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Formation of Defected Cadmium Ferrite during Hydrothermal Storage of Cadmium–Iron Hydroxides

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The storage of amorphous coprecipitated $Cd(OH)_2 \cdot 2Fe(OH)_3$ gel in mother liquor at 150 ± 2°C for 20 hr leads to a crystalline species which, according to X-ray analysis, is composed of cadmium hydroxide nitrate, $Cd_3(OH)_5NO_3$, cadmium hydroxide, $\beta Cd(OH)_2$, and a strongly ferrimagnetic spinel phase. The Curie point at 270–280°C was found by thermomagnetic analysis. At that temperature the decomposition of the spinel phase and of the accompanying nonmagnetic phases takes place. IR spectra indicate that during thermomagnetic recording the liberated cadmium oxide and iron oxide form antiferromagnetic cadmium ferrite, with frequencies somewhat displaced in comparison to $CdFe_2O_4$ annealed at 1000°C. The results indicate that the ferrimagnetic phase (having spinel structure, a unit-cell parameter a of about 8.37 ± 0.01 Å, and a T_c point differing by more than 300°C from that of pure maghemite, γFe_2O_3) is likely to be a defected solid solution of maghemite and cadmium ferrite, of the formula $Cd_x^{2+}Fe_{1-x}^{3+}[Fe_{(5+x)/3}^{3+}\square_{(1-x)/3}]O_4$.

INTRODUCTION

When amorphous mixtures of $Cd(OH)_2/2Fe(OH)_3$ coprecipitated from the corresponding nitrates are hydrothermally stored, the products are multiphasic with strongly ferrimagnetic behavior, instead of the expected antiferromagnetic cadmium ferrite, $CdFe_2O_4$. The phase responsible for ferrimagnetism is hard to identify because of the poor crystalline state of the product and the presence of other phases. Hence its magnetic properties were earlier ascribed to maghemite, γFe_2O_3 (1, 2). Due to progress in instrumental equipment, the phase has been more recently identified as a defected solid solution of maghemite and cadmium ferrite (3, 4), which, by the way, better justified the high value of saturation magnetization.

The main crystalline phase present on the X-ray diffraction pattern can now be identified by comparison with a cadmium hydroxide nitrate (5). The X-ray diffraction pattern recorded after hydrothermal storage of $Cd(OH)_2/2Fe(OH)_3$ has been indexed, and the study of its evolution during further thermal treatment becomes possible. The point is that the preparation of $Cd(OH)_2/2Fe(OH)_3$ gel free of anions cannot be obtained, since the precipitated $Cd(OH)_2$ at pH 10 turns into a sol during washing. Thus, in order to preserve a stoichiometry of Cd(II)/Fe(III) = 0.5, the hydrothermal storage must take place with the accompanied anions, leading to the formation of the newly described cadmium hydroxide nitrate (5) beside other phases.

The purpose of this paper is to identify the product of hydrothermal treatment of the Cd/Fe-hydroxides gel and to describe the phase transformations during thermal treatment.

EXPERIMENTAL

To a mixture of titrated Cd(II) and Fe(III) nitrates of the molar ratio 1 : 2 in a teflon vessel, sodium hydroxide was added to reach pH 10 in order to preserve full precipitation of $Cd(OH)_2$. The coprecipitated gel was put into an autoclave and kept at 150 ± 2°C for 20 hr. Washing and drying of the preparation at 20°C, as well as all the earlier operations, were carried out in N_2 atmosphere in order to avoid forming $CdCO_3$. The dried product was ground in an agate mortar. In powder form it was subjected to X-ray, thermal, magnetic, thermomagnetic, and infrared (IR) investigations. Preparations after the various thermal treatment techniques were studied similarly.

Thermomagnetograms (TM) were obtained on the GEAR X-Y Recorder 240, and the thermogravimetric curve (TG) was taken with the help of a TG-A50-Shimadzu instrument. Infrared spectra were recorded on Perkin–Elmer-180 spectrophotometer using CsBr pellets.

RESULTS AND DISCUSSION

The best X-ray diffraction instrumental conditions revealed three crystalline phases in the product after 20 hr storage at 150 ± 2°C, as shown in Fig. 1. The most abundant phases are cadmium hydroxide nitrate, $Cd_3(OH)_5NO_3$, cadmium hydroxide, $\beta Cd(OH)_2$, and a spinel structure. Unfortunately, the reflections of the first two phases overlap to a large extent the characteristic lines of the spinel phase. Thus the (220)-line representative for cations in tetrahedral positions in the spinel lattice

