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VACANCY CONTENTS IN MnZn FERRITES FROM TG CURVES

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Abstract

Expressions for calculating the cation vacancy contents of MnZn ferrites from thermogravimetric curves are presented together with some experimental data. In a single-phase MnZn ferrite synthesized by conventional ceramic procedures, the O_2 evolution accompanying ferrite formation follows the formal equation.

$$\mathrm{Mn}^{2+}_{\sigma'\alpha}\mathrm{Zn}_{\sigma'\beta}\mathrm{Fe}^{3+}_{2\sigma'(1-\gamma)}[V\,]_{\frac{\sigma'}{4}(1-2\gamma)}\mathrm{O}_4=\frac{\sigma'}{\sigma}\mathrm{Mn}^{2+}_{\sigma(\alpha-2\varphi)}\mathrm{Zn}_{\sigma\beta}\mathrm{Fe}^{2+}_{2\sigma\theta}\mathrm{Mn}^{3+}_{2\sigma\varphi}\mathrm{Fe}^{3+}_{2\sigma(1-\gamma-\theta)}[V\,]_{\frac{\sigma}{4}(1-2\gamma-3\varphi)}\mathrm{O}_4+\frac{\sigma'\phi}{2}\mathrm{O}_2\,(\mathrm{g})$$

where α and β denote the MnO and ZnO mole fractions in the primary mixture $\gamma=\alpha+\beta$, θ and φ depend on the quantities of Fe^{2+} and Mn^{3+} formed, respectively, $\phi=\theta-\varphi$ and σ'/σ is a function of the former parameters. Even though the relative amounts of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} remain uncertain, the vacancy content $[V]$ of the ferrite can be determined because it depends on ϕ alone, which is related to the change in mass of the sample as the synthesis takes place through the equation

$$\phi=(1.5-\gamma)\frac{\mu_{\mathrm{B}}}{\mu_{\mathrm{O_2}}}\left(1-\frac{m_{\mathrm{f}}}{m_{\mathrm{i}}}\right)$$

Here, m_{i} and m_{f} are the masses of the sample before and after O_2 evolution, μ_{B} is the formula mass of the ferrite and $\mu_{\mathrm{O_2}}$ is the O_2 molar mass. Practically vacancy-free single-phase MnZn ferrite samples were obtained by sintering in air at 1250°C and cooling in pure N_2.

Keywords: MnZn ferrite, TG

Introduction

Thermogravimetric analysis has shown to be useful for the appraisal of Fe^{2+} and cation vacancy concentrations in NiZnCo and LiZnTi spinel ferrites synthesized by ceramic procedures [1, 2]. It seems that this procedure could also be effective for the analysis of interstitials in garnets [3]. Vacancy concentrations, together with other crystalline de-

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fects, modify the cation diffusion paths in a significant range of temperatures. This may be important in processes involving cation rearrangements in the material, e.g. in some types of induced anisotropy and in disaccommodation processes. Disaccomodation is often associated with the time stability of the magnetic properties at room temperature [4]. The change in mass taking place on sintering is caused mainly by the O_2 evolution associated with the transition $Fe^{3+}\rightarrow Fe^{2+}$, which can be formally represented as $Fe_2O_3\rightarrow 2FeO+1/2O_2(g)$. Earlier reports on thermogravimetric analysis relating to MnZn ferrites with cubic spinel crystalline structure, or referred to the related magnetite, were based on the analysis of some parameter associated with the oxygen content, but without connecting this parameter to the vacancy and Fe^{2+} concentration [5], or involving too complex or loose approximations [6].

From a technical point of view, the spinel ferrite system Fe_2O_3–MnO–ZnO is a very important one. A great amount of the world's soft ferrite production involves inductance and transformer cores of sintered MnZn ferrite [7]. In these materials, the presence of a certain amount of Fe^{2+} is necessary to attain the required magnetic properties; Fe^{3+} and Fe^{2+} have different occupational preferences for the tetrahedral and octahedral sites of the ferrimagnetic spinel structure; they also differ in their atomic magnetic moments and in their contributions to the magnetocrystalline anisotropy [8]. The electromagnetic behaviour is also affected by the possible electronic interchange $Mn^{3+}+Fe^{2+}\leftrightarrow Mn^{2+}+Fe^{3+}$. Electric neutrality considerations for the crystal as a whole indicate that $[Fe^{2+}]$ and the vacancy concentration $[V]$ are not independent: as concerns iron-excess NiZnCo ferrites, formula (5) in reference [1] states that

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

where γ is a parameter associated with the amount of Fe_2O_3 present in the original mixed reagents. Below, we derive expressions to calculate the vacancy contents of MnZn ferrites from the change in mass taking place as the ferrite is being formed, and apply them to the experimental results obtained on samples with nominal composition Fe_2O_3:MnO:ZnO=53.5:34.5:12.0 mol%. This composition is cited in the literature as having a high saturation induction, adequate for the production of power transformer cores [9].

