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On the possible existence of unusual higher oxidation states of iron in the Na–Fe–O system

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Abstract

The study of the Na_2O_2–Fe_2O_3 system allowed us to obtain new information about compounds of iron in higher oxidation states. At a 10:1 molar ratio of these oxides the phase with parameters of Mössbauer spectra $\delta = -0.01 \pm 0.01$ mm s^{-1}, $\Delta E = 0.40 \pm 0.01$ mm s^{-1}, $\Gamma = 0.24 \pm 0.01$ mm s^{-1} at 291 K and $\delta = 0.12 \pm 0.01$ mm s^{-1}, $\Delta E = 0.42 \pm 0.01$ mm s^{-1}, $\Gamma = 0.42 \pm 0.01$ mm s^{-1} at 77 K was obtained, a six-line spectrum ($\delta = 0.09 \pm 0.02$ mm s^{-1}, $\Delta E = 0.21 \pm 0.02$ mm s^{-1}, $H = 257 \pm 1$ kOe and $\Gamma = 0.27 \pm 0.02$ mm s^{-1} for central lines) at 5 K was observed (δ given relative to sodium nitroprusside). The compound decomposes quickly which leads to the formation of unusual iron states. This process was observed by Mössbauer and EPR techniques.

Keywords: Sodium ferrate; Mössbauer spectroscopy; Oxidation state; Hyperfine magnetic interaction; Quadrupole splitting

1. Introduction

Transition elements exhibit a wide spectrum of oxidation states. That is why the synthesis and the study of iron compounds with iron in higher oxidation states are of great importance and interest in present-day inorganic chemistry. Information about such compounds is necessary for different modern physico-chemical methods too. On the one hand, it makes it possible to check the reliability of the theoretical suppositions. On the other hand, it allows us to expand the experimental base of empirical laws which have no quantitative theoretical descriptions at present. Compounds of iron in higher oxidation states have high reaction capacity and are unstable. This can explain unsatisfactory research of their synthesis methods and properties. As for the system Na–Fe–O, the reliable information about derivatives of iron in higher oxidation states is very limited. Mössbauer spectroscopy is a very convenient research method for iron-containing systems. In particular it can define the oxidation state of iron. Earlier works [1,2] made possible the accumulation of interesting data about sodium ferrates (IV) and (VI) in the solid state [1] and for iron oxidation states + 4, + 6, + 8 in base solutions [2]. Moreover, in Kopelev et al. [1] the formation of sodium ferrate (V) was not excluded. However, in a number of cases the interpretation given is not convincing.

In the present paper new data about derivatives

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of iron in higher oxidation states in the sodium–iron–oxygen system are presented.

2. Experimental

The sodium peroxide used in this work and the products of reactions have extremely high reaction capacity and easily interact with water and carbon dioxide present in the air. That is why all manipulations with the substances were performed in glove boxes under a dry oxygen atmosphere. Specimen for measurements were enclosed in a hermetically sealed special container or ampoule.

To get the substance, the mixture of Na_2O_2 and Fe_2O_3 in the desired ratio was thoroughly ground to powder and poured into a silver boat with a cover. Then it was heated at approx. 480°C in a special reactor with oxygen passing over it.

The Mössbauer spectroscopic data were obtained with the spectrometers 'PERSEY' and 'ROSTOV' of Russian origin. EPR spectra were examined with modernized 'Varian' spectrometer. X-ray diffraction research was carried out on different types of diffractometers in special containers.

3. Results and discussion

Using a 10:1 molar ratio of sodium to iron, we were able to get a phase of iron in higher oxidation state. Its Mössbauer spectrum at 291 K is given in Fig. 1a and is a doublet with chemical shift $\delta = -0.01 \pm 0.01$ mm s^{-1}, quadrupole splitting $\Delta E = 0.40 \pm 0.01$ mm s^{-1} and half width $\Gamma = 0.24 \pm 0.01$ mm s^{-1}. At 77 K spectrum lines broadened (Fig. 1b) which, we believe, is a result of the beginning of magnetic interactions ($\delta = 0.12 \pm 0.01$ mm s^{-1}, $\Delta E = 0.42 \pm 0.01$ mm s^{-1}, $\Gamma = 0.42 \pm 0.01$ mm s^{-1}). At 5 K (Fig. 2) a splitting by internal hyperfine magnetic field (HMF) $H = 257 \pm 1$ kOe ($\delta = 0.09 \pm 0.02$ mm s^{-1}, $\Delta E = 0.21 \pm 0.02$ mm s^{-1}, $\Gamma = 0.27 \pm 0.02$ mm s^{-1} for central lines) was observed.

