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Gas Phase Composition over $\text{Y}_3\text{Fe}_5\text{O}_{12}$

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Abstract. The account of the gas phase composition over $\text{Y}_3\text{Fe}_5\text{O}_{12}$ in dependence on temperature and partial pressure of oxygen Po_2 at the total pressure in system $P = 10^5$ Pa was performed with the use of the program Astra.4. Polynomials was offered for account of heats capacities $C_p(T)$ solid solutions $\text{Ln}_{3-x}\text{Ln}_x\text{Fe}_5\text{O}_{12}$ (Ln: Lanthanide Elements and Y). It is shown, that dissociation of garnet results in formation in gas phase of substances: Fe, FeO, YO_2 , O, O_2 , over 900 K and at further increase of temperature in addition will be formed: Fe^+ , YO, YO^+ . The presence of FeO (that is ions Fe^{2+}) in gas phase is one more proof of reaction: $\text{Y}_3\text{Fe}_5\text{O}_{12} \rightarrow 3/2 \text{O}_2 + 3 \text{V}_o'' + 6 \text{Fe}'$.

1. INTRODUCTION

The studies of thermodynamic stability of condensed phases in systems $\text{Ln}_2\text{O}_3 - \text{FeO} - \text{Fe}_2\text{O}_3$ (Ln: Lanthanide Elements and Y) are published [1, 2]. The conclusions [2] about comparative stability of LnFeO_3 and $\text{Ln}_3\text{Fe}_5\text{O}_{12}$ were used [3] to synthesize $\text{Nd}_3\text{Fe}_5\text{O}_{12}$, $\text{Pr}_3\text{Fe}_5\text{O}_{12}$. However, a quantitative knowledge of the gas phase composition over $\text{Ln}_3\text{Fe}_5\text{O}_{12}$ (mass - spectrometer, for example) as a function of temperature and partial pressure is still lacking. This knowledge can be used to bring changes into the technology of ferrite-garnets synthesis and will promote definition of a species of defects in them. The most complete experimental data on main thermodynamic functions and their temperature dependences are available for yttrium iron garnet (YIG) and phases coexisted with it. That is why in present work a composition of a gas phase over $\text{Y}_3\text{Fe}_5\text{O}_{12}$ is calculated in dependence on temperature and partial pressure of oxygen Po_2 at the total pressure in system $P = 10^5$ Pa and $T = 423 \div 1723$ K.

2. CALCULATION

The accounts were performed with the use of the program Astra.4 [4]. The program algorithm is based on the decision of system of equations for the equilibrium concentration of the thermodynamic system components. Formation of the following substances in gas phase: Ar, O_2 , O, O_3 , Fe, FeO, Fe^+ , Y, YO, YO_2 , YO^+ and in the condensed phase Fe, Y, Fe_3O_4 , Fe_2O_3 , Y_2O_3 , YFeO_3 , YFe_2O_4 , $\text{Y}_3\text{Fe}_5\text{O}_{12}$ has been taken into account. The analysis of phase and chemical equilibrium of thermodynamic system is possible if main thermodynamic properties of its components (heat capacity – C_p , changes of Gibbs free energy – ΔG , enthalpy – H , entropy – ΔS ,) are known. The database of the program Astra.4 contains the thermodynamic functions of the majority of components of system. For condensed phases $\text{Y}_3\text{Fe}_5\text{O}_{12}$, YFeO_3 , YFe_2O_4 the thermodynamic functions of reactions of formation from elements – ΔG_f , ΔH_f , ΔS_f [1] were used. The temperature dependences of the thermodynamic functions were calculated using the following expressions:

$$\Delta H_T = \Delta H_{298} + \int \Delta C_p dT, \Delta S_T = \Delta S_{298} + \int \Delta C_p / T dT, \Delta G_T = \Delta H_T - T \Delta S_T,$$

where ΔC_p – the difference of heat capacities of products of reaction and initial substances. For yttrium iron garnet of values of heats capacities C_p are determined [5] for several temperatures. The temperature dependence $C_p(T)$ in researched interval of temperatures was determined by following technique:

a) The deviation $\delta C_p(T)$ of experimental values of temperature dependences of heats capacities [6] $\text{Ln}_3\text{Fe}_5\text{O}_{12}$ ($\text{Ln}^{3+} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}$) from sum of heat capacities of oxides were calculated:

$$\delta C_p(T) = C_p(T) - \{3/2 C_p(\text{Ln}_2\text{O}_3) + 5/2 C_p(\text{Fe}_2\text{O}_3)\} \quad (1)$$