Theory

Let us consider a conventional ceramic synthesis procedure and an initial composition MnO:ZnO:Fe_2O_3=$100\alpha:100\beta:100(1-\gamma)$ mol%, where $\gamma=\alpha+\beta<0.5$. If there were no Fe^{2+} or Mn^{3+} present in the final single-phase product, the chemical formula of the formed ferrite could be written as

$$Mn_{\alpha}Zn_{\beta}Fe_{2(1-\gamma)}O_{3-2\gamma} \qquad (1)$$

However, let us assume that, as usually happens in practice, in the sintering stage a certain amount 2θ of Fe^{3+} is transformed to Fe^{2+} and, for the sake of generality, also that a certain fraction 2φ of Mn^{2+} is changed to Mn^{3+} at the same time. For the pure oxides, the reactions can be written as

$$\theta Fe_2^{3+}O_3 = 2\theta Fe^{2+}O + \frac{\theta}{2}O_2(g) \tag{2}$$

$$2\varphi Mn^{2+}O + \frac{\varphi}{2}O_2(g) = \varphi Mn_2^{3+}O_3 \tag{3}$$

If Eq. (1) is added to both sides of Eq. (2) and the resultant equation is combined with Eq. (3), arrangement of the terms and the introduction of $\phi=\theta-\varphi$ leads to

$$Mn_{\alpha}Zn_{\beta}Fe_{2(1-\gamma)}O_{3-2\gamma} = Mn_{\alpha-2\varphi}^{2+}Zn_{\beta}Fe_{2\theta}^{2+}Mn_{2\varphi}^{3+}Fe_{2(1-\gamma-\theta)}^{3+}O_{3-2\gamma-\phi} + \frac{\phi}{2}O_2(g) \tag{4}$$

To maintain the usual 4 oxygen atoms per formula of the spinel structure without changing the total mass and the cation/anion ratio, let us multiply the coefficients and formula of the right-hand side of Eq. (4) by the fraction $\sigma=4/(3-2\gamma-\phi)$ and its inverse. A similar procedure can be applied to the left-hand term with $\phi=0$. In this case, $\sigma'=4/(3-2\gamma)$. The substitutions lead to

$$\frac{1}{\sigma'}Mn_{\sigma'\alpha}Zn_{\sigma'\beta}Fe_{2\sigma'(1-\gamma)}O_4 = \frac{1}{\sigma}Mn_{\sigma(\alpha-2\varphi)}^{2+}Zn_{\sigma\beta}Fe_{2\sigma\theta}^{2+}Mn_{2\sigma\varphi}^{3+}Fe_{2\sigma(1-\gamma-\theta)}^{3+}O_4 + \frac{\phi}{2}O_2(g) \tag{5}$$

In the formulae in Eq. (5), the electric balance holds, but the characteristic quotient of the stoichiometric spinel (cations/oxygen=3/4) does not hold, as can readily be seen by adding the cation coefficients. Instead, in the chemical formulae we must consider a vacancy concentration with coefficients δ and δ'. For the formula on the right, δ is given by $\delta=3-\sigma(\alpha-2\varphi)-\sigma\beta-2\sigma\theta-2\sigma\varphi-2\sigma(1-\gamma-\theta)$. For the one on the left, a similar procedure follows. Substitution leads to $\delta=(\sigma/4)(1-2\gamma-3\phi)$; $\delta'=(\sigma'/4)(1-2\gamma)$ and to the final equation:

$$\begin{aligned} &Mn_{\sigma'\alpha}^{2+}Zn_{\sigma'\beta}Fe_{2\sigma'(1-\gamma)}^{3+}[V]_{\frac{\sigma'}{4}(1-2\gamma)}O_4 = \\ &\frac{\sigma'}{\sigma}Mn_{\sigma(\alpha-2\varphi)}^{2+}Zn_{\sigma\beta}Fe_{2\sigma\theta}^{2+}Mn_{2\sigma\varphi}^{3+}Fe_{2\sigma(1-\gamma-\theta)}^{3+}[V]_{\frac{\sigma}{4}(1-2\gamma-3\varphi)}O_4 + \frac{\sigma'\phi}{2}O_2(g) \end{aligned} \tag{6}$$

Equation (6) indicates that the vacancy content δ is a function of the O_2 evolution associated with ferrite formation through the parameter ϕ and also that it does not depend on the Fe^{2+} or Mn^{3+} content separately. This allows the calculation of δ from the experimental data on the change in mass without the need to know the Fe^{2+} or Mn^{3+} concentration beforehand.

