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DEFECT CONCENTRATION IN Ti-SUBSTITUTED YIG FROM TG CURVES

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The article discusses theory and experiment about the measurement of defect concentration in Ti-substituted yttrium iron garnet by means of thermogravimetry techniques. The two possible cases arising from oxygen interchange with atmosphere, oxygen vacancies and interstitial cations, may be analyzed quantitatively from the derived expressions. The possibility of another type of defects being present in the samples, not associated to oxygen evolution, is not excluded. Measurements were carried out in air and CO_2 for different Ti contents. The substitution tends to increase slightly the defect parameter θ in YIG, while a CO_2 reducing atmosphere is much more effective than the Ti substitution for increasing θ. Calculations for a given single-phased sample sintered in air show two possibilities: a deficit of one oxygen atom for every 2.5 unit cells of 96 atoms, or one excess cation for every 3.5 cells. Other samples show very similar results. The accuracy involved in the measurements is about 2–3%.

Keywords: *garnets, lattice defects, thermogravimetry*

Introduction

Defect concentration may become a very important parameter in solid-state processes. For instance, in solid reactions at high temperature, the defect content in the reactants or in the intermediate products may severely affect the kinetics and densification of the samples. Moreover, several factors such as minor changes in stoichiometry or in the sintering atmosphere may noticeably affect the final defect content [1, 2]. Another type of defect control occurs in some magnetic ceramics, associated to vacancies and low temperature diffusion processes. Defects may affect different specific time-dependent magnetic properties severely; i.e. after-effects such as disaccommodation may be significantly speeded up or delayed. As for the type of defects involved in yttrium iron garnet (YIG), it is not clear from the literature the dominance of vacancies, interstitials or the so-called cation 'antisite disorder' [3–5]. It is possible to find extended theoretical discussions about the energies involved in each type of defect in garnets [5–8], but the literature about experimental procedures for assess the defect concentration in the samples is scarce, mostly based on indirect methods [9, 10]. Recently, TG curves have been used to characterize the oxygen interchange and formation of spinel compounds [11], oxide thin films [12] and co-precipitated manganese ferrite powders [13]. Also, oxygen defects have been studied in calcium titanate perovskites, but by means of diffusion techniques [14].

In the following, we present some results about the use of TG techniques to study the influence of Ti substitution on the defect content linked to oxygen evolution in YIG. These techniques have been applied before in different spinel and garnets [15, 16].

Theory

YIG

Let us consider the usual solid-state, high-temperature synthesis of YIG from the oxides,

$$\frac{3}{2}Y_2O_3+\frac{5}{2}Fe_2O_3=Y_3Fe_5O_{12}$$

when sintering in a reducing atmosphere, some mass loss is observed above 1300°C, associated to the $Fe^{3+}\rightarrow Fe^{2+}$ transition and the consequent oxygen evolution. Assuming single-phased samples, the process taking place may be represented explicitly by the equation

$$\frac{3}{2}Y_2O_3+\frac{5}{2}Fe_2O_3=Y_3F^{2+}_{2\theta}Fe^{3+}_{5-2\theta}O_{12-\theta}+\frac{\theta}{2}O_2 \quad (1)$$

As a first impression, the formula at the right suggests the presence of oxygen vacancies in the material, θ being the defect parameter. However, more elaborated considerations about ion sizes and the relatively 'loose' structure of garnets, which includes many unoccupied cation sites, brings to mind the possibility of cation in-

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terstitials instead of oxygen vacancies being present in the samples [17]. Taking this latter point of view as the valid one, Eq. (1) may be rearranged as [11]:

$$\frac{3}{2}\mathrm{Y_2O_3}+\frac{5}{2}\mathrm{Fe_2O_3}= \\ =\frac{12-\theta}{12}\mathrm{Y}^{3+}_{\frac{36}{12-\theta}}\mathrm{Fe}^{2+}_{\frac{24\theta}{12-\theta}}\mathrm{Fe}^{3+}_{\frac{12(5-2\theta)}{12-\theta}}\mathrm{O}_{12}+\frac{\theta}{2}\mathrm{O}_2(g) \tag{2}$$

where now a cation/oxygen ratio larger than the YIG's stoichiometric 2/3 (or 8/12) appears. Subtracting number 8 from the addition of the Y, $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$ cation coefficients, we get the amount of additional cations or interstitials $[I]$:

$$[I]=\frac{8\theta}{12-\theta} \tag{3}$$

Therefore, if θ is known, the corresponding coefficient for interstitials in Eq. (2) can be determined from Eq. (3), along with the remaining cation coefficients. The complete and adjusted formula would be then:

$$\frac{3}{2}\mathrm{Y_2O_3}+\frac{5}{2}\mathrm{Fe_2O_3}= \\ =\frac{12-\theta}{12}\mathrm{Y}^{3+}_{\frac{36}{12-\theta}}\mathrm{Fe}^{2+}_{\frac{24\theta}{12-\theta}}\mathrm{Fe}^{3+}_{\frac{12(5-2\theta)}{12-\theta}}[I]_{\frac{8\theta}{12-\theta}}\mathrm{O}_{12}+ \\ +\frac{\theta}{2}\mathrm{O}_2(g) \tag{4}$$