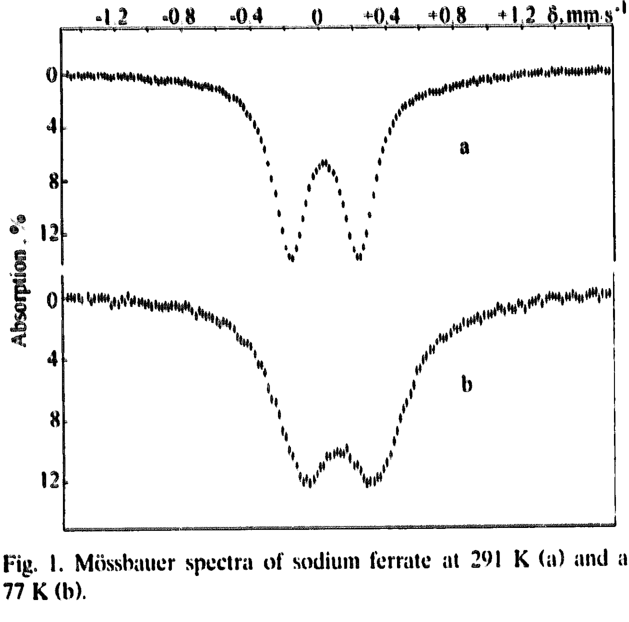

Fig. 1. Mössbauer spectra of sodium ferrate at 291 K (a) and at 77 K (b).

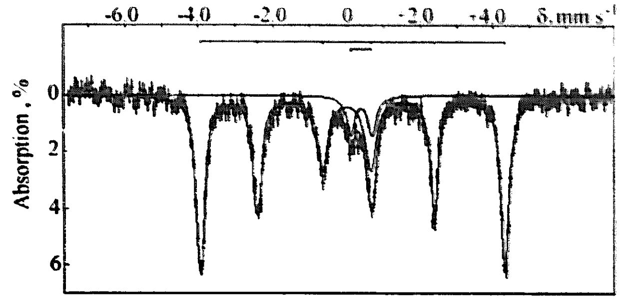

Fig. 2. Mössbauer spectrum of sodium ferrate at 5 K (the doublet of decomposition product is present).

There is a definite relationship between the oxidation state of iron in oxygen arrangement and the chemical shift of the Mössbauer spectrum [3]. From that relationship the chemical shift of our ferrate can be ascribed to either a tetra- or pentavalent iron.

A definite relationship can be also observed between the iron valency and the value of HMF in splitted spectra. The values of HMF for hexavalent iron are in the region 118–151 kOe (2.8 K) according to Herber and Johnson [4]. This value for La_2LiFeO_6 [5] is equal to 232 ± 2 kOe (4.2 K). For $CaFeO_3$ at 4 K disproportionation $2Fe^{4+} \rightarrow Fe^{5+} + Fe^{3+}$ was seen, HMF values 279 kOe and 416 kOe respectively (average value 348 kOe) for these states were obtained [6]. Finally the tetravalent iron state in $SrFeO_3$ is characterized at 4 K by a HMF value of 331 kOe [6]. The HMF value for our ferrate agrees well with known values of the state + 5.

The use of different X-ray diffraction techniques did not provide any information about crystal structure. According to the results of this method the substance is amorphous.

At room temperature the phase decomposes quickly. It can be easily seen in Mössbauer spectra (Fig. 3). Together with the lines in the trivalent iron region, there appear lines with $\delta \approx -1.4$ mm s^{-1} and $\delta \approx -1.1$ mm s^{-1}. According to Kopelev et al. [2] and Menil [3] these values can be related to derivatives of octa- and heptavalent iron. However, these lines can also be components of doublets with large quadrupole splitting. Nevertheless, even in this case they correspond to an iron oxidation state of no less than + 5.

