Curie temperature measurement by thermomagnetic analysis (TMA) and differential scanning calorimetry (DSC)

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Introduction

Thermomagnetic analysis and differential scanning calorimetry are two experimental techniques commonly used for physical chemical analysis. However, they could be useful in the determination of the Curie temperature which is an important characteristic of magnetic materials. This work is related to a large study into the preparation of yttrium iron garnets (YIG) by coprecipitation [1-4]. Its aim is to study the effect of Fe^{3+} substitution by non-magnetic Al^{3+} ions for $Y_3Fe_{5-x}Al_xO_{12}$ garnets. The variation of the Curie temperature (T_c) as a function of the degree x of substitution are compared with the results already obtained by other authors [5].

I. Thermomagnetic analysis (TMA)

The principle of the TMA method is based on Faraday's theory.

If a sample is placed in a non-homogeneous magnetic field $\vec{H}$, a force $\vec{F}$ is exerted upon it:

$$\vec{F} = \vec{\text{grad}}\left(\vec{M}.\vec{H}\right) = m\,\chi\,H\frac{\partial H}{\partial x}\vec{x} \qquad (1)$$

as: $\vec{M} = m\,\chi\,\vec{H}$

where: m: mass of the sample

$\vec{M}$: magnetization of the material

χ: magnetic susceptibility per unit mass.

If we use an electromagnet whose magnetic poles have a "Weiss" profile, we obtain between the two poles the presence of a small volume in which the product $H\,\partial H/\partial x$ is uniform (fig. 1).

This method cannot be applied rigourously to the study of ferro- or ferrimagnetic materials as, in this case, the magnetization does not vary linearly with the intensity of the magnetic field.

However, we can solve this problem by using a low magnetic field for which, as a first approximation the magnetization $\vec{M}$ becomes:

$$\vec{M} = \alpha\,(T)\,\vec{H}$$

and thus:

$$\vec{F} = \alpha\,(T)\,H\frac{\partial H}{\partial x}\vec{x}$$

where α (T) is a function of the temperature and is independant of H.

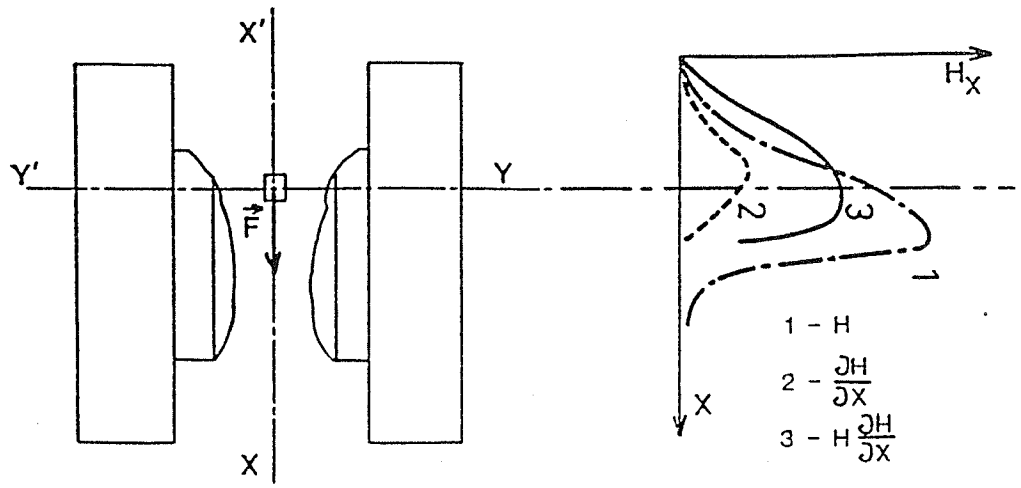


Fig. 1. Variation of the product H ($\partial H/\partial x$) as a function of x for poles with a Weiss profile

