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Formation of cadmium-containing W-type hexagonal ferrite

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The main steps of the phase formation processes which take place in samples of W-type hexaferrites containing cadmium, prepared by chemical coprecipitation, have been analysed. The processes were followed by Mössbauer spectroscopy, powder X-ray diffraction, thermomagnetic analysis and magnetic measurements. For samples heated in the temperature range 1000–1100 °C, the phase formation processes are the same as those verified for the other zinc, nickel, cobalt W-type compounds: for $T_h = 1000$ °C the only phases present are $SrFe_{12}O_{19}$ (M-type ferrite) and $CdFe_2O_4$ (spinel ferrite); in contrast, for $T_h > 1100$ °C, the solid state reaction between the M-type and the spinel phases does not take place and the spinel phase decomposes, leading to the formation of α-Fe_2O_3.

1. Introduction

Until now W-type hexagonal ferrites with composition (Sr, Ba) $Me_2^{2+}Fe_{16}O_{27}$ (Me = Fe, Co, Ni, Mn, Mg, Zn) have been prepared both as polycrystalline and single-crystal specimens and studied in detail. However, efforts devoted to the preparation of single-phase samples of W-hexaferrite containing Cd^{2+} have not given satisfactory results. It is worth bearing in mind that the Cd^{2+} ion has an ionic radius of 0.097 nm which is intermediate between that of the light divalent cations ($r_i = 0.075$ and 0.074 nm for Fe^{2+} and for Zn^{2+}, respectively) and that of the heavy divalent cations ($r_i = 0.129$ and 0.110 nm for Ba^{2+} and Sr^{2+}, respectively). In this paper the main steps of the phase formation processes taking place in samples with the stoichiometric composition of Cd_2-W are discussed. The powders were prepared by chemical coprecipitation and then subsequently heat treated. This method of preparation does not include a grinding stage which could affect both the intrinsic and the extrinsic properties of the particles.

The crystalline structure and the general properties of the W-type ferrites have been described extensively in the literature [1–3], but in order to help in the following discussion, their main structural and magnetic features are summarized in Table I. The Me^{2+} and Fe^{3+} cations are distributed among seven different crystallographic sites. The magnetic properties are often grouped into five magnetic sublattices following a scheme suggested by Gorter for an easy axis spin configuration [4].

Cd^{2+} ions have a preference for tetrahedral sites and, according to the Gorter scheme, they should occupy the 4e and 4f spin-down sublattices. This should decrease the number of spin-down magnetic ions and thus increase the overall saturation magnetization. The situation is similar to that of Zn_2-W compound [5] because Zn^{2+} ions also show a marked preference for the tetrahedral sites. In this compound it is known [5] that the presence of Zn^{2+} in 4e and 4f tetrahedral sublattices perturbs the equilibrium of superexchange interactions, leading to a deviation from the axial order predicted by the Gorter scheme. Because of the large difference in the ionic radii of Cd^{2+} and Zn^{2+}, this perturbation is expected to be different in the two cases. For these reasons, Cd_2-W is of interest both for possible applications and for the study of fundamental properties.

In recent years, some papers on Cd_2-W hexagonal ferrite have been published [6, 7]. However, the phase-formation process in this compound seems to be different from that observed in other W ferrites, and the check of phase homogeneity in the final products is not so straightforward.

2. Experimental procedure

Polycrystalline samples with the stoichiometric composition of $SrCd_2Fe_{16}O_{27}$ were prepared by chemical coprecipitation. The precipitating agent was a hydroxide–carbonate buffer solution with a ratio of $NaOH:Na_2CO_3$ suitable for ensuring a pH value higher than 10 (see Table II). The coprecipitation was achieved by adding 200 ml of a solution containing 2.66 g $SrCl_2 \cdot 6H_2O$, 3.95 g $CdCl_2 \cdot 4H_2O$ and 43.25 g $FeCl_3 \cdot 6H_2O$ (a stoichiometric ratio of 1:2:16), to 400 ml of a solution containing $NaOH:Na_2CO_3$. The filtered solution was then tested using standard specific anions in order to check the complete precipitation of Sr^{2+}, Cd^{2+} and Fe^{3+} cations. Finally, the precipitate obtained was washed with cold distilled water

