

## Evaluation of vacancies and interstitials by thermogravimetry

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Received 16 July 1999; received in revised form 22 November 1999; accepted 29 November 1999

### Abstract

A procedure to determine the vacancy concentration [V] in magnetite from TG curves when heating  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in a reducing atmosphere is presented, together with some experimental results. The procedure correlates vacancy and cation concentration with the weight change due to oxygen evolution through the charge and mass balance in the sample. The results are presented together with a generalized summary of previous findings on mixed spinel ferrites and yttrium iron garnet. It is shown that in all cases the procedure leads to the same general expression

$$\theta = \Gamma \frac{\mu_B}{\mu_{O_2}} \left( 1 - \frac{m_f}{m_i} \right)$$

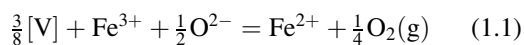
where  $m_f$  and  $m_i$  are the final and initial mass of the sample,  $\mu_B$  the formula mass of the initial oxide reagents,  $\mu_{O_2}$  the oxygen molar mass and  $\theta$  a parameter associated with the oxygen evolution. The parameter  $\Gamma$ , together with the explicit dependence [V]( $\theta$ ) (or interstitial concentration  $I(\theta)$  in the case of YIG) must be determined in every case from the specific chemical equations. The  $\Gamma$  values derived for different ferrite materials are tabulated together with the corresponding [V]( $\theta$ ) or [I]( $\theta$ ). The procedure allows the calculation of the Fe<sup>3+</sup> → Fe<sup>2+</sup> enthalpy from the equilibrium  $\ln(K)$  versus  $1/T$  curves deduced from the TG data and the Van't Hoff equation. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Vacancy; Interstitial; Ferrite; Enthalpy; Thermogravimetry

### 1. Introduction

Vacancy concentration may become a very important parameter for the study of after-effects in magnetic ceramics. Diffusion processes, which could severely affect specific magnetic properties, may be speeded up or delayed depending on the amount of vacancies in the sample. For instance, in iron-excess perminvar-type ferrites the presence of vacancies, together with the presence of Co<sup>2+</sup> ions, is essential to obtain the

characteristic properties of perminvar [1–3]. Vacancies can also be important in the control of disaccommodation processes, associated with the time stability of the magnetic properties at room temperature [4]. Most ferrite materials are able to include in the lattice some Fe in excess over the stoichiometry without segregating additional phases. Depending on the oxygen partial pressure ( $p_{O_2}$ ) and the temperature, the interchange



may take place in either direction [5]. Here  $1/2 O^{2-}$  means the oxygen linked to the lattice and [V] a cation vacancy. From (1.1) it follows that, as a general rule,

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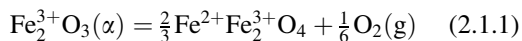
iron excess single-phased ferrite samples sintered at high temperature are apt to contain a certain amount of both  $\text{Fe}^{2+}$  and vacancies. However, earlier attempts to make use of thermogravimetry (TG) procedures as an analytical tool were usually referred to the oxygen or the  $\text{Fe}^{2+}$  contents, without stressing the point of the vacancy concentration. Further, these attempts are frequently based on estimations or approximations not always entirely justified [6–10].

The aim of this report is to summarize a general procedure that allows the estimation of the vacancy (or interstitial) concentration from TG curves of ferrites synthesized by conventional ceramic methods. In the following, the expressions to compute the vacancy content in magnetite when heating  $\alpha\text{-Fe}_2\text{O}_3$  in a reducing atmosphere are derived and presented together with a generalized summary of previously reported results for mixed spinel and garnet ferrites.

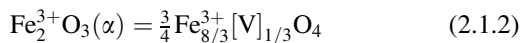
## 2. Results

### 2.1. Magnetite

As it is well known, cubic magnetite  $\text{Fe}_3\text{O}_4$  can be obtained by heating trigonal hematite  $\alpha\text{-Fe}_2\text{O}_3$  at high temperature in a suitable reducing atmosphere [11]. However, the interchange described in (1.1) implies that, depending on the particular treatment applied, some vacancy content could be present after cooling the sample. To evaluate the vacancy content by TG procedures let us assume that not all the hematite has transformed to magnetite, but that some of it transformed to maghemite  $\gamma\text{-Fe}_2\text{O}_3$ , with the same cubic crystalline structure but also with one of every nine Fe cation sites vacant. If we write the hematite–magnetite transformation as



the assumed hematite–maghemite transition can be represented as follows:



Let us suppose that on heating the  $\alpha\text{-Fe}_2\text{O}_3$  a single-phased solid solution of magnetite and maghemite is formed; that is, only a molar fraction  $\theta$  of the hematite transforms to magnetite and the remainder  $(1-\theta)$  transforms to  $\gamma\text{-Fe}_2\text{O}_3$ . Adding and adjusting coefficients in

(2.1.1) and (2.1.2), grouping like terms and multiplying formula and coefficients by the appropriate factor to keep four oxygen atoms by formula leads to

$$\begin{aligned} \text{Fe}_2\text{O}_3(\alpha) &= \frac{(9-\theta)}{12}\text{Fe}_{8\theta/(9-\theta)}^{2+}\text{Fe}_{8(3-\theta)/(9-\theta)}^{3+} \\ &\times [\text{V}]_{3(1-\theta)/(9-\theta)}\text{O}_4 + \frac{\theta}{6}\text{O}_2(\text{g}) \end{aligned} \quad (2.1.3)$$

Note that (2.1.1) and (2.1.2) may be arranged and simplified to obtain (1.1). From (2.1.3) it is seen that for every  $q$  transformed formulas of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $q\theta/6$  moles of  $\text{O}_2$  must appear. Therefore, the evolved mass of oxygen would be

$$m_i - m_f = \frac{q\theta}{6}\mu_{\text{O}_2} \quad (2.1.4)$$

where  $m_i$  and  $m_f$  are the initial and final mass of the sample and  $\mu_{\text{O}_2}$  is the oxygen molar mass. Besides,  $m_i = q\mu_{\text{B}}$ ,  $\mu_{\text{B}}$  being the  $\alpha\text{-Fe}_2\text{O}_3$  formula mass. The substitution of  $q$  in (2.1.4) leads to

$$\theta = 6\frac{\mu_{\text{B}}}{\mu_{\text{O}_2}}\left(1 - \frac{m_f}{m_i}\right) \quad (2.1.5)$$

and from (2.1.5) it follows that, on measuring  $m_i$  and  $m_f$ , the vacancy and remaining coefficients in the chemical formula can be computed from (2.1.3):  $[\text{V}] = 3(1-\theta)/(9-\theta)$ ,  $[\text{Fe}^{2+}] = 8\theta/(9-\theta)$  and  $[\text{Fe}^{3+}] = 8(3-\theta)/(9-\theta)$ .

Fig. 1 shows the TG curve of an  $\alpha\text{-Fe}_2\text{O}_3$  sample heated to  $T_{\text{max}} = 1400^\circ\text{C}$  in a  $\text{CO}_2$  atmosphere. From

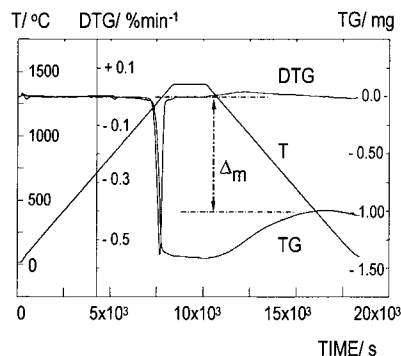


Fig. 1. TG curve of  $\alpha\text{-Fe}_2\text{O}_3$  (44.2 mg) heated in a TGDTA-92 SETARAM thermobalance,  $\text{CO}_2$  atmosphere,  $T_{\text{max}} = 1400^\circ\text{C}$ , heating and cooling rates  $10^\circ\text{C}/\text{min}$ .

the TG curve in the range 1000°C to room temperature with  $m_i=44.2$  mg it was computed that  $\Delta m=1.02$  mg. Substitution in (2.1.5) leads to  $\theta=0.691$ . Since  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> segregation was not observed in the cooling stage, the chemical formula of the resulting spinel material at room temperature could be written as Fe<sub>0.665</sub><sup>2+</sup>Fe<sub>2.223</sub><sup>3+</sup>[V]<sub>0.112</sub>O<sub>4</sub>

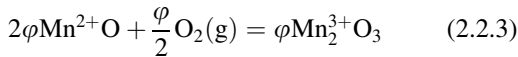
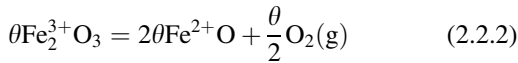
## 2.2. Mixed spinel ferrites