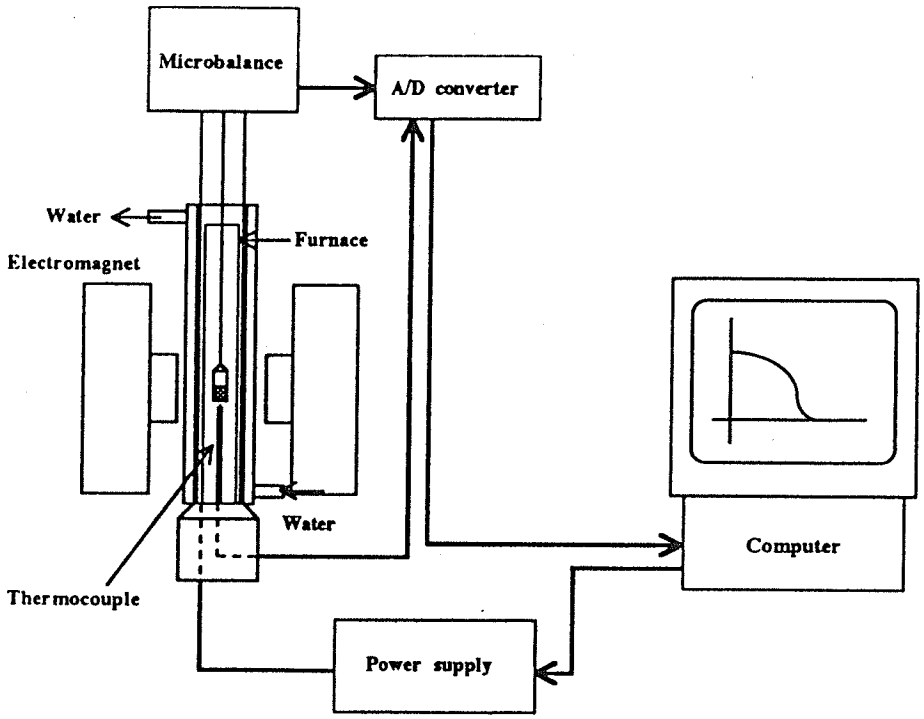


Fig. 2. Diagram showing the apparatus used for thermomagnetiç analysis

In the gap of air between the two poles of the magnet, the direction and intensity of the force can be evaluated through the use of a microbalance. A non-inductive furnace is used to follow the variation of the signal measured as a function of the temperature (fig. 2).

As this signal is proportional to the magnetization, the curve obtained describes the variation of M. We can determine the Curie temperature from this curve (fig. 3) by taking the temperature at the intesection between the tangent at the point of inflexion of the curve and the abscissa.

The plot of the signal measured against the sample temperature shows an hysteresis. To ensure reproducible results, the measurement of T_c is systematically taken from the curve obtained as the temperature increases.

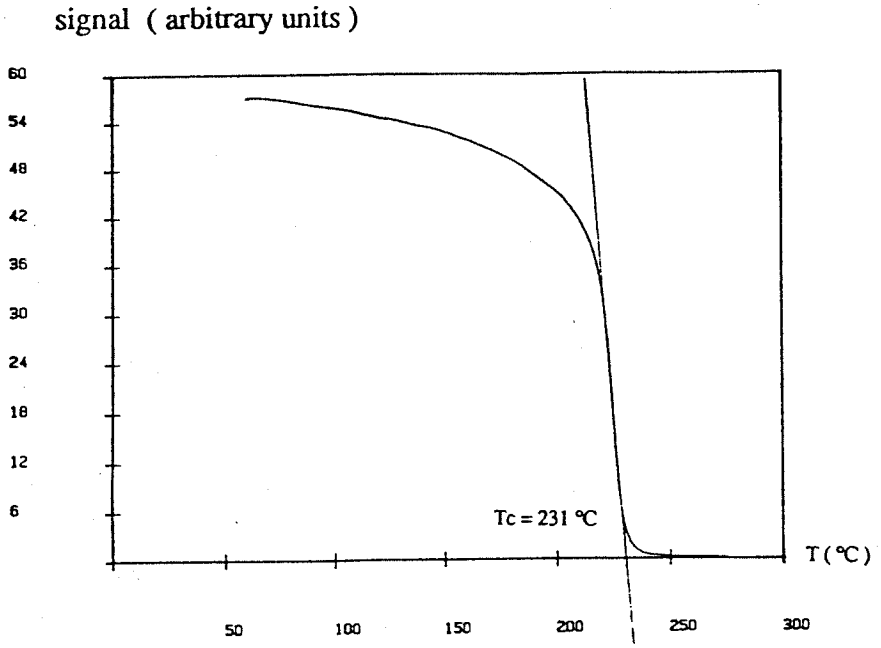


Fig. 3. Example of curve obtained from TMA. The sample's formula is $Y_3Al_{0.4}Fe_{4.6}O_{12}$