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TABLE I Number of ions, coordination and spin orientation for the various cation sublattices of W-type hexagonal ferrite

Magnetic sublattice	Sublattice	Coordination	Number of ions per formula unit	Block	Spin
k	12k	Octahedral	6	R-S	Up
f_{IV}	4e	Tetrahedral	2	S	Down
	$4f_{IV}$	Tetrahedral	2	S	Down
f_{VI}	$4f_{VI}$	Octahedral	2	R	Down
a	6g	Octahedral	3	S-S	Up
	4f	Octahedral	2	S	Up
b	2d	Hexahedral	1	R	Up

TABLE II Solubility products and pH values at the start and finish of precipitation for $Cd(OH)_2$ and $Fe(OH)_3$.

Hydroxide	Solubility product	Start of precipitation $[Me^{n+}]$ ($g\,ion\,l^{-1}$)	pH	Complete precipitation $[Me^{n+}]$ ($g\,ion\,l^{-1}$)	pH
$Cd(OH)_2$	1.2×10^{-14}	1	7.0	10^{-6}	10.0
		10^{-1}	9.3		
$Fe(OH)_3$	3.8×10^{-38}	0.8	1.5	10^{-6}	3.5
		10^{-2}	2.2		

until all chloride ions were eliminated. The coprecipitated powders were annealed at different temperatures (T_h) for 6 h, a time sufficient to reach equilibrium.

The samples were characterized using the following techniques: temperature dependence of the initial permeability (thermomagnetic analysis, TMA), single point detection (SPD) technique for the measurement of the magnetic anisotropy field (H_a); X-ray powder diffraction using CoK_α radiation; vibrating sample magnetometer for measuring the saturation magnetization (σ_s) and coercive field ($_iH_c$), scanning electron microscopy (SEM), Mössbauer spectroscopy using a ^{57}Co in rhodium source.

3. Results and discussion

The coprecipitated particles, before any heat treatment, were analysed by SEM. They show a high morphological homogeneity and grain sizes ranging from 0.05–0.075 μm (Fig. 1). SEM was also used to perform an X-ray microanalysis of the grains in order to determine the relative amounts of barium, cadmium and iron. The average chemical composition of the grains agreed with the starting stoichiometry. The iron in the coprecipitated powder is in the trivalent ionic state within hydroxide complexes: the Mössbauer spectrum shows a quadrupole doublet with a splitting $\Delta Q = 0.65 \pm 0.05$ mm s^{-1} and an isomer shift $\Delta = 0.25 \pm 0.05$ mm s^{-1} (Fig. 2a).

The Mössbauer spectrum of the sample heated at 500 °C (Fig. 2b) shows a low-intensity sextet with parameters typical of α-Fe_2O_3 and an intense doublet ($\Delta Q = 0.85 \pm 0.05$ mm s^{-1}) attributable to α-Fe_2O_3 superparamagnetic particles. This high value of the splitting compared to that of α-Fe_2O_3 large particles ($\Delta Q = 0.1$ mm s^{-1}) can be explained in terms of surface effects on the crystalline field around Fe^{3+} ions in very small particles [8]. However, in our samples, the interpretation is more intriguing due to the fact that the $CdFe_2O_4$ spinel phase, which is expected to be present in the early stages of the phase formation

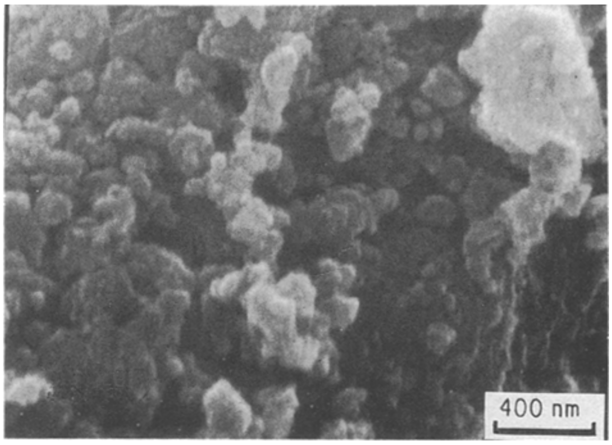

Figure 1 Scanning electron micrograph of coprecipitated powders before the heat treatment.