### 2.2.1. MnZn ferrite

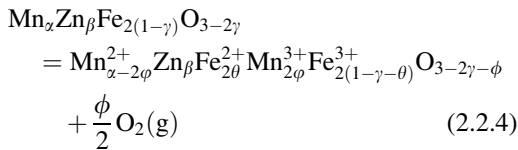
Let us consider an initial composition MnO:ZnO:Fe<sub>2</sub>O<sub>3</sub>=100 $\alpha$ :100 $\beta$ :100(1- $\gamma$ ) mol%, where  $\gamma=\alpha+\beta<0.5$ , synthesized by a conventional ceramic procedure from the oxides or carbonates [12]. If there were not Fe<sup>2+</sup> or Mn<sup>3+</sup> ions present in the final single-phased product, the chemical formula of the formed ferrite could be written as



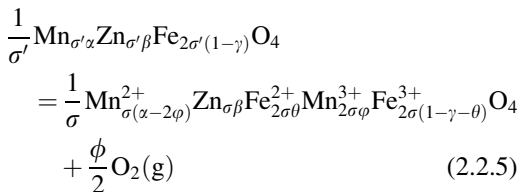
However, as usually happens in practice, let us assume that while the synthesis at high temperature is taking place some amount  $2\theta$  of Fe<sup>3+</sup> cations transforms to Fe<sup>2+</sup> and, for the sake of generality, that also some fraction  $2\varphi$  of Mn<sup>2+</sup> changes to Mn<sup>3+</sup> at the same time. For the pure oxides the reactions can be written as follows,



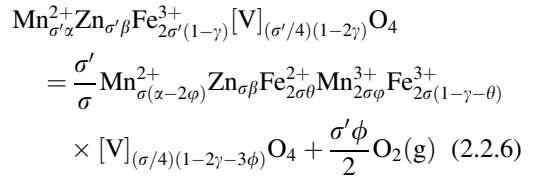
Combining these equations and letting  $\phi=\theta-\varphi$ , leads to



Multiplying coefficients and formula of the right term in (2.2.4) by the fraction  $\sigma=4/(3-2\gamma-\phi)$  and its inverse respectively, and applying a similar procedure to the left term with  $\phi=0$  (in this case  $\sigma'=4/(3-2\gamma)$ ) leads to



Since in this expression the characteristic spinel quotient [cat]/[ox]= $\frac{3}{4}$  does not hold (the addition of the cation coefficients is less than 3), we must consider a vacancy concentration  $\delta=3-\Sigma$  (cat. coeff.). For the formula at the right,  $\delta=(\sigma/4)(1-2\gamma-3\phi)$ . For the one at the left a similar procedure follows and  $\delta'=(\sigma'/4)(1-2\gamma)$ . This leads to



Eq. (2.2.6) tells us that the vacancy content  $\delta$  is a function of the oxygen evolution associated with the ferrite formation through the parameter  $\phi$ , and also that it does not depend on the Fe<sup>2+</sup> or Mn<sup>3+</sup> content separately. This allows the estimation of  $\delta$  from the experimental weight change without the need to know either the Fe<sup>2+</sup> or Mn<sup>3+</sup> concentration beforehand.

Although the exact reaction mechanism of the ferrite formation is unknown, if we know that the final product is single phased, due to mass conservation it is possible to assume for the calculations that the reaction (2.2.6) actually takes place. Calling  $\mu_B$  the formula mass of the ferrite when  $\phi=0$  it follows from (2.2.6) that  $\mu_B=\sigma'[\alpha\mu_{\text{Mn}}+\beta\mu_{\text{Zn}}+2(1-\gamma)\mu_{\text{Fe}}]+2\mu_{\text{O}_2}$ , where  $\mu_{\text{Mn}}$ ,  $\mu_{\text{Zn}}$  and  $\mu_{\text{Fe}}$  are the atomic masses of Mn, Zn and Fe. Therefore, since for every  $q=m_i/\mu_B$  moles of initial ferrite transformed  $q\sigma'\phi/2$  moles of O<sub>2</sub> must appear, a similar reasoning as the one carried out in Section 2.1 leads to

$$\phi = (1.5 - \gamma) \frac{\mu_B}{\mu_{\text{O}_2}} \left( 1 - \frac{m_f}{m_i} \right) \quad (2.2.7)$$

Once  $\phi$  is known from the experiment, the vacancy content ( $\delta$ ) is given by the corresponding coefficient in the right side of (2.2.6) with  $\sigma=4/(3-2\gamma-\phi)$ . Using this procedure it was possible to verify the attainment of vacancy-free single phased MnZn ferrite samples after sintering in air at a maximum temperature of 1250°C and cooling afterwards in pure N<sub>2</sub> [12].