II. Differential scanning calorimetry

The magnetic order transitions such as the transition ferrimagnetic → paramagnetic (which we study here) are of the second order. For such a transformation, the molar volume V and the molar entropy S which are first order partial derivatives of the Gibbs energy G are continuous functions of T and P. Thus, a second order transformation cannot be characterized by a technique such as differential thermal analysis because no thermal effect is associated with it. However, any transformation of this type is associated with a discontinuity of the second order partial derivatives of G and therefore also of the dilatation coefficient α, the compressibility χ_T and the heat capacity C_p.

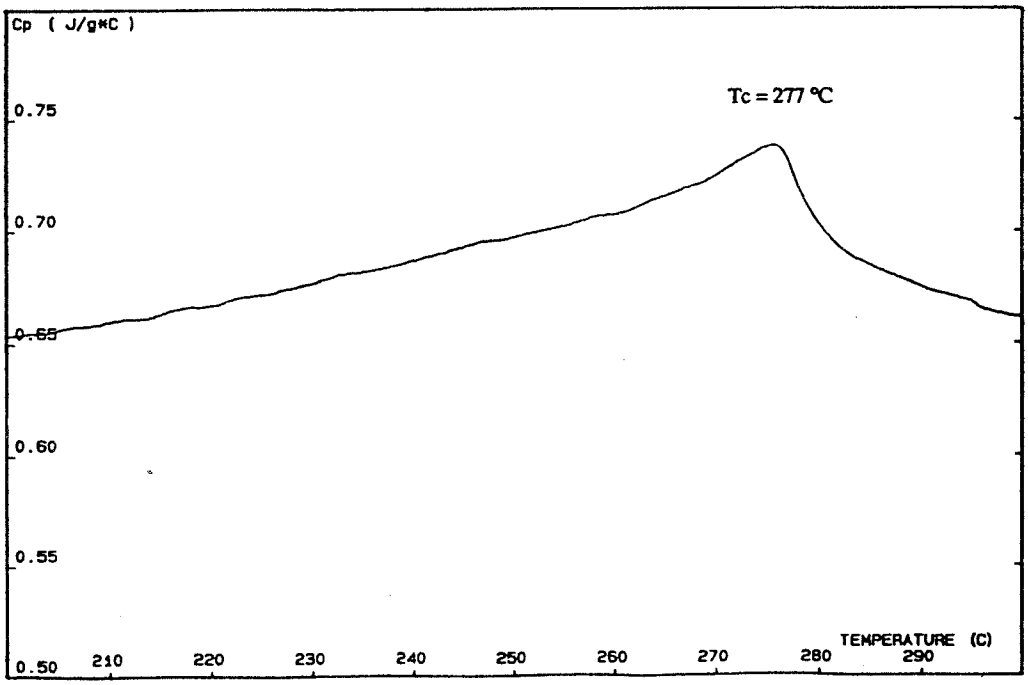


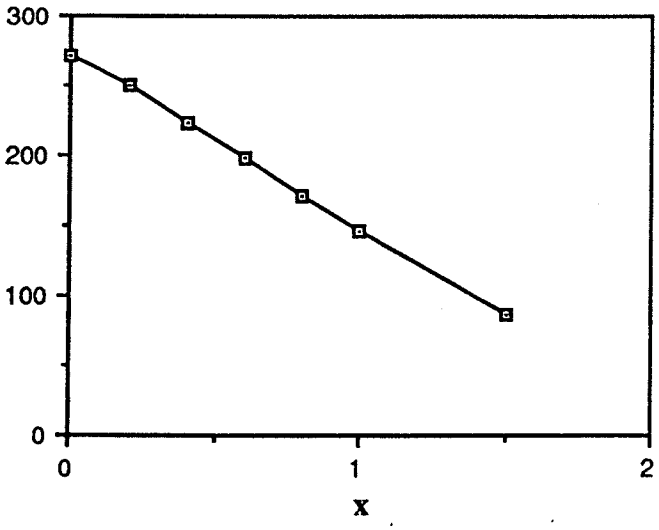
Fig. 4. Variation of C_p versus T for YIG from DSC analysis

The differential scanning calorimetric analysis allows us to follow the variation of C_p as a function of the temperature. In this way, it is possible to characterize the transformation by the discontinuity of the heat capacity at the time of the transition which shows up as a well-defined peak (fig. 4). The Curie temperature can be determined from the curve obtained from the measurement of the temperature corresponding to the maximum of C_p.

