means that in this case iron plays a role of the network former and only about 23% of Fe³⁺ iron is a network modifier of the iron-phosphate glass structure.

In the case of the investigated glasses, O/P ratio is equal to 3.5 which means that they are polyphosphate glasses built of PO₄ tetrahedra. Two oxygen anions are bridging and create the P-O-P bonds. The rest of the oxygen ions are non-bridging and form the P=O bond. The structure of such glass is built of long tetrahedrally coordinated PO₄ chains, terminated by the PO₄ tetrahedra with three non-bridging oxygen ions. The existing FeO₄ tetrahedra alternate with PO₄ tetrahedra to maintain charge neutrality. These tetrahedra could be present in FePO₄-like regions having only even-membered chains alternating tetrahedra within general phosphate network [10]. The remaining Fe³⁺O₆, Fe²⁺O₆ and possible Fe²⁺O₅ are probably surrounded by non-bridging oxygen ions and iron cations play a role of the glass network modifiers [7]. The network modifiers start opening the weak P=O bonds and create much stronger P-O-Fe bonds permanently linking non-bridging oxygen ions and cross-linking the iron-phosphate chains which makes the glass network more rigid. The network forming tetrahedral Fe³⁺ alternates weaker P-O-P bonds by the stronger P-O-Fe. Both of these could increase the chemical durability of the iron-phosphate glasses making them a good candidate for matrix to immobilization of radioactive waste.

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