### 2.2.2. NiZnCo ferrite

In the case of an iron excess NiZnCo ferrite [13] with nominal molar composition Fe<sub>2</sub>O<sub>3</sub>:NiO:ZnO:CoO=59:19.5:20.5:1, the procedure described before

leads to the equation

$$\text{Me}_{2\gamma/(3-\gamma)}\text{Fe}_{4(2-\gamma)/(3-\gamma)}^{3+}[\text{V}]_{(1-\gamma)/(3-\gamma)}\text{O}_4 = \frac{m}{2(3-\gamma)}\text{Me}_x\text{Fe}_y^{2+}\text{Fe}_z^{3+}[\text{V}]_\delta\text{O}_4 + \frac{\theta}{(3-\gamma)}\text{O}_2(\text{g})$$

where Me means NiZnCo,  $x=4\gamma/m$ ,  $y=8\theta/m$ ,  $z=8(2-\gamma-\theta)/m$ ,  $\delta=(2-2\gamma-3\theta)/m$ ,  $m=6-2\gamma-\theta$ ,  $\gamma=2\{1-0.01(\text{Fe}_2\text{O}_3 \text{ mol}\%) \}$  and

$$\theta = (3-\gamma) \frac{\mu_{\text{B}}}{\mu_{\text{O}_2}} \left\{ 1 - \frac{m_{\text{f}}}{m_{\text{i}}} \right\} \quad (2.2.8)$$

being

$$\mu_{\text{B}} = \frac{2\gamma}{(3-\gamma)}\mu(\text{Me}) + \frac{4(2-\gamma)}{(3-\gamma)}\mu(\text{Fe}) + 4\mu(\text{O})$$

It is worth noting that the approximations involved in [13] associated to the removal of  $\theta$  in the former expressions can be discarded. When doing so, we arrive at the more exact expressions

$$[\text{Fe}^{3+}] = -\frac{(4-\gamma)}{2(3-\gamma)}[\text{Fe}^{2+}] + \frac{4(2-\gamma)}{(3-\gamma)} \quad (2.2.9a)$$

$$[\text{V}] = -\frac{(4-\gamma)}{4(3-\gamma)}[\text{Fe}^{2+}] + \frac{(1-\gamma)}{(3-\gamma)} \quad (2.2.9b)$$

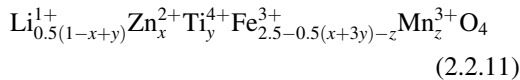
and to the equilibrium constant

$$k = \frac{2(3-\gamma)[\text{Fe}^{2+}]p_{\text{O}_2}^{1/4}}{8(2-\gamma) - (4-\gamma)[\text{Fe}^{2+}]} \quad (2.2.10)$$

The evaluation of the experimental data in [13] using the exact expression (2.2.10) and the Van't Hoff equation leads to  $\Delta H=0.47\pm 0.01$  eV for the  $\text{Fe}^{3+}\rightarrow\text{Fe}^{2+}$  transition (see Fig. 2). This is a slightly larger value than the one reported in [13] and suggests that the relative size of the octahedral and tetrahedral sites in different mixed ferrite compounds may have a minor but detectable influence on the corresponding bond energy, larger than the experimental error.

### 2.2.3. LiZnTiMn ferrite

When applying the procedure to a LiZnTiMn spinel with nominal composition



if some amount  $\alpha$  of  $\text{Fe}_2\text{O}_3$  is in excess over stoichio-

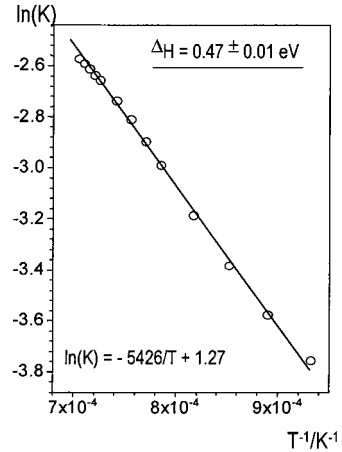
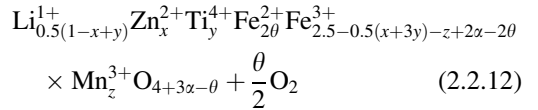
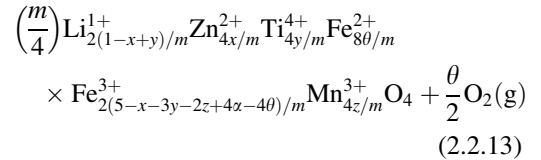