The process of decomposition can be seen in successively obtained EPR spectra. At 77 K in these spectra one can see an anisotropic signal ($g_{\parallel} = 2.190 \pm 0.001$, $g_{\perp} = 1.999 \pm 0.001$). The intensity of the signal increases with time.

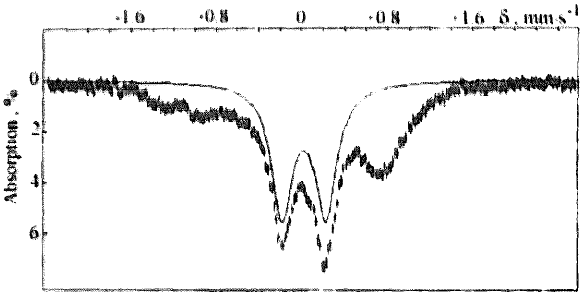

Fig. 3. Mössbauer spectrum of decomposing sodium ferrate at 291 K.

To increase the content of constituent with very low chemical shifts we tried to stimulate decomposition process by increasing the quantity of oxidation agent in initial mixture. The use of monoisotopic $^{57}Fe_2O_3$ allows to obtain spectra of good quality with a sodium to iron molar ratio of 100:1. Spectra of one of the samples, obtained at a ratio of 100:1 and under the same conditions of synthesis, are given in Fig. 4. It can be seen that the content of constituent in the area of approx. -1.4 mm s^{-1} increased greatly and the original doublet practically disappeared. However, in the area of tetravalent iron an intensive line remains, so it is not clear if we obtained a singlet of octavalent iron or a doublet of iron + 5 or + 6. But still it must be stressed that neither situation has been described yet. Measurements at liquid helium temperature do not make these questions clear, as the splitting by HMF was not observed.

4. Conclusions

The system Na–Fe–O is prospective for the study of derivatives of iron in higher oxidation states. The use of oxidizer in abundance in solid-state oxidation synthesis can get novel information about valent possibilities of transition metals. For the first time the data about quadrupole and magnetic interactions of iron in higher oxidation state in Na–Fe–O system were obtained. Complementary studies on this system are going on.

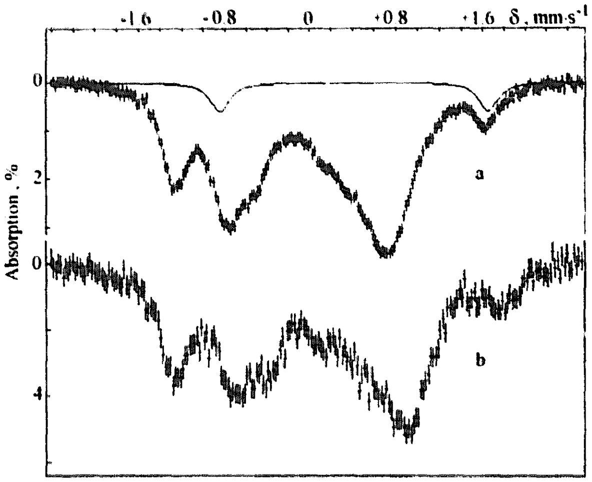

Fig. 4. Mössbauer spectrum of iron in sodium peroxide matrix at 291 K (a) [the two inserted lines are the central lines of iron(III) sextet] and at 5K (b).

Acknowledgements

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References

[1] N.S. Kopelev, Yu.D. Perfiliev, Yu.M. Kiselev, J. Radioanal. Nucl. Chem. 162 (1992) 239.
[2] N.S. Kopelev, Yu.D. Perfiliev, Yu.M. Kiselev, J. Radioanal. Nucl. Chem. 157 (1992) 401.
[3] F. Menil, J. Phys. Chem. Solids 46 (1985) 763.
[4] R.H. Herber, D. Johnson, Inorg. Chem. 18 (1979) 2786.
[5] G. Demazeau, B. Buffat, F. Menil, Mater. Res. Bull. 16 (1981) 1465.
[6] Y. Takeda, S. Naka, M. Takano, T. Shinjo, T. Takada, M. Shimada, Mater. Res. Bull. 13 (1978) 61.