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# Matrix Effects in Obtaining Pentavalent Oxidation States of Iron

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**Abstract**—The possibility of obtaining pentavalent iron in glassy potassium manganate (V) matrices has been shown.

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The iron oxidation state +5 is chemically unstable. Reliable direct information on this oxidation state is scarce, and its identification became possible only after the advent of Mössbauer spectroscopy [1]. The iron(V) state has been obtained, in particular, by the matrix isolation method [2], in which the unstable ion of an element is isomorphously substituted into a stable compound of another element. To stabilize the $Fe^{5+}$ ion, potassium manganate(V) $K_3MnO_4$ [3] was used since the iron and manganese ions have close ionic radii in any oxidation states and, hence, are capable of isomorphous substitution. Potassium manganate was synthesized by a known procedure [4], although the sample turned out to be amorphous. This suggests that unstable ions can be stabilized by highly disperse or even glassy substances in matrices that are not fully crystalline. To check this suggestion, in this work, iron was introduced into different mixtures prepared from potassium superoxide $KO_2$ and manganese oxides $Mn_2O_3$ and $MnO_2$, which, as might be expected by analogy with phosphate and vanadate matrices [5], can give glasses.

## EXPERIMENTAL

Mixtures of potassium peroxide (Merck, pure for analysis) and manganese oxide (pure for analysis, Russian State Standard) containing 1–3 at. % iron were placed in a silver boat into an oven, heated for 30 min to 800°C, and kept at this temperature for 1 h. Synthesis was carried out in a dry oxygen atmosphere. To cool the sample, the quartz tube with the boat was removed from the oven and placed in a water flow. All operations for loading the initial mixture and removing the resulting sample were carried out in a dry box. This procedure is close to the procedure used for preparing potassium manganate $K_3MnO_4$ [1].

Mössbauer absorption spectra were recorded on an MosTek MS1101E spectrometer (Russia) or on a Persei high-precision spectrometer (Russia) with laser calibration and stabilization of velocities. The standard $^{57}Co(Rh)$ source was used. Chemical shifts were measured relative to α-iron. The spectra were processed by the least-squares method with the Univem software (MosTek, Russia).

## RESULTS AND DISCUSSION

A molar ratio >3 : 1 of the components of the $KO_2$–$MnO_2$ system was chosen to considerably exceed the stoichiometric amount of the reagent required for the formation of potassium manganate $K_3MnO_4$ and to facilitate the formation of a glassy matrix. All samples prepared at 800°C were blue-green in color, hygroscopic, and X-ray amorphous. Before being ground to a powder, the samples were a shiny homogeneous mass typical of glass.

The sample with the potassium-to-manganese ratio 8 : 1 has the simplest spectrum as a virtually symmetric well-resolved doublet with the inner slopes being gen-

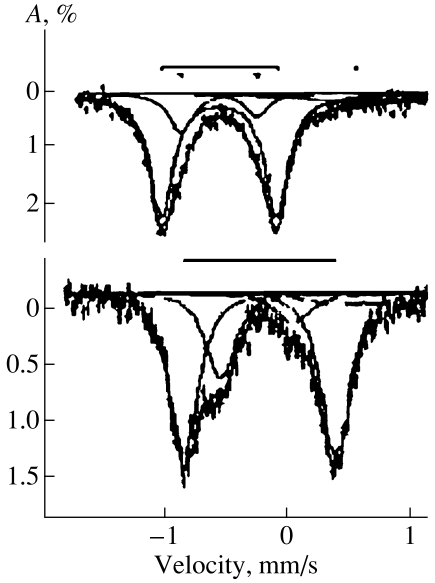

**Fig. 1.** Mössbauer spectra of the sample with the ratio $[KO_2] : [MnO_2] = 8 : 1$ at (top) 295 and (bottom) 80 K.

tler than the outer ones. This spectrum can be represented by two doublets or by a doublet and two singlets (Fig. 1). The line parameters for both models are given in Table 1. Our calculations show that the spectra are satisfactorily described by a superposition of lines of nearly Lorentzian shape. In all models, the isomer shift of the major doublet, for example, –0.538(2) mm/s at 295 K, in model 3, is evidence that it arises from pentavalent iron [3]. The other doublet in model 1 can also correspond to the oxidation state +5. In model 2, the isomer shift of one of the singlets $\delta = 0.90(2)$ mm/s precisely coincides with the isomer shift of potassium ferrate(VI), whereas the position of the second singlet is also acceptable for the $Fe^{4+}$ ion [1].

