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MAGNETIC AND MÖSSBAUER SPECTROSCOPY STUDIES OF CERAMIC GARNET PROCESSING

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Résumé. — L'analyse thermomagnétique et la spectrographie Mössbauer au voisinage du point de Curie sont des méthodes utiles mais relativement peu exploitées pour l'étude de la formation des céramiques magnétiques. L'effet du processus de fabrication et du traitement thermique sur le degré de réaction et l'homogénéité chimique peut être directement évalué et relié aux performances finales du matériau.

Abstract. — Thermomagnetic analysis and Mössbauer spectroscopy near \( T_c \) are useful and relatively unexploited tools for studying the formation of magnetic ceramics. The effect of processing and heat treatment on the extent of reaction and chemical homogeneity can be readily evaluated and related to final application performance.

1. Introduction. — The major testing and evaluation of magnetic ceramics is carried out on the fired (sintered) product. We discuss measurements which are not commonly used in monitoring ceramic processing but which may be useful in the production of magnetic ceramics. The measurements are thermomagnetic analysis and Mössbauer spectroscopy near the Curie temperature \( (T_c) \). These tests add to the understanding of prior processing steps and directly correlate with engineering properties such as microwave loss tangent and resonance line width. They are ideally suited to garnets with partial substitution for Fe by diamagnetic ions, but also apply in principle to spinels.

Examples are taken from our studies [1, 2] of the garnet \( (Y_{2.66}Gd_{0.34})_2Fe_{4.19}Al_{0.67}Mn_{0.09}O_{12} \) where \( x \) has a value close to 4.22, used in microwave phase shifters.

2. Thermomagnetic Analysis. — This measurement of the magnetization (\( \sigma \)) as a function of temperature in magnetic fields \( (H) \) sufficient to produce technical saturation is well known in the physics of magnetic materials [3]. The information is richer than that obtainable from \( \sigma_{\text{sat}} \) (room temp.) alone. The presence of several magnetic phases is readily detected. Also, the shape of the \( \sigma \) vs. \( T \) curve and the values of \( \sigma(RT) \) and \( T_c \) permit estimates of the extent, composition and approach to homogeneity of the phase formed.

The steps of the conventional ceramic process are:

a) mix oxides for a time \( t_{\text{mix}} \); b) calcine (prefire) for time \( t_{\text{calc}} \) at temperature \( T_{\text{calc}} \); c) ball-mill for a time \( t_{\text{mill}} \), or jet (fluid energy) mill; and d) press to shape and fire for time \( t_{\text{fired}} \) at temperature \( T_{\text{fired}} \). Thermomagnetic analysis is well suited for measuring on powder the effect of \( t_{\text{mix}} \), \( t_{\text{calc}} \) and \( T_{\text{calc}} \). The technique also has application in detecting incorrect stoichiometry and mill ball abrasion.

Figure 1 shows the effect of \( t_{\text{mix}} \) on the garnet phase formed by calcination for a powder of nominal composition \( (Y_{2.66}Gd_{0.34})_2Fe_{4.19}Al_{0.67}Mn_{0.09}O_{12} \). The 10 % difference in the \( \sigma(RT) \) values is traced to a 20 C difference in approximate \( T_c \). The \( T_c \) values observed measure the progress [4] of Fe-Al oxide reaction between that for \( Y_2Fe_5O_{12} \) (280 C) and that for our composition when fully reacted (185 C). Note also that \( T_c \) is not sharply defined, which indicates a range of Fe/Al ratios in the garnet. This is also demonstrated (below) using Mössbauer spectrometry.

In figure 2, the effect of calcination temperature is shown \( (t_{\text{mix}} = 3 \text{ hr.}) \). The evolution of these curves reflects the ongoing incomplete reaction process. For comparison, the dashed curve shows a rather homogeneous (sharper \( T_c \)) fired sample.

In commercial practice milling is usually carried out in steel-ball mills [5]. The unavoidable wear of the...
steel balls is determined by analysis (often after firing) and compensation of the starting composition is made. Recently X-ray fluorescence of a minor constituent (Cr) of the steel was shown to be superior to measurements on Fe which require the subtraction of two large quantities [6]. Alternatively, the alloy abrasion can be monitored by thermomagnetic analysis on the as-milled powder. The abraded material remains metallic and is ferromagnetic above \( T_c \) of any garnet. At 300 C, the magnetization is expressible as \( \sigma = \sigma_0 + \chi H \) where \( \sigma_0 (300 \text{ C}) \) is a property of the abraded steel and \( \chi \) (300 C) depends on the garnet. Measurements at two fields (e.g. 5, 10 kOe) suffice. Our data with a martensitic (\( \sim 83 \text{ Fe}, \sim 17 \text{ Cr} \)) steel in a neoprene lined mill are shown in figure 3. The results agree with those of Palmer et al. [6] obtained on these materials by X-ray fluorescence and direct weight loss. While this steel is ferromagnetic the method can also be applied to austenitic (nonmagnetic) steels because the mechanical working partially converts the steel to a ferromagnetic form.

