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Photoacoustic monitoring of magnetite-crystal formation from iron(III) hydroxide acetate: Comparison with ESR results

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The formation of crystalline magnetite by 1-h heat treatment of iron(III) hydroxide acetate is described. This amorphous-crystalline solid transformation is monitored by electron-spin resonance and photoacoustic spectroscopies. No significant changes were detected for samples heated below 190 °C. Above this temperature both techniques presented results following a definite pattern, namely, the enhancement of ion mobility leading to particle growth and crystallization for a temperature up to 240 °C and the onset of magnetic ordering of magnetite near this temperature.

I. INTRODUCTION

The existence of noncrystalline solids is frequently due to a slow kinetics of crystallization. For example, a vitreous, amorphous phase is formed¹ whenever the rate of cooling of the melt is faster than the rate of crystallization. Amorphous solids are also formed by allowing the reagents to react faster than the crystallization time.² This is the case with the formation of many metal oxides; rapid mixing of iron salt solution and, for instance, ammonium hydroxide leads to the precipitation of amorphous hydrous iron oxide. In a recent paper³ we demonstrated that there is a temperature threshold at which amorphous iron(III) hydroxide acetate reacts upon heating to yield magnetite. This reaction is the transformation of an amorphous, paramagnetic solid into a crystalline, ferrimagnetic substance. The observed temperature threshold should be distinguished from the glass transition temperature T_g of polymers and glasses, since in the present case chemical changes are also detected. This amorphous-crystalline solid transformation was attributed to the presence, at the threshold temperature, of solid ions sufficiently mobile to allow mass transfer within the solid bulk; chemical reaction and ion reorganization are thus allowed, and crystallization occurs.

In this paper the amorphous-crystalline solid transformation occurring in the magnetite formation from iron(III) hydroxide acetate (IHA) is further investigated using both electron-spin resonance (ESR) and photoacoustic (PA) techniques. The PA technique⁴ looks directly at the heat generated in a sample, due to nonradiative deexcitation processes, following the absorption of light. In the conventional PA experimental arrangement a sample enclosed in an airtight cell is exposed to a chopped light beam. As a result of the periodic heating of the sample, the pressure in the chamber oscillates at the chopping frequency and can be

detected by a sensitive microphone coupled to the cell. The PA signal depends not only on the amount of heat generated in the sample (i.e., on the optical absorption coefficient and the sample light-into-heat conversion efficiency), but also on how this heat diffuses through the sample. The quantity that measures the rate of heat diffusion in the sample is the thermal diffusivity α , defined by

$$\alpha = k / \rho c, \quad (1)$$

where k is the thermal conductivity, ρ is the density, and c is the heat capacity at constant pressure. The importance of α as a physical parameter to be monitored is due to the fact that, like the optical absorption coefficient, it is unique for each material. This can be appreciated from the tabulated values⁵ of α for a wide range of materials, such as metals, minerals, foodstuffs, biological specimens, and polymers. Furthermore, the thermal diffusivity is also known to be extremely dependent upon the effects of compositional and microstructural variables⁶ as well as processing conditions, as in the cases of polymers,⁶⁻⁸ glasses,⁹ and ceramics.¹⁰ The PA technique may either be used as a spectroscopic technique^{11,12} to monitor the chemical and structural changes or as a thermal monitoring technique.^{8,9} As a thermal monitoring technique one uses the PA technique to look how the heat diffusion is being affected by the chemical and structural changes. This latter aspect of the PA technique is the one which we explore in this paper, and it consists of using the PA technique for measuring the thermal diffusivity.

II. SAMPLE PREPARATION

The IHA was prepared¹³ by adding 50 ml of concentrated (28%) aqueous NH_4OH to 250 ml of a solution containing 101 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 14 ml of glacial acetic acid in 90% vol % aqueous ethanol. The admixture was made as rapid as possible, under vigorous stirring. The precipitate was centrifuged and rinsed 6 times with 90% vol % aqueous

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FIG. 1. X-ray diffractograms of IHA samples heated at various temperatures for 2 h under nitrogen.

ethanol. The resulting solid was dried in an oven at 120 °C.

