CRYSTALLIZATION OF IRON PHOSPHATE GLASSES

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Differential thermal analysis (DTA), thermogravimetric analysis (TG), X-ray diffraction and Mössbauer spectroscopy were employed in the investigation of crystalline products of $FeO_x - P_2O_5$ glasses generated by various heat treatments. In glasses with a high value of $\alpha = Fe^{2+}/(Fe^{2+} + Fe^{3+})$, absorption of oxygen occurs in a broad temperature range identified by TG. Depending on the value of α, two exotherms appear in the DTA curves, the low-temperature one corresponding to crystallization of the $Fe_3(PO_4)_2$ type regions, and the high-temperature one being related to various phases with dominating $FePO_4$. Each exotherm has its own transformation region, identical in absolute value. The Mössbauer spectra of glasses which underwent thermal treatment at higher temperatures exhibit some indication of phases of the types $Fe_3(PO_4)_2 \cdot xH_2O$ and $FePO_4 \cdot xH_2O$.

It is assumed that the transport of charge in iron phosphate glasses is due to the migration of charge carriers between Fe ions of various valencies. In our recent paper devoted to the analysis of $FeO_x - P_2O_5$ glasses, using the thermostimulated depolarization method (TSD) we predicted the presence of microscopic regions of the dispersed phase inserted in the homogeneous matrix of the glass [1]. The mechanism of devitrification, studied in this connection by means of transmission electron microscopy [2], as well as some indirect structural conclusions based on ac and dc characteristics measurements [3] and considerations of the phase separation of phosphate glasses [4, 5], assume the existence of several phases.

It is the aim of this paper to investigate the crystallization of $FeO_x - P_2O_5$ glasses in a non-isothermal way (using differential thermal analysis, DTA, and thermogravimetry, TG), to identify crystalline phases generated by heat treatment (using X-ray analysis and Mössbauer spectroscopy), and to judge the possibility of liquid–liquid phase separation.

Experimental

Sample preparation

Reagent-grade P_2O_5, Fe_2O_3 and dextrose were carefully mixed in the desired proportion and then approximately 15 g of the mixture was placed in an SiO_2 crucible and melted in an electric muffle furnace. An argon atmosphere under normal conditions was present during the preparation of glasses with $\alpha > 0.5$

$\alpha = Fe^{2+}/(Fe^{2+} + Fe^{3+})$, while glasses with $\alpha \leq 0.5$ were prepared in air. The temperature increase in the furnace was approximately 300°/h; the duration of melting at 1250° was 15 min. The melts were stirred from time to time in order to improve their homogeneity, poured into a stainless steel mold maintained at 300°, and subsequently cooled down to room temperature at a cooling rate of 15°/min. Wet chemical analysis and Mössbauer analysis were used to determine the concentrations of Fe^{2+} and Fe^{3+} as well as Fe_{total}. Details are given in our previous paper [1]. The non-crystalline state of each sample was established by means of X-ray analysis (CoK_α radiation).

Thermal analysis

A Du Pont Thermal Analyzer with a high-temperature DTA cell as well as a TG 951 cell were employed. For DTA, 33 mg of pulverized sample was placed each time into a Pt pan and scanned at 10°/min over the temperature range desired under an argon atmosphere flow. TG was performed on a fine pulverized sample of 23 mg at 20°/min in an oxygen atmosphere.

X-ray and Mössbauer analyses

Commercial Phillips PW 1049 and KFKI devices were used, respectively. 57 Co in an Rh lattice was used as a source for Mössbauer spectroscopy, with measurement at room temperature at a constant acceleration and evaluation by means of a 1024-channel analyzer.