The spectra recorded at liquid nitrogen temperature allow us to choose model 2. In this case, the spectral resolution is improved due to some increase (to 1.36 mm/s) in the quadrupole splitting for the +5 ion since the lines of the doublet are shifted in opposite directions with decreasing temperature. Taking into account the quadratic Doppler effect (temperature dependence of the isomer shift), the lines of the +6 and +4 ions, as expected, are shifted in one direction.

The decomposition of the spectrum is improved by introducing yet another doublet (model 3). Its intensity is low (8%), and, therefore, the parameters of this doublet are not exactly determined. However, they undoubtedly correspond to the iron state +3 (Table 1). Upon the introduction of this doublet, the parameters of the lines of the other iron forms remain virtually unaltered. The quadrupole splitting of Fe(V) (1.067(10) mm/s) differs noticeably from the quadrupole splitting observed when the Fe(V) ion is stabilized in $K_3MnO_4$ (0.158(5) mm/s [3]).

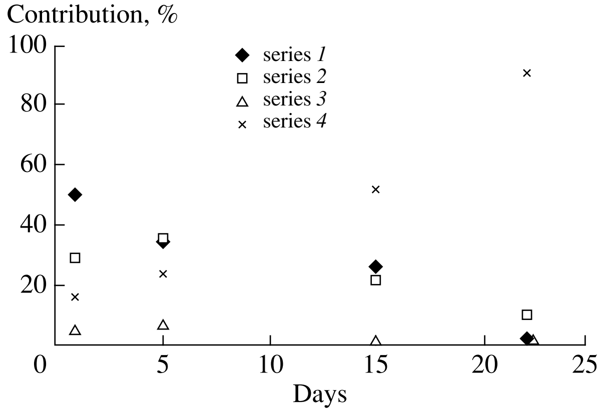

**Fig. 2.** Contribution of iron species as a function of the storage time of the sample: (series *1*) Fe(V), (series *2*) Fe(VI), (series *3*) Fe(IV), and (series *4*) Fe(III) (error, 4%).

**Table 1.** Mössbauer spectra of the sample with $[KO_2] : [MnO_2] = 8 : 1$ ($\delta$, isomer shift; $\Delta$, quadrupole splitting; $\Gamma_{exp}$, experimental line width at half maximum; $S$, the surface above the line of a corresponding species; $\chi^2$, the sum of squared deviations of the spectrum from the approximating function)

| Temperature of measurement (calculation model) | Iron species | $\delta$, mm/s | $\Delta$, mm/s | $\Gamma_{exp}$, mm/s | $S$, % (±4%) | $\chi^2$ |
|---|---|---|---|---|---|---|
| 295 K (model 1) two doublets | Fe(V) | −0.530(2) | 1.073(8) | 0.26(1) | 79 | 1.6 |
| | | −0.540(6) | 0.70(3) | 0.24(1) | 21 | |
| 295 K (model 2) doublet and two singlets | Fe(V) | −0.534(2) | 1.08(1) | 0.25(1) | 77 | 1.5 |
| | Fe(VI) | −0.90(2) | 0 | 0.25(2) | 13 | |
| | Fe(IV) | −0.18(2) | 0 | 0.25(2) | 10 | |
| 295 K (model 3) two doublets and two singlets | Fe(V) | −0.538(2) | 1.067(10) | 0.26(1) | 73 | 1.0 |
| | Fe(VI) | −0.89(2) | 0 | 0.27(3) | 12 | |
| | Fe(IV) | −0.19(3) | 0 | 0.28(4) | 8 | |
| | Fe(III) | 0.80(8) | 0.52(11) | 0.62(6) | 8 | |
| 80 K (model 2) | Fe(V) | −0.42(1) | 1.36(1) | 0.30(1) | 70 | 1.5 |
| | Fe(VI) | −0.78(1) | 0 | 0.30(2) | 18 | |
| | Fe(IV) | −0.02(4) | 0 | 0.53(8) | 12 | |
| 80 K (model 3) | Fe(V) | −0.422(6) | 1.36(1) | 0.307(9) | 68 | 1.2 |
| | Fe(VI) | −0.772(9) | 0 | 0.31(2) | 18 | |
| | Fe(IV) | −0.12(4) | 0 | 0.36(8) | 7 | |
| | Fe(III) | 0.5(3) | 0.5(2) | 0.6(2) | 7 | |
| 295 K (model 2) five days after the preparation | Fe(V) | −0.54(1) | 1.08(2) | 0.25(2) | 42 | 1.2 |
| | Fe(VI) | −0.93(3) | 0 | 0.29(6) | 12 | |
| | Fe(IV) | −0.11(2) | 0 | 0.38(4) | 23 | |
| | Fe(III) | 0.56(2) | 0 | 0.67(6) | 23 | |

