ISSN 1070-4272, *Russian Journal of Applied Chemistry*, 2019, Vol. 92, No. 2, pp. 181−185. © Pleiades Publishing, Ltd., 2019.
Russian Text © L.B. Vedmid', O.M. Fedorova, V.M. Dimitrov, 2019, published in *Zhurnal Prikladnoi Khimii*, 2019, Vol. 92, No. 2, pp. 149−153.

INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Structure and Thermodynamic Stability of $LuFe_2O_4$

L. B. Vedmid'[a,b], O. M. Fedorova[a],*, and V. M. Dimitrov[a]

[a] *Institute of Metallurgy, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*
[b] *Ural Federal University, Yekaterinburg, Russia*
**e-mail: fom55@mail.ru, elarisa100@mail.ru*

Received September 28, 2018; revised November 22, 2018; accepted November 29, 2018

Abstract—Synthesis of a multiferroic of composition $LuFe_2O_4$ at a temperature of 1363 K and low oxygen pressures, its crystal structure, and thermodynamic properties are reported. The $LuFe_2O_4$ ferrite was obtained by using an improved method of synthesis in a controlled atmosphere. The stability range of this compound was determined in relation to the partial pressure of oxygen in the gas atmosphere under a thermal treatment. At room temperature, the sample has a rhombohedral structure ($R\bar{3}m$ space group). The X-ray diffraction method was used to determine the structural characteristics of the compound, and its thermodynamic properties were found by the static method in a vacuum circulation installation.

Keywords: multiferroics, partial oxygen pressure, mixed valence, structure, thermodynamic properties.

DOI: 10.1134/S1070427219020022

Materials based on transition metal oxides, which possess a mixed valence of cations and combine ferromagnetic and ferroelectric properties, are attributed to the special class of multiferroics, which makes promising their technological application in information and energy-saving technologies [1]. Their particular properties are due to the relationship between the spin, charge, and orbital kinds of ordering. The mechanisms by which the ferromagnetic and ferroelectric ordering appears in this class of compounds differ rather strongly, to the point of mutual exclusion. [2]. To obtain compounds of this kind and prognosticate their properties, it is necessary to have information about their existence conditions and structural and thermodynamic characteristics. At present, there is information about the classification by the presence of compounds of the homological series $LnFeO_3 \cdot nFeO$ in Ln–Fe–O systems (Ln is a rare-earth element) in the temperature range 1423–1523 K and some phase diagrams have been reported [3, 4]. Depending on the presence of a rare-earth ion Ln^{3+} in compounds and on thermodynamic conditions, the classification subdivides the systems into four groups. The compounds $LnFeO_3$ and $Ln_3Fe_5O_{12}$ are synthesized in air at temperatures higher than 1273 K for all Ln. The homologs $LnFe_2O_4$ (Ln = Y, Ho–Lu) and $Ln_2Fe_3O_7$ (Ln = Y, Yb, Lu), which contain aliovalent iron ions Fe^{2+}, Fe^{3+}, are, as a rule, obtained in a reducing mixture of gases $CO–CO_2–H_2–H_2O$ at temperatures above 1423 K [3–6]. The oxide $LuFe_2O_4$ is a representative of materials of this kind. At present, there are no data on the possibility of synthesizing the compound $LuFe_2O_4$ at temperatures below 1473 K. Lutetium ferrite attracts researchers' interest because the charge ordering occurs in this material at room temperature, and its structure changes as the temperature is lowered [5]. There is published evidence about the crystal structure and physical properties of $YbFe_2O_4$ [7, 8], YFe_2O_4, $ErFe_2O_4$ [9], $TmFe_2O_4$ [10], but no data are available on the thermodynamic stability of these compounds.

The goal of our study was to find conditions for synthesis of $LuFe_2O_4$ at temperatures below 1423 K, obtain thermodynamic characteristics at lowered oxygen pressures, and examine the structure in more detail in a wide temperature range. The availability of evidence of this kind is important for practical application of this class of compounds.