Results and discussion

The TG of an iron phosphate glass sample with $\alpha = 0.93$ is shown in Fig. 1. A detectable increase in weight of the sample already appears below the glass transition temperature $T_g \sim 480°$; it increases in the viscoelastic and crystallization temperature regions I and II, with the slope $\tau_1 = 1.05 \cdot 10^{-3}$ degree^{-1}. After complete melting in the temperature interval ΔT_m characterized by several
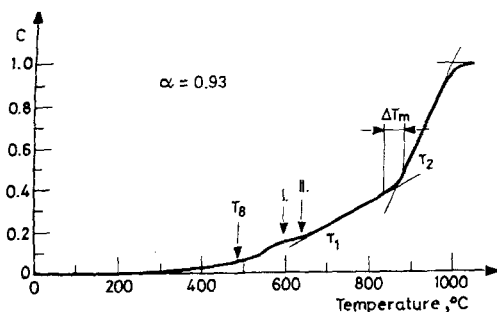

Fig. 1. TG of iron-phosphate glass (c — degree of conversion)

endothermic DTA effects, a maximum dynamic absorption of oxygen appears with $\tau_2 = 0.44-10^{-3}$ degree^{-1}. Under our experimental conditions the TG effects are saturated at the temperature 1050°, where the original value $\alpha = 0.93$ decreases to $\alpha = 0.65$. In order to follow the changes occurring during heat treatment, we employed an inert (argon) atmosphere. In some papers published so far, this fact has not been considered. However, Fig. 1 shows that the heat treatment of samples with $\alpha > 0.5$ above the temperature T_g can substantially change the chemical composition of the sample, thus making questionable the structural changes deduced in [2, 3, 6].
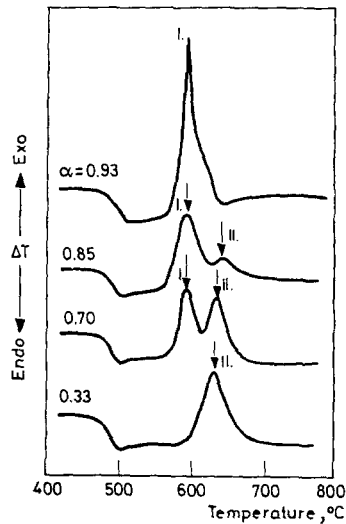

Fig. 2. DTA curves of iron-phosphate glasses

DTA curves for various values of α are given in Fig. 2. The temperature of glass transition T_g, defined in this paper as the extrapolated onset, is (within the framework of our experimental errors) not dependent on the value of α, and is always $T_g = 480 \pm 2°$. Endothermic effects occurring on the melting of the samples were irreproducible and are not presented here. The number of crystallization exotherms depends on the value of α. The position of exotherm I, with maximum peak value $T_m = 590 \pm 3°$, and that of exotherm II, with $T_m = 630 \pm 7°$, are typical for all α values. The ratio of enthalpies I and II well characterizes parameter α.

From the thermoanalytical viewpoint, the most acceptable explanation of the observed curves is the assumption of the existence of two glassy phases coexisting in the given glass and crystallizing separately in the temperature ranges I and II, respectively. In this case each glass phase (and thus that crystallizing at the temperature T_{mII}) must exhibit its own glass transition. A way of determining such a T_g for a sample with $\alpha = 0.7$ is shown in Fig. 3. Partial crystallization I was completely performed by the first DTA measurements and after free cooling in a DSC

cell a new curve was produced. The remaining crystallization exotherm II is characterized by a glass transition region at the same temperatures as those recorded in all the other measured samples. Thus, the separated glassy phases have identical temperature ranges of glass transitions. The idea of phase separation well explains the ac and dc characteristics of thermally treated samples [3], with no need to consider the presence of small crystalline phase fractions in as-prepared glasses.