Fig. 2. Van't Hoff plot for the  $\text{Fe}^{3+}\rightarrow\text{Fe}^{2+}$  transformation in a NiZnCo ferrite sample. The experimental points fits to the straight line  $\ln(K)=-A/T+B$  where  $A=5426\pm 70$   $\text{K}^{-1}$  and  $B=1.27\pm 0.05$ .

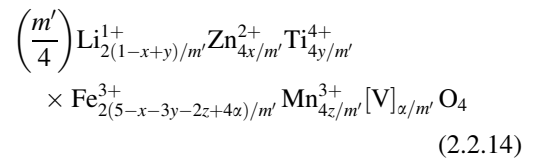
metry, the chemical formula may be written as



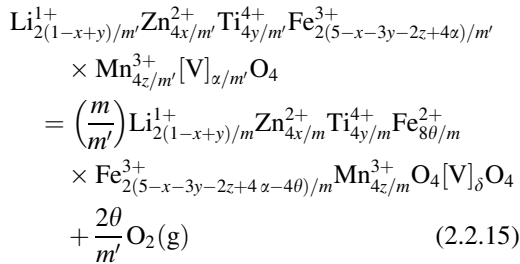
Multiplying coefficients and formula by the factors  $4/m$  and  $m/4$  respectively, where  $m=4+3\alpha-\theta$  leads to



This equation keeps the charge neutrality, but the characteristic quotient  $[\text{cat}]/[\text{ox}]=3/4$  does not hold anymore due to the presence of cation vacancies. Since the addition of the cation coefficients leads to  $4(3+2\alpha)/m$ ,  $\delta$  may be expressed as  $\delta=3-\{4(3+2\alpha)/(4+3\alpha-\theta)\}=(\alpha-3\theta)/m$ . If during a first stage the experimental sintering conditions were such that no  $\text{Fe}^{2+}$  formation was allowed, then  $\theta=0$ ,  $m=m'=4+3\alpha$  and  $\delta=\alpha/m'$ . In this case the equation may be written as



The normalized reaction describing the reaction process is obtained by combining (2.2.13) and (2.2.14) and multiplying by  $4/m'$ .



Following a similar reasoning to that leading to (2.2.6), it was found that  $\theta$  depends on the evolved mass of oxygen as

$$\theta = \frac{4 + 3\alpha \mu_{\text{B}}}{2 \mu_{\text{O}_2}} \left(1 - \frac{m_{\text{f}}}{m_{\text{i}}}\right) \quad (2.2.16)$$

where

$$\begin{aligned} \mu_{\text{B}} = & \frac{2(1-x+y)}{m'} \mu(\text{Li}) + \frac{4x}{m'} \mu(\text{Zn}) + \frac{4y}{m'} \mu(\text{Ti}) \\ & + \frac{2(5-x-3y-2z+4\alpha)}{m'} \mu(\text{Fe}) \\ & + \frac{4z}{m'} \mu(\text{Mn}) + 4\mu(\text{O}) \end{aligned}$$

Here  $m=4+3\alpha-\theta$ ,  $m'=m-\theta$  and  $\delta=(\alpha-3\theta)/m$ . These equations were used to estimate  $\delta$  and  $[\text{Fe}^{2+}]$  in samples synthesized by a conventional ceramic process with  $x=0.25$ ,  $y=0.83$ ,  $z=0.05$  and with different amounts of iron defect in the nominal composition [14]. The iron defect was introduced with the aim of making up for the additional  $\alpha\text{-Fe}_2\text{O}_3$  included in the slurry in the comminution stage due to mill contamination. It was found that, for a given iron deficit, the more oxidative the sintering atmosphere the higher the vacancy content ( $\delta$ ) and the less the  $\text{Fe}^{2+}$  content. The sensitivity of  $\delta$  to the atmosphere changes was much higher than that of  $[\text{Fe}^{2+}]$ ; the increase in the iron deficit ( $k$ ) up to 0.06 practically did not affect  $[\text{Fe}^{2+}]$  when sintering in  $\text{O}_2$ ; however, in the same sintering conditions this increase reduced drastically the amount of vacancies. The vacancy reduction could be correlated with the decrease of the microwave ferromagnetic losses of the material at room temperature; i.e., with the narrowing of the ferromagnetic resonance line width ( $\Delta H$ ) which, in these samples,

shows a sharp change around  $k=0.06$  when measured at 0.8 GHz [15].