EXPERIMENTAL

$LuFe_2O_4$ samples were synthesized from a mixture of oxides Fe_2O_3 (analytically pure) and Lu_2O_3 (99.9%), both

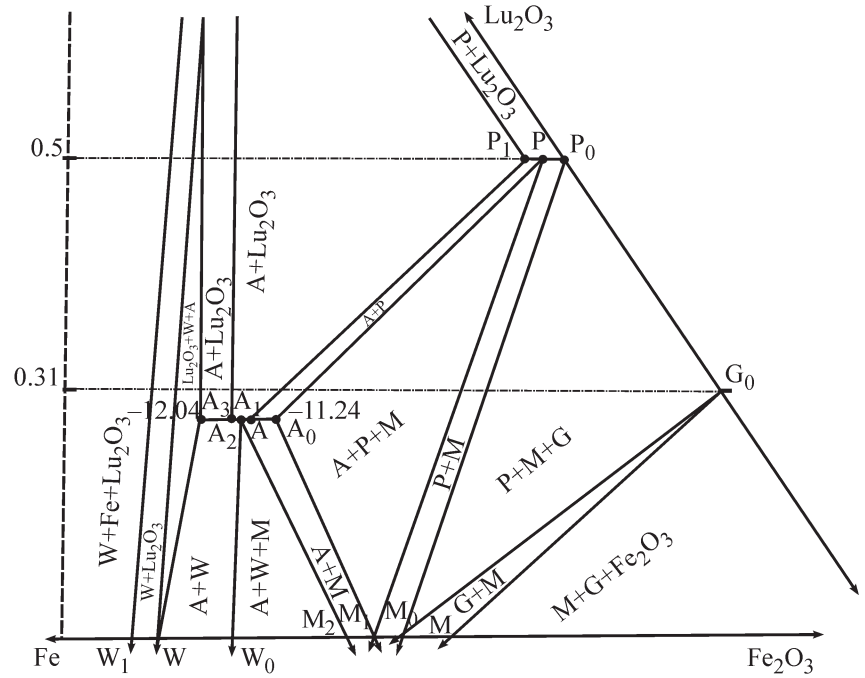

Fig. 1. Fragment of the phase diagram of the Lu–Fe–O system at a temperature of 1363 K. Phase designations: A = LuFe$_2$O$_{4\pm\delta}$, P = LuFeO$_{3\pm\delta}$, G = Lu$_3$Fe$_5$O$_{12}$, W = FeO, M = Fe$_3$O$_4$.

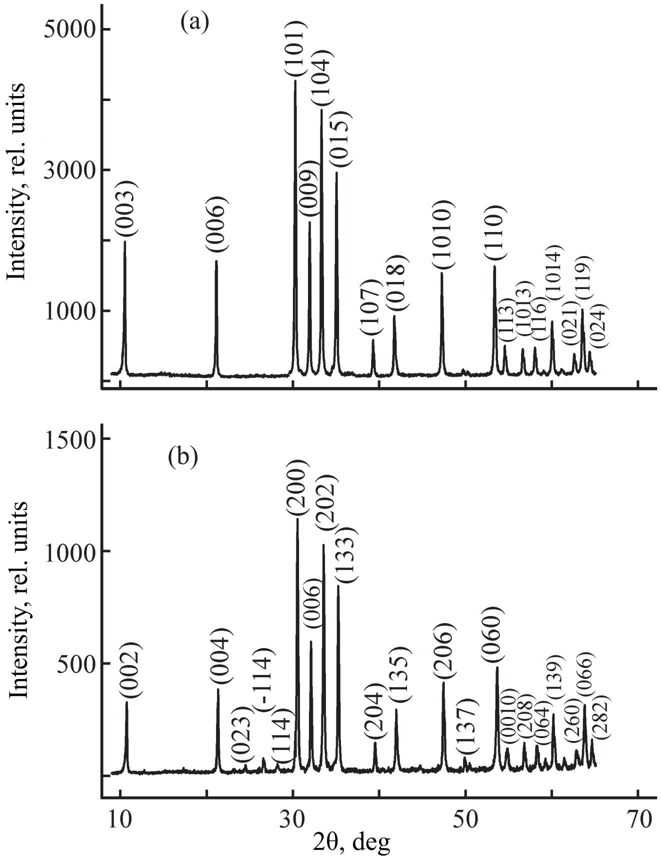

Fig. 2. Diffraction patterns of LuFe$_2$O$_4$ samples at (a) 300 and (b) 150 K. Miller indices are shown for (a) rhombohedral and (b) monoclinic structures.