X-ray diffraction and Mössbauer spectroscopy were used for the identification of crystalline products arising on various heat treatments of the glasses. Figure 4 shows schematic X-ray diffraction patterns of glasses with $\alpha = 0.70$ and $\alpha = 0.33$, respectively. The product of partial crystallization of the glass with $\alpha = 0.70$ (as shown in exotherm I, Fig. 3) was assigned according to [7] to $Fe_3(PO_4)_2$. The complete crystallization of this glass leads to the formation of other diffraction lines (Fig. 4, $T_t = 660°$) with the qualitative spectrum comprising the diffraction spectrum of the fully crystallized sample with $\alpha = 0.33$ (Fig. 4, $T_t = 800°$). Therefore, the crystallization product of exotherm II (Fig. 3), together with the main crystallization product of the sample with $\alpha = 0.33$, was indexed as $FePO_4$. The diffraction spectrum according to Fig. 4 ($\alpha = 0.33$) further characterizes crystalline regions with chemical compositions Fe_2O_3 and FeO.
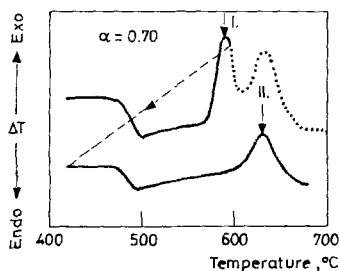

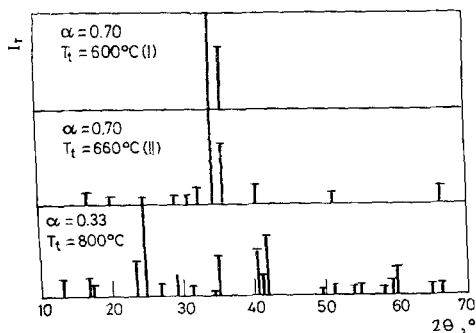Fig. 3. DTA curves of partial and complete crystallization of glass with $\alpha = 0.70$

Fig. 4. Schematic X-ray (CoK_α) diffraction patterns after various heat treatments T_t
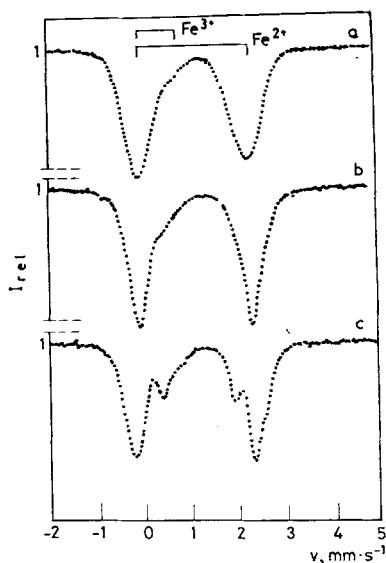
Fig. 5. Mössbauer spectra of glass with $\alpha = 0.85$ after various heat treatments

The Mössbauer spectrum of the glassy sample with $\alpha = 0.85$ consists of components corresponding to Fe^{2+} and Fe^{3+} (Fig. 5a). An approximation of the spectrum by two doublets of the Lorentzian curves was not precise enough and therefore Gaussian distribution was employed [8], according to which the spectrum exhibits the line widths $\Gamma_{Fe^{2+}} = 2.235$ mms^{-1} and $\Gamma_{Fe^{3+}} = 0.563$ mms^{-1}, the mean quadrupole splitting values $\Delta_{Fe^{2+}} = 2.235$ mms^{-1} and $\Delta_{Fe^{3+}} = 0.898$ mms^{-1}, the isomeric shifts being $\delta_{Fe^{2+}} = 1.078$ mms^{-1} and $\delta_{Fe^{3+}} = 0.264$ mms^{-1}. The relative Fe^{2+} content determined from the line width intensity is in good agreement with the wet chemical analysis result.

After heat treatment in the temperature interval I (Fig. 5b), performed in the same regime as that of the DTA experiments, the Mössbauer spectrum changes are so small that they cannot be evaluated in practice. However, the higher the temperature of further heat treatment applied to the sample, the better the distinction of doublets with a different quadrupole splitting of crystalline phases with Fe^{3+} and Fe^{2+}. In the case of thermal treatment at 900°, in the crystalline phase involving Fe^{2+} the spectrum separates into several fractions. The quadrupole splitting of Fe^{2+} in the crystalline phases ranges from 1.513 to 2.94 mms^{-1}, the isomeric shifts being 1.12 to 1.21 mms^{-1}. The remaining Fe^{3+} crystallizes in doublets with a mean quadrupole splitting of 0.76 mms^{-1} and a mean isomeric shift of 0.404 mms^{-1}.