In principle, the exact reaction mechanism of ferrite formation is unknown. However, in consequence of mass conservation, in the calculations it is possible to assume that reaction (6) actually takes place without loss of generality. With μ_B the formula mass of the ferrite when $\phi=0$, it follows from (6) that $\mu_B=\sigma'[\alpha\mu_{Mn}+\beta\mu_{Zn}+2(1-\gamma)\mu_{Fe}]+2\mu_{O_2}$, where μ_{Mn}, μ_{Zn} and μ_{Fe} are the atomic masses of

Mn, Zn and Fe and μ_{O_2} is the oxygen molar mass. Then, for every $\nu=m_i/\mu_B$ moles of initial material transformed, $\nu\sigma'\phi/2=(m_i-m_f)/\mu_{O_2}$ moles of O_2 must be evolved. Here, m_i is the initial mass and m_f is the final mass of the sample. The elimination of ν in these expressions with the substitution $\sigma'=4/(3-2\gamma)$ leads to

$$\phi=(1.5-\gamma)\frac{\mu_B}{\mu_{O_2}}\left(1-\frac{m_f}{m_i}\right) \tag{7}$$

Once ϕ is known from the experiment, the vacancy content is given by the corresponding coefficient on the right-hand side of (6) with $\sigma=4/(3-2\gamma-\varphi)$:

$$\delta=\frac{1-2\gamma-3\phi}{3-2\gamma-\phi} \tag{8}$$

Results and discussion

Samples of MnZn ferrite with composition Fe_2O_3:MnO:ZnO=53.5:34.5:12.0 mol% were prepared by conventional ceramic methods from reagent grade Fe_2O_3, ZnO and MnO_2. The powders were mixed wet for 30 min in a steel attrition mill at 120 rpm, heated at 950°C and milled again. Afterwards, they were die-conformed as small disks 12 mm in diameter and 1 mm high at a pressure of 2.5 ton cm^{-2}, using a polyvinyl alcohol binder. The compacts were sintered in a TG-DTA SDT 2960 TA Instruments Thermal Analyzer under different mixtures of air and N_2, at a flux of 40 ml min^{-1}. The maximum temperature was set between 1220 and 1250°C. The sintered compacts were analyzed by X-ray diffraction procedures, using a Siemens D5000 monochrome diffractometer. For the mentioned composition, $\alpha=0.345$, $\beta=0.12$ and $\gamma=0.465$. The use of MnO_2 instead of MnO as a precursor means that, for the vacancy content calculations, 4.41% of the total mass must be subtracted because of the evolution of the oxygen in excess.

Figure 1 shows one of the TG curves of the mixed and previously dried powders, heated at a maximum temperature of 950°C in an air flux. The small mass changes

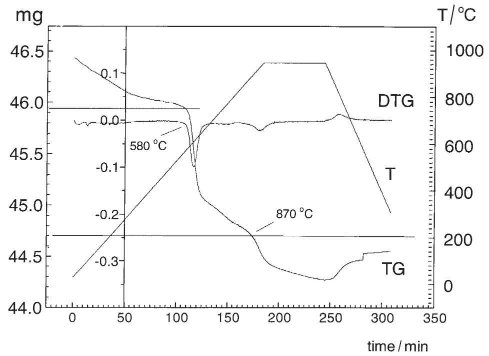

Fig. 1 TG curve of mixed powders heated at 950°C in air atmosphere

taking place below 580°C are attributed to the loss of water and possibly to remnants of volatile impurities. At least two different mechanisms of mass loss seem to be involved at higher temperatures: a first, irreversible one, beginning at 580, and a reversible second one at 870°C. The first was attributed to the O_2 evolution associated with the partial reduction of the MnO_2, reported elsewhere to begin at around this temperature. The second presumably involves some additional low-temperature reaction between the original precursors, which is difficult to estimate from the available data. The reversibility depends strongly on the cooling rate, and also on the maximum temperature attained (Fig. 2). The curve in Fig. 1 is not completely reversible in the mentioned range because, in this particular experiment, the cooling rate was specially increased in order to try to prevent the reversibility. For the assessment, we took only the irreversible mass loss taking place between 580 and 870°C. The calculations showed that this loss represents only 2.72 of the initial mass instead of the expected 4.41 mass% due to the MnO_2 oxygen excess. This means that, to be able to use formula (6), the loss of the remaining 1.69 mass% had to be subtracted in the next thermal treatment at higher temperatures.