### 2.3. Yttrium iron garnet

Oxygen loss observed in stoichiometric  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  samples sintered in a low  $p_{\text{O}_2}$  atmosphere had been associated with the presence of oxygen vacancies in the lattice [16]. However, an alternative explanation more in accordance with the loose crystalline structure of garnets, states that the oxygen loss, instead of creating oxygen vacancies, requires that a small fraction of the cations become interstitial; i.e., that they go to free sites not normally occupied in the stoichiometric compound [17]. The presence of interstitials provides an explanation for the unusual behavior of the magnetic disaccommodation spectrum observed in YIG, where accommodation instead of disaccommodation, is detected below 130 K. The interstitial approach together with the electric and mass balance criteria leads to the equation

$$\begin{aligned} & \text{Y}_3^{3+} \text{Fe}_5^{3+} \text{O}_{12} \\ & = \frac{(12-\theta)}{12} \text{Y}_{36/(12-\theta)}^{3+} \text{Fe}_{24\theta/(12-\theta)}^{2+} \\ & \quad \times \text{Fe}_{12(5-2\theta)/(12-\theta)}^{3+} \text{O}_{12} + \frac{\theta}{2} \text{O}_2(\text{g}) \end{aligned} \quad (2.3.1)$$

where the amount of interstitials is computed from the coefficients in (2.3.1) by simple subtraction from the stoichiometric formula:  $[\text{I}]_{\text{V}}=3\theta/(12-\theta)$ ;  $[\text{I}]_{\text{Fe}}=5\theta/(12-\theta)$ . We have not found reports in the literature connecting interstitials in garnets with TG curves. However, from (2.3.1) it readily follows that the amount of interstitials might be estimated using the method outlined in the former sections. The application of the procedure leads to

$$\theta = 2 \frac{\mu_{\text{B}}}{\mu_{\text{O}_2}} \left(1 - \frac{m_{\text{f}}}{m_{\text{i}}}\right) \quad (2.3.2)$$

where  $\mu_{\text{B}}$  is the formula mass of the stoichiometric YIG [17].

### 3. Conclusions

The vacancy concentration of synthesized spinels and the amount of interstitials in garnets may be expressed as a function of a certain parameter  $\theta$ ,

Table 1  
The  $\Gamma$  values for the different materials

| Sample        | $\Gamma$        | $[V](\theta)$ or $[I](\theta)$           |
|---------------|-----------------|--|
| Magnetite     | 6               | $3(1-\theta)/(9-\theta)$                 |
| MnZn spinel   | $1.5-\gamma$    | $(1-2\gamma-3\theta)/(3-2\gamma-\theta)$ |
| NiZnCo spinel | $3-\gamma$      | $(2-2\gamma-3\theta)/(6-2\gamma-\theta)$ |
| LiZnTi spinel | $(4+3\alpha)/2$ | $(\alpha-3\theta)/(4+3\alpha-\theta)$    |
| YIG           | 2               | $8\theta/(12-\theta)$                    |

associated with the oxygen evolved in the high temperature treatments. This parameter depends on the mass change ratio  $m_f/m_i$  through an equation of the general form

$$\theta = \Gamma \frac{\mu_B}{\mu_{O_2}} \left( 1 - \frac{m_f}{m_i} \right)$$

where  $\mu_B$  is the formula mass of the oxide reagents and  $\mu_{O_2}$  the oxygen molar mass. The parameter  $\Gamma$ ,  $\mu_B$  and the dependence  $[V](\theta)$  or  $[I](\theta)$  must be derived in each case from the chemical equations. The procedure allows the calculation of the  $Fe^{3+} \rightarrow Fe^{2+}$  enthalpy from the Van't Hoff equation and the equilibrium  $\ln(K)$  versus  $1/T$  curves derived from the TG experimental data. The  $\Gamma$  values for the different materials analyzed here are summarized in Table 1, where  $\phi$  has been changed into  $\theta$  in (2.2.7) for the sake of uniformity.

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