Analysis of the measured parameters according to [9, 10] indicates the presence of further crystalline phases of composition $Fe_3(PO_4)_2 \cdot xH_2O$ and $FePO_4 \cdot xH_2O$. According to [9] the Fe^{2+} phase has a monoclinic structure, with two non-equivalent Fe^{2+} locations with a relative ratio 1 : 2. From the viewpoint of Mössbauer

spectroscopy each spectrum of such a compound consists of two quadrupole doublets with a relative ratio of areas 1 : 2; moreover, the individual doublets can be asymmetric. The spectrum from Fig. 5c presents the case of bivalent Fe, being a superposition of several doublets corresponding to the composition $Fe_3(PO_4)_2$, together with a varying number of H_2O molecules. A similar situation occurs during the incorporation of trivalent Fe into $FePO_4$, in which the presence of crystalline water is evidenced by the superposition of several doublets.

Conclusions

(1) During heat treatment in an oxygen atmosphere, Fe^{3+}-reduced iron phosphate glasses tend to absorb oxygen, thus causing a change of the factor α.

(2) The crystallization of iron phosphate glasses runs in two stages, depending on the ratio Fe^{2+}/Fe^{3+}. The dominant crystalline phases produced by heat treatment are $Fe_3(PO_4)_2$ and $FePO_4$, respectively. Each crystalline stage has its own (the same in absolute value) glass transition region.

(3) Crystallization by-products appearing during the heat treatment of iron phosphate glasses are the following phases: Fe_2O_3, FeO, $Fe_3(PO_4)_2 \cdot xH_2O$ and $FePO_4 \cdot xH_2O$.

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ZUSAMMENFASSUNG — Differentialthermoanalyse (DTA), thermogravimetrische Analyse (TG), Röntgendiffraktion und Mössbauerspektroskopie wurden bei der Untersuchung (von kristalliner Produkte) durch verschiedene thermische Behandlungen hergestellten FeO_x—

P_2O_5 Gläsern eingesetzt. In den Glasarten mit einem hohen Wert von $\alpha = Fe^{2+}/(Fe^{2+} + + Fe^{3+})$ erfolgt die Sauerstoffabsorption in einem durch $TG_{\lceil}$nachgewiesenen breiten Temperaturbereich. In Abhängigkeit von dem α-Wert erscheinen zwei Exothermen in den DTA-Kurven, von denen der bei niedriger Temperatur die Kristallisation des $Fe_3(PO_4)_2$ entspricht, und jener bei höheren Temperaturen in verschiedenen Phasen dem $FePO_4$. Jede Exotherme hat ihr eigenes Umwandlungsgebiet, das in absolutem Wert identisch ist. Die Mössbauer-Spektren der Gläser welche einer Wärmebehandlung bei höheren Temperaturen unterzogen worden sind, weisen einige Indikationsphasen der Typen $Fe_3(PO_4)_2 \cdot xH_2O$ und $FePO_4 \cdot xH_2O$ auf.

Резюме — ДТА, ТГ, рентгенодиффрактометрия и мессбауэровская спектроскопия были использованы для исследования кристаллических продуктов стекол FeO_x—P_2O_5, получаемых путем различной тепловой обработки. С помощью ТГ было установлено, что в стеклах с высоким значением $\alpha = Fe^{2+}/(Fe^{2+} + Fe^{3+})$ поглощение кислорода наблюдается в широкой области температур. В зависимости от значения α, на ДТА-кривых наблюдаются две изотермы: низкотемпературная изотерма соответствует области кристаллизации $Fe_3(PO_4)_2$, а высокотемпературная — кристаллизации различных фаз с преобладанием $FePO_4$. Каждая экзотерма имеет собственную область превращения, идентичных по абсолютному значению. Мессбауэровские спектры стекол, подвергнутых термообработке при высоких температурах, представили некоторые указания на существование фаз типа $Fe_3(PO_4)_2 \cdot xH_2O$ и $FePO_4 \cdot xH_2O$.