The operation of magnetic ceramics in microwave devices demands single phase material [7] within a narrow composition range near to the stoichiometric formula [2, 8]. Overmilling sometimes occurs and the consequence is Fe-rich second phase(s) in the fired piece with degradation of physical properties. The (excess-iron) secondary phases may be either (strongly magnetic) spinel or (weakly magnetic) hematite accompanied by spinel. The technique for monitoring ball abrasion can detect small amounts of ferrimagnetic phase. Spinel present as a second phase, even minutely, is responsible for an unacceptable microwave loss. This is demonstrated in figure 4 by the correlation between \( \tan \delta_M \) at 3 GHz and \( \sigma_0 \) (300 C), starting from a base loss attributed to the garnet host. The equation for this line is \( \tan \delta_M \text{ (garnet)} \approx 0.0006 + f \tan \delta_M \text{ (spinel), where } f = \sigma_0 \text{ (300 C, sample)} / \sigma_0 \text{ (300 C, spinel)} \). As a representative \( \sigma_0 \) value for a spinel which is iron-rich (as indicated by microprobe analysis), we pick \( \sigma_0 \text{ (300 C, spinel)} \approx 50 \text{ emu/g} \) [9]. From figure 4, \( \tan \delta_M \) (spinel) is about 2.3 and in agreement with a range of values for NiFe\(_2\)O\(_4\) between 1.5 and 3 at 3 GHz (p. 269 of ref. [9]).

3. Mössbauer spectroscopy near \( T_c \).—This is a uniquely sensitive technique to monitor chemical homogeneity owing to the marked difference between paramagnetic and ferrimagnetic Mössbauer spectra. In high homogeneity garnets van der Kraan et al. [10] have shown that the coexistence region of the two spectra is quite narrow, ranging from less than 1 C up to 5 C. The coexistence region, which measures the spread of Curie temperatures, \( \Delta T_c \), is related to chemical fluctuations, presumably in the Fe/Al ratio in the family under study here.

The Mössbauer technique was applied to the powders whose thermomagnetic curves are reported in figure 1. Figure 5 shows \( F(T) \), the fraction which is ferrimagnetic (area of spectrum which shows hyperfine splitting divided by total area). \( \Delta T_c \) is defined as the range \( \Delta T_c = T_{c2} - T_{c1} \) where \( F(T_{c2}) = 0.1 \), \( F(T_{c1}) = 0.9 \). \( \Delta T_c \) values of 50 C are typical for calcined (unfired) powder confirming the assertion that the lack of sharpness of the thermomagnetic \( T_c \) arises from composition fluctuations. The offset of these \( F(T) \) curves for differing \( t_{\text{mix}} \) indicates differences in the amounts of unreacted material at this stage. When these powders are fired, but with a gentle comminution and sieving substituted for milling, a
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FIG. 5. — Mössbauer ferrimagnetic fraction $F$ vs. temperature in as-calcined powder. Effect of $t_{\text{mix}}$ on garnet formation during calcination ($t_{\text{cal}} = 4$ hr., $T_{\text{cal}} = 1300$ C, air). Magnetic Curie points from Fig. 1.

difference in their $T_c$ values of 10 C persists from the differing $t_{\text{mix}}$ periods. This translates in the Mössbauer measurement to the data of figure 6. The sample for $t_{\text{mix}} = 3$ hr. sharpens its $\Delta T_c$ markedly to 9 C while that for $t_{\text{mix}} = 1$ hr. remains rather inhomogeneous with $\Delta T_c \approx 25$ C.

In [1] we concentrated on the approach to homogeneity with $\Delta T_c$ decreasing from 9 C to about 3 C as $t_{\text{mix}}$ went from 3 hr. to 66 hr. The passage of the calcined sample through a fluid energy mill before firing is at least as effective as 60 hr. additional sintering time. A significant correlation between resonance line width (9.5 GHz) and this Mössbauer measure of single phase homogeneity was demonstrated.

FIG. 6. — Mössbauer ferrimagnetic fraction $F$ vs. temperature: Effect of $t_{\text{mix}}$ on residual inhomogeneity after calcining and firing.

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