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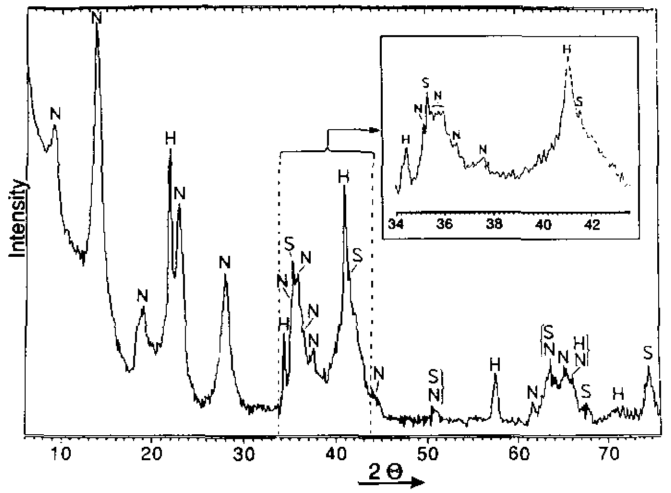

FIG. 1. X-ray powder diffraction spectrum (Co$K\alpha$ radiation) of products after hydrothermal storage of amorphous $Cd(OH)_2 \cdot 2Fe(OH)_3$ at 150 ± 2°C for 20 hr. Peak labels are (N) $Cd_3(OH)_5NO_3$, (H) $\beta Cd(OH)_2$, and (S) spinel phase.

is covered by the (023)-line of orthorhombic basic cadmium nitrate, provided that the lattice parameter of the spinel ferrimagnetic phase is near that of γFe_2O_3 ($d_{220} \sim$ 2.95 Å). The most intense (311)-line in the spinel structure appears as a hardly visible offset on the shoulder of the strongest (101)-line of cadmium hydroxide ($d \sim 2.55$ Å). To make identification more convincing, the $2\theta = 34$–44° region, where these two spinel lines should occur, is also represented for other instrumental conditions in the inset of Fig. 1. Two separate lines, (023) of $Cd_3(OH)_5NO_3$ with $d = 2.97$ Å and the (220) spinel line with $d = 2.96$ Å may be seen. Furthermore, the offset visible as a shoulder on the (101)-line of $\beta Cd(OH)_2$ forms its own peak with $d_{(311)S} = 2.52$ Å. The next weak spinel line (400) with $d = 2.09$ Å forms a rather broad maximum because of the proximity of the (043)-line from $Cd_3(OH)_5NO_3$ (d = 2.07 Å). From the very characteristic triad of spinel structure reflections (422), (511), and (440), the last two are sufficiently resolved to interpret them correctly. Particularly well formed is the last member of this triad, the (440)-line with $d \sim 1.48$ Å. Further reflections of the spinel phase (531), (642), and (800) at higher 2θ, although more suitable for exact determination of lattice parameters in a well-crystallized single-phase system, cannot be used in the system under discussion because of difficulties in determining their maxima. With only the set of spinel lines visible in Fig. 1 available, we can roughly assume that the unit-cell parameter a of the phase responsible for ferrimagnetic behavior of the species is equal to 8.36–8.37 Å, markedly greater than the γFe_2O_3 a-parameter, even for very fine particles (6–8). Unfortunately, it is not possible to determine the composition formula of that phase on the basis of chemical analysis. Any reagent which might remove the accompanying phases affects its integrity, which is manifested by the decrease of magnetization instead of an increase.

Before returning to the ferrimagnetic phase, let us consider first the thermal stability of $Cd_3(OH)_5NO_3$ when accompanied by the other phases. As shown in Fig. 2, the (001)- and (011)-lines in the original preparation lose intensity after heating for 3 hr at the same temperature at which it has been hydrothermally obtained. In another thermal treatment, of the pure $Cd_3(OH)_5NO_3$ prepared by the interdiffusion method, the decomposition begins at about 160°C (5). In this work, the full disappearance of the first line should occur at about 220°C, while the strongest line, successively displaced toward higher angles, vanishes at 300°C, making free CdO. This enriches the CdO stemming from the decomposition at this temperature of $Cd(OH)_2$. It is important to stress that, according to our experimental results, the $Cd(OH)_2$, which precipitated separately from the nitrate solution and was stored with the nitrate ions at the same conditions (i.e. at 150 ± 2°C for 20 hr) does not transform even in traces into $Cd_3(OH)_5NO_3$. It seems, then, that the presence of iron hydroxide undergoing the transformation into ferrimagnetic phase stimulates the formation of the Cd(II) basic nitrate.