III. Experimental results

We have prepared by a coprecipitation method some samples of Al substituted YIG whose formula is given by $Y_3Fe_{5-x}Al_xO_{12}$. After six hours of heat treatment at 1000°C, the powders obtained are of a pure garnet phase without any other crystallized phase.

By the use of the two characterization methods described above, it is possible to study the variation of the Curie temperature T_c as a function of the degree x of substitution. In both cases, the curves obtained (figures 5 and 6) are in good agreement. It was impossible to determine T_c for x = 1.5 by the DSC method as the signal was too low to be measured with any precision.



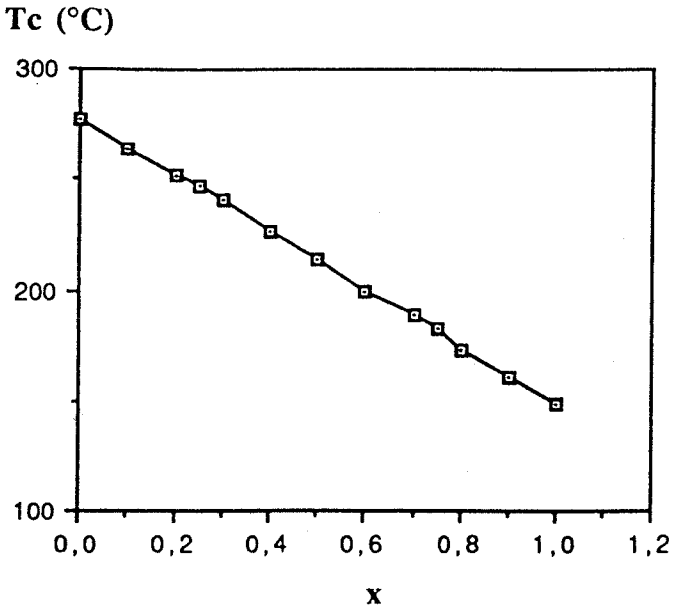
x	Tc (°C)
0	272
0,2	250
0,4	224
0,6	199
0,8	172
1	146
1,5	86

Fig. 5. Tc versus x for $Y_3Fe_{5-x}Al_xO_{12}$ from TMA

We can observe from these curves a continuous decrease of T_c as x increases. This behaviour is related to the reduction of the number of superexchange interactions between Fe^{3+} ions. Some statistical models have been established to describe this phenomenon. The first was from Gilleo [8] which was in good agreement with his experimental results for small amounts of substituting ions in the octahedral sites.

In the case of the substitution by Al^{3+} ions, the use of this model is more difficult as Al^{3+} enters simultaneously both the tetrahedral and octahedral sites. We cannot compare the theory and experimental results because we have no knowledge of the fraction f_T of Al^{3+} ions entering tetrahedral sites.

Gilleo and Geller [8] note that calculated values of f_T by magnetization measurements cannot be used to calculate the corresponding Curie temperatures due to the model's lack of precision. We can see however the good agreement between our values of T_c and those of Gilleo which were obtained from the point of inflection method.



x	Tc (°C)
0	277
0,1	264
0,2	251
0,25	246,5
0,3	240
0,4	226
0,5	214
0,6	200
0,7	188
0,75	183
0,8	173
0,9	160
1	148

Fig. 6. Tc versus x for $Y_3Fe_{5-x}Al_xO_{12}$ from DSC analysis

Conclusion

This work shows that TMA and DSC could be equally used to measure the Curie temperature of a material. However, it appears that the differential scanning calorimetry is the simpler of the two methods. T_c can also be determined through this method in a more objective manner. Nevertheless, TMA does allow us to follow the variation of the magnetization versus the temperature. This is of great interest for rare earth ions substituted YIG as magnetic rare earth ions form a sublattice whose magnetization is opposed to the resulting magnetization of the two Fe^{3+} ions sublattices.

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