preliminarily dried at a temperature of 550°C. Equimolar amounts of the starting oxides were mixed and ground in an agate mortar for 1 h. The resulting mixture was used to compact pellets 10 mm in diameter on a hydraulic press under a pressure of 150 kPa cm^{-2}, and the pellets were calcined in a closed-volume installation [11] in a quartz reactor at T = 1363 K in a gas atmosphere with variable oxygen pressure during 18 h. Under the experimental conditions, the maximum possible synthesis temperature is 1363 K, which is determined by using quartz as the reactor material. The partial oxygen pressure in the gas atmosphere is monitored during the whole run with the use of an oxygen cell including an oxygen sensor and an oxygen pump. The operation of the oxygen cell is controlled by a programmed oxygen-pressure regulator. The gas medium was formed from a purified mixture of an inert gas (Ar) and O$_2$. In this case, only an oxygen exchange can occur as a result of the interaction of a sample with components of the gas mixture, in contrast to the case of a mixture of gases, CO–CO$_2$–H$_2$–H$_2$O, in which carbides can be formed. An X-ray diffraction (XRD) analysis of quenched LuFe$_2$O$_4$ samples was made with a Shimadzu XRD 7000 diffractometer (CuK_α radiation) at angles $10° < 2\theta < 70°$ with a step of 0.2°. A full-profile XRD analysis was made by the Rietveld method with EXPGUI software complex [12], with the model described in [8] served as the starting model. The thermal stability of $LuFe_2O_4$ samples was examined in a vacuum circulation installation by the static method [13]. Changes in the thermal properties of the compounds were recorded by the method of differential scanning calorimetry (DSC) on a Netzsch DSC 204 F1 instrument. Measurements were made in aluminum crucibles in the atmosphere of nitrogen in the temperature range 110–373 K at a heating rate of 10 deg min^{-1}.

RESULTS AND DISCUSSION

The process in which compounds of the type RFe_2O_4 (R = Dy–Lu) can be represented by the scheme

$$R^{3+}Fe^{3+}O_3^{2-} + Fe^{2+}O^{2-} \rightarrow R^{3+}Fe^{3+}Fe^{2+}O_4^{2-} \rightarrow RFe_2O_4. \quad (1)$$

Fixing one parameter, temperature, while varying another parameter, oxygen pressure, when synthesizing samples made it possible to find the stability range of the $LuFe_2O_4$ compound. When the partial oxygen pressure at a temperature of 1363 K changes to more than $P_{O_2} = 10^{-11.24}$ atm, the XRD analysis demonstrates the presence of $LuFe_2O_4$, $LuFeO_3$, and Fe_3O_4 phases. Lowering the oxygen pressure to below $P_{O_2} = 10^{-12.04}$ atm results in that the Ln_2O_3 and FeO phases appear in addition to the main phase $LnFe_2O_4$ (Fig. 1). At the boundaries of this range of oxygen pressures, samples retain a single-phase rhombohedral structure.

The single-phase $LuFe_2O_4$ samples have a rhombohedral structure and belong to the $R\bar{3}m$ space group with hexagonal packing; their unit cell parameters are the following: $a = 3.4403(1)$ Å and $c = 25.272(2)$ Å (Fig. 2a).

When $LuFe_2O_4$ is cooled to below 250 K, a transition from the rhombohedral ($R\bar{3}m$ space group) to the monoclinic ($C2/m$ space group) structure is observed. In the XRD patterns, this process is manifested in that peaks appear at angles in the 2θ range 25–28° (Fig. 2b). According to our data, the temperature of this transition somewhat differs from that obtained in [5]. A probable reason may be the difference between the methods used to produce the samples. In the spatial structure of the ferrite $LuFe_2O_4$, the anionic polyhedra containing in the disordered state aliovalent iron cations form layers perpendicular to the principal axis z of the unit cell. Iron cations are situated within a trigonal bipyramids in fivefold environment of oxygen anions. The environment of Lu is an octahedron with six oxygen anions moved apart in the x–y plane. The triangular faces of this octahedron are oriented perpendicularly to the principal axis [14].