**Table 2.** Contribution of different iron oxidation states as the sample is aged (temperature of measurements, 295 K; calculation model 3)

| Sample | Iron species | δ, mm/s | Δ, mm/s | $\Gamma_{exp}$, mm/s | *S*, % (±4%) | $\chi^2$ |
|---|---|---|---|---|---|---|
| Initial | Fe(V) | −0.54(1) | 0.99(3) | 0.38(4) | 50 | 1.5 |
| | Fe(VI) | −0.83(1) | 0 | 0.36(5) | 29 | |
| | Fe(IV) | −0.38(4) | 0 | 0.25(12) | 5 | |
| | Fe(III) | 0.5(7) | 0.8(8) | 0.9(6) | 16 | |
| 5 days after the preparation | Fe(V) | −0.541(8) | 1.03(2) | 0.30(3) | 34 | 1.2 |
| | Fe(VI) | −0.877(4) | 0 | 0.28(1) | 35 | |
| | Fe(IV) | −0.34(3) | 0 | 0.32(10) | 7 | |
| | Fe(III) | 0.24(5) | 0.72(7) | 0.71(13) | 24 | |
| 15 days after the preparation | Fe(V) | −0.53(1) | 0.99(2) | 0.29(3) | 26 | 1.1 |
| | Fe(VI) | −0.863(1) | 0 | 0.30(3) | 22 | |
| | Fe(IV) | – | – | – | 0 | |
| | Fe(III) | 0.19(1) | 0.72(2) | 0.49(3) | 52 | |
| 22 days after the preparation | Fe(V) | – | – | – | 0 | 1.2 |
| | Fe(VI) | −0.88(2) | 0 | 0.45(6) | 7 | |
| | Fe(IV) | – | – | – | 0 | |
| | Fe(III) | 0.218(3) | 0.657(4) | 0.439(8) | 93 | |
| 22 days after the preparation, model 4 (three doublets and two singlets) | Fe(V) | – | – | – | 0 | 0.8 |
| | Fe(VI) | −0.81(2) | 0 | 0.53(6) | 10 | |
| | Fe(IV) | – | – | – | 0 | |
| | Fe(III) | 0.21(1) | 0.61(2) | 0.42(2) | 73 | |
| | Fe(III) | 0.38(5) | 1.1(2) | 0.55(14) | 17 | |

According to the isomer shift, this form should be assigned to the Fe(V) ion in a tetrahedral oxygen environment [1]. The new Fe(V) state is unstable and gradually disappears (Table 2, Fig. 2). This state is quite stable at liquid nitrogen temperature.

Figure 2 shows that, over the first five days, the decrease in the content of pentavalent iron at 295°C is accompanied by an increase in the contribution of the +4 and +6 forms, which presumably reflects the disproportionation of the +5 form. It is worth noting that the yield and the rate of disappearance of Fe(V) vary within noticeable ranges and depend on difficult-to-control experimental conditions. When iron ions are almost completely transformed into the +3 state, the calculation without constraints gives two doublets (model 4, Table 2). According to their isomer shifts, these doublets can be assigned to the ions in the tetrahedral (73%) and octahedral (17%) oxygen environment [6].

Thus, we identified a new form of pentavalent iron unstable at room temperature. The fact that its Mössbauer parameters are virtually independent of the composition near the ratio $[KO_2] : [MnO_2] = 8 : 1$ most likely supports the formation of an individual compound rather than a continuous solid solution of iron(V) oxide in potassium oxide.

## ACKNOWLEDGMENTS

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