Figure 2 presents the TG curve of a previously calcined, milled and compacted sample, sintered at 1220°C and cooled in air. It reveals a loss in mass below 300°C, caused by the evolution of the polyvinyl alcohol used as binder. Another loss beginning near 800°C is very well defined. A change in slope is also observed in the cooling stage of the curve, at about the same temperature. These changes reproduce well in different samples; however, the reproducibility of the onset temperatures in the cooling stage was poor; the onset temperatures ranged between 760 and 840°C without apparent reason on cooling at a rate of 300°C h^{-1}. Nevertheless, in all cases the fast mass gain stopped at about 600°C. Room temperature X-ray diffraction procedures verified that the mass gain is associated with the presence of a large amount of α-Fe_2O_3 in the sample, additional to the spinel content. Figure 3 shows the TG curve of a sample taken from the same batch and sintered under the same general conditions, but now cooled from 1250°C in 99.999% pure N_2 to avoid the formation of Fe_2O_3. It is seen that the change in slope in the cooling stage at about 800°C has completely disappeared and that there is no appreciable gain in mass in the stage. The

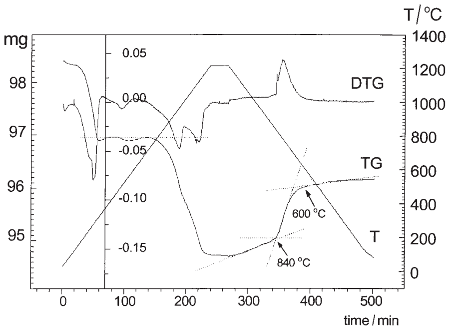

Fig. 2 Sintering of sample in air, cooled in air

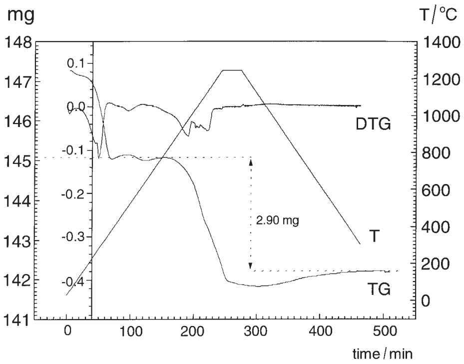

Fig. 3 Sintering of sample in air, cooled in N_2

room temperature X-ray diffraction pattern of this sample appears in Fig. 4. It exhibits only the very well-defined spinel peaks and no traces of α-Fe_2O_3. The cell parameter of this ferrite, determined from the high angle reflections, was 8.480±0.002 Å.

For the given composition, μ_B=231.24 and σ'=1.9324. From Fig. 3 and Eq. (7) it follows that ϕ=0.02356, with an estimated instrumental error of about 1%. Substitution in Eq. (8) gives δ<0.001; as compared with the approximate 3 total cations per formula unit, this means less than 0.03% of vacant cation sites in the crystal. It is noteworthy that the vacancy coefficient δ' in Eq. (6) provides the maximum allowed vacancy concentration for a single-phase ferrite; for this particular composition, δ'=0.034 (more than 1%), which is much larger than the measured value. Given the conditions of sintering and the uncertainty in the experimental error, we consider that these results demonstrate that the analyzed sample contained practically no vacancies.

It is concluded that, in spite of the unknown amounts of Fe^{2+} and Mn^{3+}, the vacancy content of MnZn ferrites sintered by ceramic procedures can be estimated from

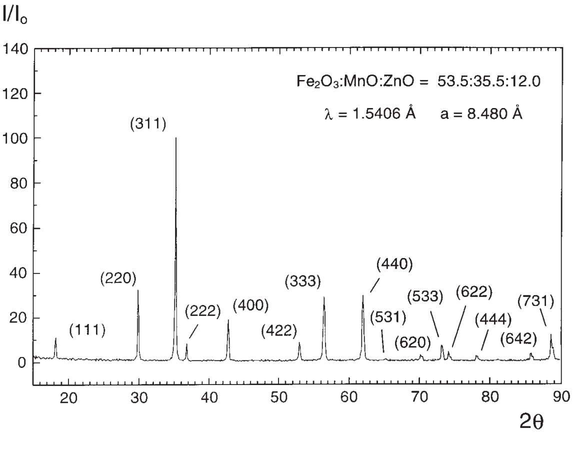

Fig. 4 Room temperature X-ray diffraction pattern of sample referred to in Fig. 3

TG curves. However, a drawback of the method is that δ is very sensitive to the difference $m_f – m_i$, especially when its value is near zero, and to obtain reproducible results the mass change must be measured with the highest possible accuracy. Sintering the samples in air at a maximum temperature of 1250°C and cooling in pure N_2 from that temperature provided MnZn ferrite samples with practically no vacancies.

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