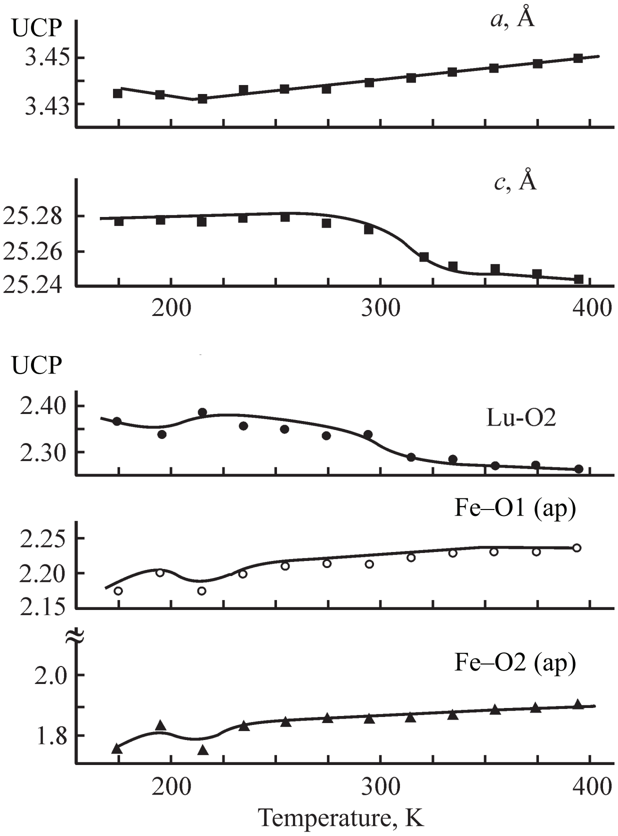

Fig. 3. Temperature dependences of the unit cell parameters (UCPs) and bond lengths in $LuFe_2O_4$.

Figure 3 shows the temperature dependence of the unit cell parameters of $LuFe_2O_4$ with rhombohedral structure and that of the lengths of Lu–O_2 bonds and Fe–O1 and Fe–O2 apical bonds. It can be seen in Fig. 3 that the parameter a of lutetium ferrite slightly decreases in the temperature range 150–210 K, with the lengths of Fe–O1 and Fe–O2 bonds also insignificantly decreasing. Then an increase in the parameter a is observed up to a temperature of 400 K. This rise is accounted for by the thermal expansion of a sample.

The parameter c remains nearly unchanged at temperatures of 150 to 290 K, and then sharply decreases in the temperature range 295–313 K. This behavior of the parameter c is correlated with the behavior of the Lu–O2 bond length. Within the same range, the DSC curve shows a minimum. The decrease in the parameter c of lutetium ferrite at 310 K and the endothermic effect in the DSC curve in the same temperature range may be indicative of the charge ordering in $LuFe_2O_4$. This temperature

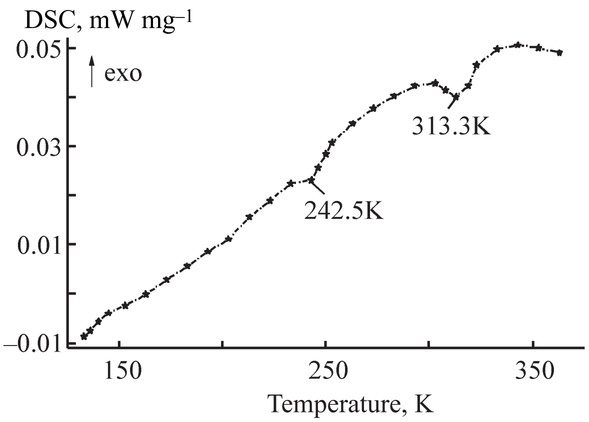

Fig. 4. DSC curve for the $LuFe_2O_4$ compound.

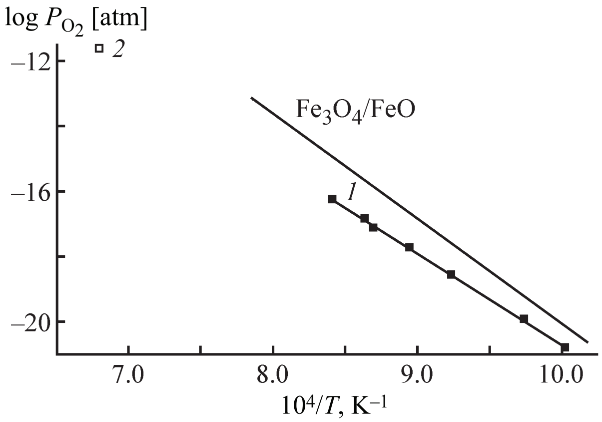

Fig. 5. Temperature dependence of the equilibrium partial oxygen pressure in dissociation of the $LuFe_2O_4$ compound Black squares (*1*) our data, white square (*2*) data of [6].

coincides with the data of [5], in which study the charge ordering in this material was confirmed by neutron diffraction analysis. The second endothermic effect at a temperature of 242.5 K is associated with the structural transition from $R\bar{3}m$ space group to $C2/m$ (Fig. 4).