Judging from the thermomagnetogram (20°C/min) and from the TG-curve (10°C/min) (Fig. 3), both $Cd_3(OH)_5NO_3$ and the ferrimagnetic phase decompose simultaneously. It may be seen that the ferrimagnetic phase has an extraordinarily high initial magnetization, taking into account that the sample contains large amounts of nonmagnetic $Cd_3(OH)_5NO_3$, $Cd(OH)_2$, and free water. The Curie point

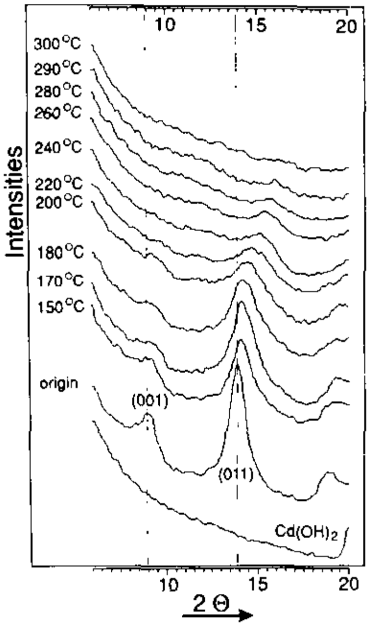

FIG. 2. Decline in intensity of the two strongest reflections of $Cd_3(OH)_5NO_3$ during successive thermal treatment (3 hr at a given temperature in °C).

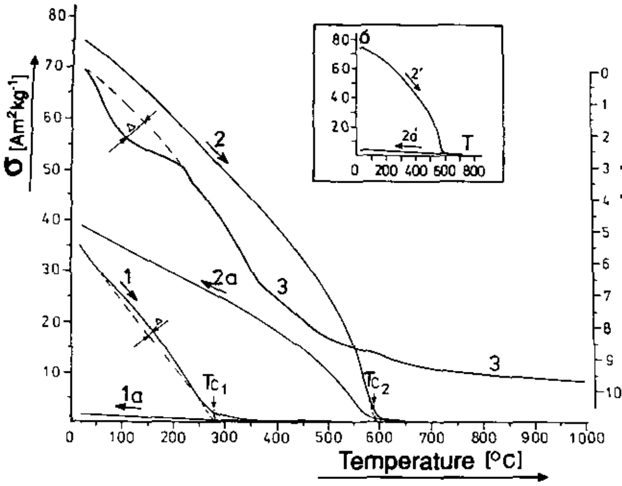

FIG. 3. Thermomagnetogram of the new ferrimagnetic phase (1) and of maghemite, γFe_2O_3 (2). (2′) The same γFe_2O_3 as in (2), measurement run with half-filled holder only (14 mm^3). (3) TG-curve (at a rate of 10°C/min).

of the ferrimagnetic phase appears to be about 270–280°C. In the temperature region where the sharpest loss of water takes place in the TG-curve, the TM-curve shows a rapid drop on the saturation magnetization. Apparently, the increase in magnetization due to the loss of H_2O exceeds the decrease caused by the rising temperature. In Fig. 3 we present a thermomagnetogram recorded in identical conditions of a pure maghemite, γFe_2O_3; this was obtained via goethite ($\alpha FeOOH$) → hematite (αFe_2O_3) → magnetite (Fe_3O_4) → maghemite (γFe_2O_3), i.e., by the procedure used for tape-recording medium. The initial values of magnetization and the Curie point correspond to the values usually found in the literature (9, 10). Here, its TM-curve does not return along the original pathway as a consequence of advanced irreversible transformation $\gamma Fe_2O_3 \rightarrow \alpha Fe_2O_3$ as the temperature rises to 650°C. It may return parallel to the temperature axis as with the new ferrimagnetic phase, by decreasing the rate of the temperature rise during TM-recording, by repeating the run, or by diminishing the γFe_2O_3 volume in the holder, so that conditions are created for full irreversible transformation of maghemite into hematite. On the basis of this very large discrepancy between the Curie points of γFe_2O_3 and of the magnetic phase under study, we conclude that there is a distinct spinel phase. In the case of TM-curve 1, because of the temperature increase, the liberated iron oxide reacts with the available cadmium oxide CdO, forming antiferromagnetic cadmium ferrite, $CdFe_2O_4$ (see also the IR results).

Since the (440)-spinel X-ray diffraction line is very well developed and does not overlap reflections of the other phases, we studied the changes in its position after thermal treatment, always keeping the preparations for 3 hr at given temperatures up to a temperature at which saturation magnetization assumes the value of a normal, antiferromagnetic cadmium ferrite, i.e., until the σ-value falls below 1 A m^{2}kg^{-1}. As Fig. 4 demonstrates, the position of the (440)-line varies between 2θ angles corresponding to $d = 1.4776$ Å and $d = 1.5327$ Å. Up to 250°C it displays a constant d value; from 250 to 300°C the displacement is slight, but above this temperature the (440)-maximum changes its position rather suddenly toward lower angles. In the same temperature range the value of specific magnetization also falls very rapidly. The preparation obtained hydrothermally at 150°C preserves some loosely bound water, which is liberated during warming of sample for 3 hr at the same temperature (150°C); hence a small increase in magnetization appears (from 35.6 to 36.2 A m^{2}kg^{-1}). The unit-cell parameter a of the original preparation, determined from the position of the (440)-line only, is equal to 8.3586 Å. After heating at 420°C (σ = 0.9 A m^{2}kg^{-1}) a increases to 8.6703 Å, which is near the literature value for $CdFe_2O_4$ (11, 12).