The former expressions hold only when there is no a secondary phase segregation in the final product, which can be ascertained, from instance, by ordinary X-ray powder diffraction procedures. The defect parameter θ may be computed from accurate mass change measurements as follows [15, 16]. Let m_i be the initial mass of reagents in Eq. (1), m_f the final mass after the oxygen evolution and μ(YIG) the stoichiometric YIG formula mass. Hence, for every $\nu=m_\mathrm{i}/\mu(\mathrm{YIG})$ moles of stoichiometric YIG transformed to the oxygen deficient phase, an amount of

$$\frac{\nu\theta}{2}=\frac{(m_\mathrm{i}-m_\mathrm{f})}{\mu(\mathrm{O_2})}$$

moles of gaseous oxygen must evolve. Removing ν in these two expressions we arrive at:

$$\theta=2\frac{\mu(\mathrm{YIG})}{\mu(\mathrm{O_2})}\frac{m_\mathrm{i}-m_\mathrm{f}}{m_\mathrm{i}} \tag{5}$$

The result is valid for both possible cases: oxygen vacancies or interstitial cations, Eqs (1) and (4). Note that the formula mass of the initial reagents in Eq. (1), matching that of the ideal stoichiometric YIG, may be written as: $\mu(\mathrm{YIG})=3\mu(\mathrm{Y})+5\mu(\mathrm{Fe})+6\mu(\mathrm{O_2})$, (which adds to 737.93535 g).

Ti-substituted YIG

In the case of a Ti-substituted YIG, there are some minor changes in the equations. Assuming no second phase segregation, the chemical formula is

$$\mathrm{Y}^{3+}_3\mathrm{Fe}^{2+}_\mathrm{x}\mathrm{Fe}^{3+}_{(5-2\mathrm{x})}\mathrm{Ti}^{4+}_\mathrm{x}\mathrm{O}_{12}$$

and the corresponding chemical Eqs (1) and (4) become

$$\mathrm{Y}^{3+}_3\mathrm{Fe}^{2+}_\mathrm{x}\mathrm{Fe}^{3+}_{(5-2\mathrm{x})}\mathrm{Ti}^{4+}_\mathrm{x}\mathrm{O}_{12}= \\ =\mathrm{Y}_3\mathrm{Fe}^{2+}_{\mathrm{x}+2\theta}\mathrm{Fe}^{3+}_{5-2\mathrm{x}-2\theta}\mathrm{Ti}_\mathrm{x}\mathrm{O}_{12-\theta}+\frac{\theta}{2}\mathrm{O}_2$$

$$\mathrm{Y}_3\mathrm{Fe}^{2+}_\mathrm{x}\mathrm{Fe}^{3+}_{(5-2\mathrm{x})}\mathrm{Ti}_\mathrm{x}\mathrm{O}_{12}= \\ =\frac{\beta}{12}\mathrm{Y}_{\frac{36}{\beta}}\mathrm{Fe}^{2+}_{\frac{12}{\beta}(\mathrm{x}+2\theta)}\mathrm{Fe}^{3+}_{\frac{12}{\beta}(5-2\mathrm{x}-2\theta)}\mathrm{Ti}_{\frac{12\mathrm{x}}{\beta}}\mathrm{O}_{12}[I]_{\frac{8\theta}{\beta}}+ \\ +\frac{\theta}{2}\mathrm{O}_2(g) \tag{6}$$

where β=12–θ. The coefficient of interstitials remains the same since the parameter *x* cancels when adding the cation coefficients to obtain Eq. (3). The only difference introduced in Eq. (5) is that now $\mu(\mathrm{YIG})=3\mu(\mathrm{Y})+(5-x)\mu(\mathrm{Fe})+x\mu(\mathrm{Ti})+6\mu(\mathrm{O_2})$, delivering a numerical difference quite small with the former calculation when *x* is small. It may be safely disregarded in most cases when compared with the usual error of measurement.

Note that in both cases, vacancies and interstitials, some mass change due to oxygen evolution is expected to take place. On the contrary, in the case of the proposed cation antisite disorder mentioned before, with no changes in cation oxidation states, no mass change would be detected by thermogravimetry. However, when some mass change is detected, the possibility of more than one type of defects being present can not be excluded.

Experimental

Samples with compositions ranging from $x=0$ to 0.2 were prepared from reagent grade oxides by the usual ceramic method and sintered in the form of 15×∅5 mm rods in a TGDTA-92 Setaram thermobalance with atmosphere facilities, 10 μg sensitivity and heating rate of 10°C min^{-1}. They were kept 2 h at the maximum temperature of 1420°C, and fast cooled afterwards. Measurements were carried out in air and $\mathrm{CO_2}$. In all cases the cooled samples were single-phased to the X-ray diffraction analysis in a PW1710 Philips monochromator diffractometer.