The presence of acetate groups was verified by the characteristic IR absorption bands at 1600–1400 cm^{-1} and by carbon elemental analysis which gave C = 4%. The iron content was determined by $\text{K}_2\text{Cr}_2\text{O}_7$ titrimetry on samples dissolved in 18% aqueous KCl at boiling temperature, under reflux. Prior to titration, Fe(III) was reduced to Fe(II) with SnCl_2 , to determine the total iron. The resulting iron content found was Fe = 45.7%, so that the ascribed formula for the precipitate is $\text{Fe}(\text{OH})_{2.8}(\text{CH}_3\text{COO})_{0.2}x\text{H}_2\text{O}$, with $x \approx 0.3$. X-ray analysis was carried out using a Phillips PW 1140 diffractometer, and specific-area determinations were made using a CG 2000 specific-area meter, which uses a catharometer for measuring the sorbed N_2 . The x-ray diffractograms are shown in Fig. 1. The IHA samples heated to 173 and 228 °C do not show any discrete diffraction lines. Diffuse lines appear upon heating to 274 °C and get more intense as the samples are heated to higher temperatures. The diffractograms of the sample heated to 435 °C allow its identification as magnetite, by comparison with the literature data.¹³ The heat-treatment procedure adopted in this work consists of heating the sample for a given time at nitrogen atmosphere.

III. RESULTS AND DISCUSSION

The ESR measurements were carried out in a Varian E-line X-band spectrometer with a 100-kHz rectangular cavity. Contrary to the case reported in Ref. 3, the ESR spectra were recorded, at room temperature, after the samples had undergone the heat treatment outside the spectrometer at a fixed heating time of 1 h. The ESR spectra of the IHA consist of a single, broad line with $g = 2.00$ –2.80 as expected for Fe(III) compounds.^{14,15} The main features of the recorded spectra are summarized in Fig. 2 where we show the measured ESR band linewidth [Fig. 2(a)] and the g value [Fig. 2(b)] as a function of the heating temperature. The initial increase of the linewidth may be understood as follows. Below 150 °C the solid is glassy with a low-mass diffusion coefficient and the Fe(III) ions remain in the environment which they originally found during the preparation. As one

(a) HEATING TEMPERATURE (°C)

(b) HEATING TEMPERATURE (°C)

FIG. 2. (a) ESR linewidth of iron(III) hydroxide acetate samples as a function of the 1-h heat-treatment temperature; (b) g value as a function of the heating temperature.

increases the temperature, mass diffusion is enhanced and new sites are accessible to the Fe(III) ions. Consequently, the linewidth is expected to increase with increasing temperature, as shown in Fig. 2(a) in the region between 150 and 215 °C. On further increasing the temperature, the enhanced particle mobility favors particle coalescence and

FIG. 3. Iron(III) hydroxide acetate specific area as a function of a 1-h heating.

growth. The coalescence and growth of the particles was checked by specific-area, $A(m^2/g)$, and density measurements. In Fig. 3 we show the specific area of IHA as a function of the heat-treatment temperature. The particle diameter d can be estimated from the specific-area measurement by $d = 6/\rho A$. Up to 250 °C the solid density remained constant at 3.4 g/cm³. Thus, the steep decrease in the specific area between 220 and 270 °C indicates that the particle growth is taking place in this temperature range, at the same time that the x-ray diffractograms show the onset of magnetite formation above 230 °C. Indeed, one estimates that from 225 to 250 °C the particle diameter changes from 68 to 110 Å, respectively. The decrease of the ESR linewidth in the 225–250 °C temperature range is typical of the supermagnetic behavior of ultrafine magnetic particles.^{14,16–18} As described by Néel, supermagnetism is due to thermally induced fluctuations of the direction of magnetization in single-domain particles between discrete easy directions. These fluctuations contribute to the ESR linewidth according to^{18,19}

$$\Delta H = (4K/M)e^{-2KV/k_bT}, \quad (2)$$

where K is the anisotropy energy density, V is the particle volume, k_b is the Boltzmann constant, T is the sample measurement temperature, and M is the particle magnetization. Using the ESR room-temperature linewidth data and the estimated particle volume, we got $K = 4.6 \times 10^4$ erg/cm³, for the samples heat treated between 225 and 250 °C. This value of K is quite close to that reported by Rogwiller and Kündig¹⁸ for 134-Å-diam Fe₃O₄ particles (i.e., $K = 5.1 \times 10^4$ erg/cm³) and that of magnetite monocrystal²⁰ ($K = 1.1 \times 10^5$ erg/cm³). Finally, above the heating temperature of 240 °C, the linewidth exhibited a steep increase; the same steep increase was also observed with the ESR intensities as well as in the g value [Fig. 2(b)] for particle heat treated above 240 °C. This steep increase in linewidth, intensity, and g value is due to the presence of magnetic ordering due to enhanced formation of magnetite crystallinities. In this heat-treatment region the average size of the particles tend to stabilize, as deduced from the specific-area data shown in Fig. 3.

The PA monitoring of the magnetite formation was carried out by measuring the thermal diffusivity of our samples. Of the several PA methods for measuring the thermal diffusivity, we have resorted to the front-phase method as de-

FIG. 4. Schematic arrangement for the PA measurement of the thermal diffusivity.