The holder in the magnetic balance contains too little sample to make the X-ray diffractogram after recording the TM-curve. Instead this sample was used for the IR spectroscopy. Figure 5 shows four spectra recorded in the lattice vibration region (200–700 cm^{-1}), where interesting information could be expected. According to our survey of literature from the last three years, no IR studies of pure basic cadmium nitrate, $Cd_3(OH)_5NO_3$, have been carried out. We know from X-ray analysis that our $Cd_3(OH)_5NO_3$ is accompanied by some amounts of

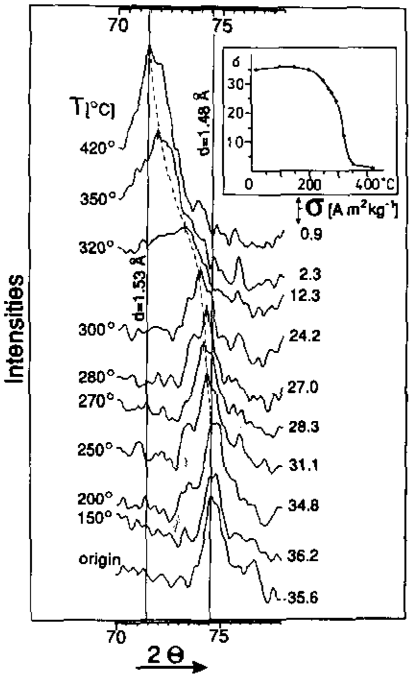

FIG. 4. Displacements of the X-ray (440)-spinel line and changes in saturation magnetization, after successive heating for 3 hr at each temperature.

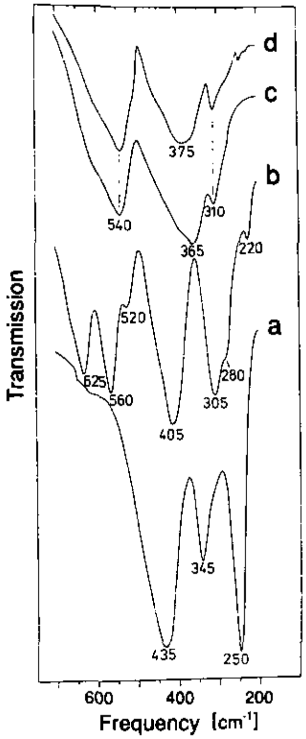

FIG. 5. Infrared spectra in the lattice vibration region of (a) pure cadmium hydroxide, (b) preparation after hydrothermal treatment of amorphous $Cd(OH)_2 \cdot 2Fe(OH)_3$ at 150 ± 2°C for 20 hr, (c) sample obtained after the thermomagnetogram recording (from Fig. 3, 1a.), and (d) normal cadmium ferrite obtained from $Cd(OH)_2 \cdot 2Fe(OH)_3$ hydroxide sintered at 1000°C.

$\beta Cd(OH)_2$ and by the ferrimagnetic spinel phase. Nonetheless, a comparison of spectrum "b" with spectra "c" and "d" indicates that the product of decomposition formed during TM-recording is indeed the cadmium ferrite. The frequencies appear slightly displaced in comparison with a sample stemming from annealing a mixture of $Cd(OH)_2/2Fe(OH)_3$ at 1000°C (Fig. 5d) and which has a correct unit-cell parameter $a = 8.7006$ Å (11).

CONCLUSIONS

A plot of a-parameter as a function of Cd^{2+} content in the composition $Cd_x^{2+}Fe_{1-x}^{3+}[Ni_{1-x}^{2+}Fe_{1+x}^{3+}]O_4$ gives a straight line (11). Knowing that the phase has a spinel structure with an a-parameter of 8.36–8.37 Å, we conclude that our phase is a defect cadmium ferrite, with the formula $Cd_xFe_{1-x}[Fe_{(5+x)/3}\square_{(1-x)/3}]O_4$, i.e., that it is a solid solution formed between maghemite and cadmium ferrite with a Cd^{2+} content roughly equal to 0.05 ~ 0.1 mole in the above formula. Such a solid solution, if in pure form, would of course have a higher resultant magnetic moment than γFe_2O_3 because of greater difference between magnetic moments in octahedral and tetrahedral sublattices. The Curie point, T_c, of our ferrimagnetic phase corresponds to its decomposition temperature, and hence the backward course of the curve is practically parallel to the temperature axis, showing the nearly zero magnetization.

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