To determine the phase equilibria and obtain temperature dependences of the equilibrium partial oxygen pressure for these equilibria, we examined the process of dissociation of the $LuFe_2O_4$ compound with the use of the vacuum circulation installation in the temperature range 990–1190 K. In the experimental conditions under the action of a reduced oxygen pressure $P_{O_2} = 10^{-11.24}$–$10^{-12.04}$ atm, the compound $LuFe_2O_4$ dissociates with evolution of oxygen into simple oxides by the reaction

$$LuFe_2O_4 = 1/2Lu_2O_3 + 2FeO + 1/4O_2. \quad (2)$$

In this case, the temperature dependence of the oxygen pressure is linear (Fig. 5, line *1*) and is expressed by the equation

$$\log (P_{O_2}, \text{Pa}^{-1}) = 12.3–27991/T \pm 0.041. \quad (3)$$

Point *2* represents the results of [6], obtained at a higher temperature of 1473 K. The change in the free Gibbs energy for reaction (2) was calculated by Eq. (3) to be

$$\Delta G_T^\circ = 133.93 - 0.0349T \pm 0.12 \text{ kJ mol}^{-1}. \quad (4)$$

Using the values of ΔH_T° and ΔS_T° for reaction (2), calculated by equation (4), and the values of the thermodynamic functions for the reaction in which the simple oxides Lu_2O_3 and FeO are formed, we calculated the changes in the standard enthalpy and entropy of formation of the compounds from elements:

$$\Delta H_T^\circ = -1610.556 \text{ kJ mol}^{-1}, \Delta S_T^\circ = 237.294 \text{ J mol}^{-1} \text{ K}^{-1}.$$

CONCLUSIONS

The conditions of synthesis of the compound $LuFe_2O_4$ at a temperature of 1363 K were studied. This made it possible to supplement with new data the *P–T–C* constitution diagram of the Lu–Fe–O system. The values of the thermodynamic characteristics of formation f the $LuFe_2O_4$ compound from simple oxides were determined. It was found that $LuFe_2O_4$ has in the temperature range 400–150 K a rhombohedral crystal structure and belongs to the $R\bar{3}m$ space group, At 295–313 K, the parameters *a* and *c* change significantly, which is not accompanied by a transition to another space group. This change can be attributed to the change in the Lu–O and Fe–O1 and Fe–O2 bond lengths. In the temperature range 295–313 K, the length of the Lu–O2 bond increases and the apical lengths of the Fe–O1(ap) and Fe–O2 bonds decreases, which causes compression of FeO_5 bipyramids and an increase in the height of the LuO_6 octahedron. The fact that the temperature ranges of charge ordering and sharp decrease in the parameter c coincide may indicate that these two processes are related.

FUNDING

The study was carried out under the State assignment to the Institute of Metallurgy, Ural Branch, Russian Academy of Sciences, on the equipment of the Ural-M Collective Use Center.

REFERENCES

1. Pyatakov, A.P. and Zvezdin, A.K., *Successes Phys. Sci.*, 2012, vol. 182, no. 6, pp. 593–620.
2. Kimizuka, N., Takenaka, A., Sasada, Y., and Katsura, T., *Solid State Commun.*, 1974, vol. 15, pp. 1321–1323.
3. Katsura, T., Sekine, T., Kitayama, K., Sugihara, T., and Kimizuka, N., *J. Solid State Chem.*, 1978, vol. 23, pp. 43–57.
4. Kimizuka, N. and Katsura, T., *J. Solid State Chem.,* 1975, vol. 15, pp. 151–157.
5. Blasco, J., Lafuerza, S., and Subias, G., *Phys. Rev.*, 2014, vol. 90, pp. 094119 (1–11).
6. Sekine, T. and Katsura, T., *J. Solid State Chem.,* 1976, vol. 17, pp. 49–54.
7. Katano, S., Matsumoto, T., Funahashi, S., Iida, J., Tanaka, M., and Cable, J.W., *Physica B*, 1995, vol. 213, pp. 218–222.
8. Hervieu, M., Damay, F., Maignan, A., and Martin, C., *Solid State Sci.,* 2015, vol. 48, pp. A1–A6.
9. Matsumoto, T., Mori, N., Iida, J., Tanaka, M., Siratori, K., Izumi, F., and Asano, H., *Physica B*, 1992, vol. 180, pp. 603–606.
10. Yoshii, K., Ikeda, N., and Nakamura, A., *Physica B*, 2006, vols. 378–380, pp. 585–586.
11. RF Patent 2 548 949 (publ. 2015).
12. Toby, B.H., *J. Appl. Crystallogr.*, 2001, vol. 34, pp. 210–213.
13. Yankin, A.M., Balakirev, V.F., Vedmid', L.B., and Fedorova, O.M., *Russ. J. Phys. Chem.*, 2003, vol. 77, no. 11, pp. 1899–1902.
14. Beznosikov, B.V. and Aleksandrov, K.S., *Perspekt. Mater.*, 2007, vol. 1, pp. 46–49.