It is found that the dependences $\delta C_p(T)$ have three temperature intervals: $298 \div T_K$ (Curie), $T_K \div 955$ and over 955 K. The deviation $\delta C_p(T)$ in the range of $298 \div T_K$ is caused [6] by the magnetic contribution to heat capacity of ferrite-garnets, and

from T_K up to 955 by phase transition ($\alpha \leftrightarrow \beta$) in Fe_2O_3 . For rare earth ferrite-garnets of values $\delta C_p(T)$ are close and in the first approach their difference is defined by accuracy of the experimental measurements (1 %) [6] and various presence of defects of garnets (1 %). Hence, the value $C_p(T)$ can be approximated by polynomials:

$$\begin{aligned}\delta C_p(T) &= -475.1 + 4.01 T - 0.011 T^2 + 9.3 \cdot 10^{-6} T^3 & (T = 298 + T_K \text{ K}) \\ \delta C_p(T) &= 328.1 - 1.31 T + 0.002 T^2 + 9.85 \cdot 10^{-6} T^3 & (T = T_K + 955 \text{ K}) \\ \delta C_p(T) &= 2.873 - 0.0147 T + 1.48 \cdot 10^{-4} T^2 & (T = 955 + 1400 \text{ K}),\end{aligned}\quad (2)$$

which are suitable for account $C_p(T)$ ferrite-garnets and of solid solutions $\text{Ln}_{3-x}\text{Ln}_x\text{Fe}_5\text{O}_{12}$.

b) The substitution of polynomials (2) in equation (1) allows to calculate temperature dependence $C_p(T)$ for $\text{Y}_3\text{Fe}_5\text{O}_{12}$, which is close to experimental values [5].

Fig. 1 An equilibrium composition of system YIG-Ar-O₂ depend on a) temperature at $P^0 = 10^5$ Pa (the condensed phase is not shown); line 1 – O₂ in equilibrium with $\text{Y}_3\text{Fe}_5\text{O}_{12}/\text{YFeO}_3/\text{Fe}_3\text{O}_4$ [1]; b) partial pressure of oxygen at $T = 1523$ K (the dotted lines show components of a condensed phase).

3. RESULTS

The results of thermodynamic accounts are plotted in fig. 1. It is shown that at the constant pressure ($P^0 = 10^5$ Pa, $P_{O_2} = 10^{-6}$ Pa) and temperatures $T > 900$ K to thermal dissociation of garnet begins and in the gas phase (fig. 1a) components FeO, Fe, YO₂, O, O₂ appear. At further increase of temperature Fe⁺, YO, YO⁺ are also formed. The experimental information about composition of a gas phase over $\text{Y}_3\text{Fe}_5\text{O}_{12}$ is lacking, therefore comparison of results (fig. 1) is impossible.

The condensed phase composition (in fig. 1 is not shown) changes only at $T > 1273$ K. Except garnet there appears the magnetite Fe_3O_4 (< 0.001 mole %), and over 1573 K the garnet is in equilibrium with Fe_3O_4 (0.03 mole %) and YFeO_3 (< 0.1 mole %), that agrees with a phase diagram [7]. The pressure of oxygen, estimated for the equilibrium $\text{Y}_3\text{Fe}_5\text{O}_{12}/\text{YFeO}_3/\text{Fe}_3\text{O}_4$, is close to experimental [2] (line 1, fig. 1a). The reduction of pressure $P_{O_2}/P^0 < 10^{-6}$ also causes dissociation of garnet on orthoferrite and magnetite, and at increase P_{O_2} up to $\sim 10^5$ Pa the garnet is in equilibrium with Fe_2O_3 (fig. 1b, the phase of garnet is not shown), that confirms conclusions [7, 8].

From fig. 1 (a, b) it is obvious, that the gas phase over YIG contains oxide FeO (< 10^{-8} mole fraction at $T = 1623$ K), the fraction of which enlarges at increase of temperature and reduction of partial pressure of oxygen. Formation of ions Fe^{2+} (in FeO) in gas phase makes it possible to assert, that the valency of iron will be changed in condensed phase according to the reaction:

That coincides data [8] - defects will be formed in YIG - divalent iron and oxygen vacancy.

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