One of the curves, built with the aid of a graphics software from the data provided by the TGDTA-92 equipment is shown in Fig. 1. The curves were indexed

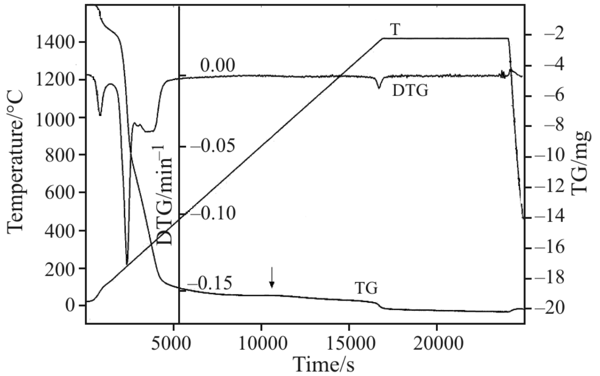

Fig. 1 TG curve of the x=0.04 sample in air (T, TG and DTG *vs*. time curves)

as TG (Δm in mg), T (temperature in °C) and DTG ($\mathrm{d}m/\mathrm{d}t$). Figures for calculations were taken directly from the accurate digital data provided by the thermobalance. Mass changes at the beginning of the heating stage below 400°C are due to the loss of water and binder (polyvinyl alcohol). A slight but steady mass loss begins at about 900°C (see arrow) and increases abruptly near 1300°C (first change of step in the TG curve) where the $\mathrm{Fe}^{3+}\rightarrow\mathrm{Fe}^{2+}$ transition is known to take place. Note that practically no mass change takes place while the temperature is held at the maximum, indicating that the equilibrium with the atmosphere is reached in a very short time. It is also seen that oxygen is partially recovered very fast from the atmosphere in the cooling stage (second inverse change of step), the absorption ending at about 900°C.

Figure 2 shows the dependence of the defect parameter θ calculated from Eq. (5) as a function of the Ti content, for samples heated up to the same maximum temperature of 1420°C. It is seen that the Ti substitution tends to increase slightly the defect parameter, while a reducing atmosphere is much more effective than the Ti substitution for increasing the amount of defects. As for the defect concentration that θ represents, let us consider, for instance, the sample shown in Fig. 1. For this sample, Eq. (4) leads to $\theta \approx 0.05$.

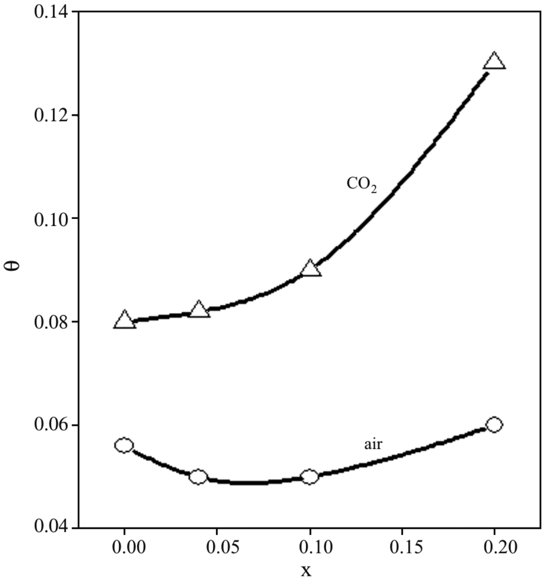

Fig. 2 Defect parameter θ as a function of the Ti doping rate for YIG samples sintered in air and CO_2

Then, if we assume oxygen vacancies as in Eq. (1), we arrive to a mean of 0.4 vacancies for every unitary cell of 96 atoms (a deficit of one oxygen atom for every 2.5 cells). In the other case, if we assume interstitials as in Eq. (4), it follows from Eq. (3) that $[I] \approx 0.035$, meaning an average of 0.28 interstitials for unitary cell, or approximately one excess cation for every 3.5 cells.

The use of error propagation procedures in Eq. (5) leads to a maximum error $\delta\theta/\theta \approx 0.011$; i.e., about 1%. This is less than half of the 2–3% repeatability observed in different samples for a given batch of powders. Therefore, for a 10 μg thermobalance sensitivity like the one used here, experimental errors due to previous sample preparation should be the main ones to watch over for improving accuracy, and not those of the TG measurement itself.

Conclusions

The two possible present cases arising from oxygen interchange with atmosphere, oxygen vacancies and interstitial cations, may be appropriately analyzed quantitatively from the derived expressions, which do not exclude the possibility of another type of defects additionally being present in the samples, not associated to oxygen evolution. While heating the samples, mass loss begins at about 900°C, increasing abruptly near 1300°C, but no mass change practically takes place while the temperature is held at the maximum. This is an indication that below 1420°C equilibrium with the atmosphere is reached in a very short time. The Ti substitution increases slightly the defect parameter θ in YIG, while a CO_2 reducing atmosphere is much more effective than the substitution for increasing that amount. With a 10 μg thermobalance sensitivity, the error of measurement due to previous sample preparation seems to be the main one affecting the accuracy of results.

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