FIG. 5. PA rear-signal amplitude for the IHA sample treated at 250 °C as a function of the modulation frequency, showing the f^{-1} frequency dependency.

scribed in Ref. 7–9. The samples were compacted (at 4 ton/cm²) in the shape of 8-mm-diam and 700-μm-thick disks. In Fig. 4 we show the schematic arrangement for the PA measurements. It consists of a 250-W halogen lamp whose polychromatic beam is mechanically chopped and focused into the sample which plays the role of a second window closing the PA cell. The sample is fixed to the cell body with silicone grease. A BK condenser microphone is mounted in one of the cell walls and is in contact with the air inside the PA chamber by means of a 1-mm-diam duct. The signal from the microphone is connected to a lock-in amplifier in which the signal amplitude and phase are both recorded as a function of the modulation frequency f . By performing a rear-illumination signal amplitude measurement, we have checked that the thermoelastic bending mechanism^{7–9,21} was the main cause responsible for the detected PA signal in the modulation frequency range of our experiments; i.e., the rear-signal amplitude varied as f^{-1} , which is the expected modulation frequency dependence of the rear signal for a thermally thick sample when the thermoelastic bending of the sample dominates the PA signal (see Fig. 5). Accordingly, as discussed in Refs. 7–9 and 21, the thermal diffusivity is obtained in this case from the fitting of the front-phase signal data to the expression

$$\phi = \phi_0 + \arctan(1/z - 1), \quad (3)$$

where $z = a\sqrt{f}$ with $a = (\pi l^2/\alpha)^{1/2}$. Thus, assuming ϕ_0 and a as adjustable parameters, the thermal diffusivity is readily obtained from the phase data fitting from the parameter a , namely, $\alpha = \pi l^2/a^2$.

In Fig. 6 we show the PA signal phase of the sample treated at 250 °C as a function of the modulation frequency. The solid curve in this figure represents the fitting of the experimental phase data to the theoretical expression given by Eq. (3). The value of α obtained from the data fitting was $\alpha = 0.0459$ cm²/s. The same procedure was applied to all the other IHA heat-treated samples. In Fig. 7, we summarize the results for the thermal diffusivity of our samples as a function of the heating temperature. For the samples heated between 220 and 240 °C, the thermal diffusivity increases

FIG. 6. PA signal phase for the IHA sample treated at 250 °C as a function of the modulation frequency. The solid curve represents the fitting of the experimental data to the expression given by Eq. (3).

with increasing heating temperature. At higher heating temperatures the thermal diffusivity decreases. Figure 7 shows that the thermal diffusivity is indeed sensitive to the transformations that take place during the material's processing and is consistent with the ESR linewidth measurements. The dramatic increase of the thermal diffusivity for the samples heated between 220 and 240 °C is interpreted as resulting from an increase of the thermal conductivity. This is consistent with the particle growth and crystallization (and onset or ordering) in this heating temperature range, as deduced from the ESR, x-ray, and specific-area measurements; a crystalline solid has higher thermal conductivity than an amorphous one. Above a heating temperature of 250 °C, the crystallites get increasingly ordered. As one increases the heat-treatment temperature, the samples get further ordered, as evidenced by the ESR linewidth and intensity steep increase, until a saturation value is reached (at the same time the samples change their color from dark brown to a full black). With increasing magnetic ordering the specific heat is expected to increase too, so that k/c may be balanced out. The observed decrease in α may then be attributed to an

FIG. 7. Iron(III) hydroxide acetate thermal diffusivity as a function of the 1-h heat-treatment temperature.

TABLE I. Thermal diffusivity and density as a function of the heat treatment.

Heating temperature (°C)	Thermal diffusivity (cm ² /s)	Density (g/cm ³)
225	0.0307	3.4
232	0.0395	3.5
240	0.0450	3.4
250	0.0459	3.3
260	0.0437	3.8
280	0.0370	4.0
325	0.0277	5.3

increase in the density of our samples. We have checked this by measuring the density. In Table I we summarize the results for the density and thermal diffusivity as a function of the heating temperature. Between 250 and 325 °C the density increases by roughly 60%, which entails that α should decrease by roughly 40% provided the ratio k/c remains constant. In fact, looking at Table I, the decrease of α in this temperature range is roughly 40% in agreement with the suggested explanation.

In conclusion, we note that the PA-determined thermal diffusivity is, indeed, a sensitive parameter for monitoring the amorphous-crystalline solid transformation occurring during the formation of magnetite from IHA. In particular, the temperature range at which the amorphous IHA reacts upon heating to yield magnetite, as determined by ESR, was clearly evident in the thermal diffusivity measurements as the heating temperature at which α undergoes a maximum.

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