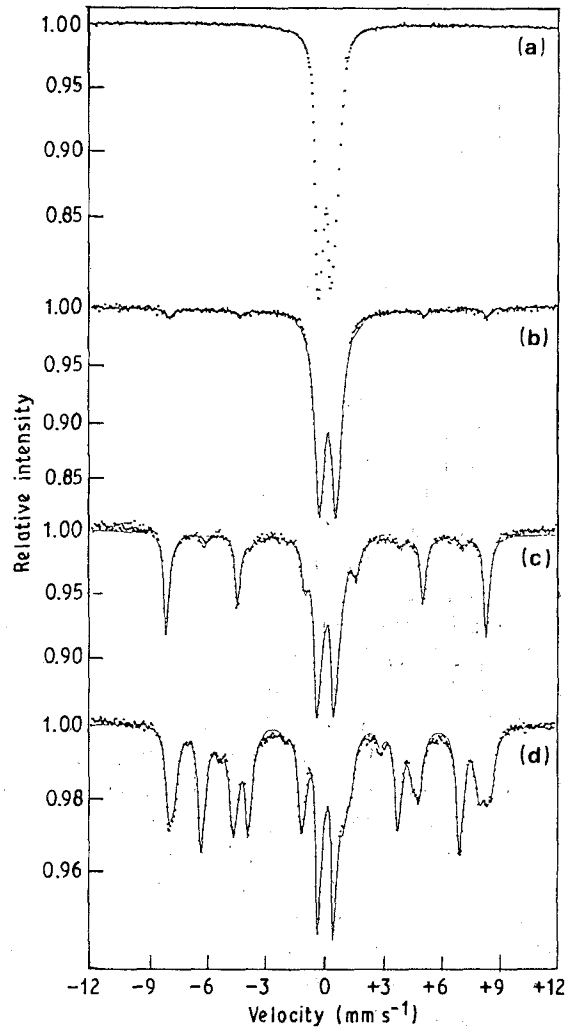

Figure 2 (a) Room-temperature Mössbauer spectra of coprecipitated powders, and after heating to different temperatures: (b) 500 °C, (c) 600 °C and (d) 1100 °C. (——) The spectrum obtained from the computer fitting.

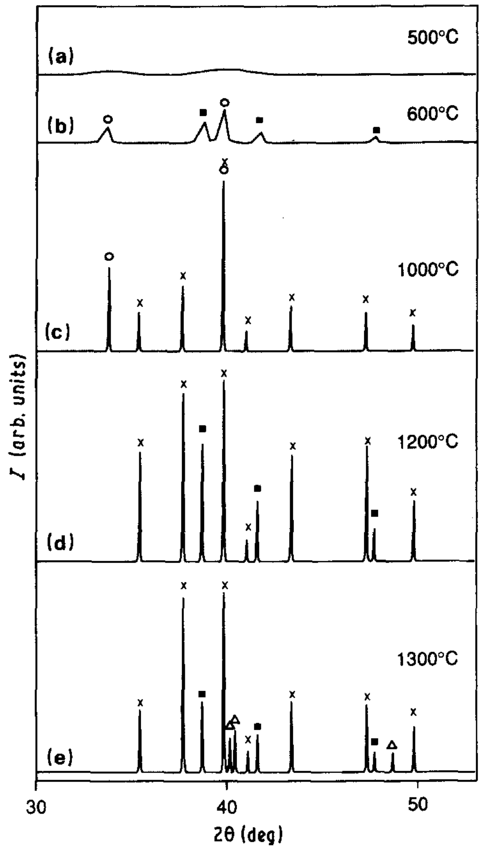

Figure 3 X-ray powder diffraction spectra for samples heated at different temperatures between 500 and 1300 °C. The phases detected are: (●) α-Fe_2O_3, (○) $CdFe_2O_4$, (×) M, (Δ) W.

process, is paramagnetic at RT and displays a Mössbauer spectrum with a quadrupole splitting equal to 0.80 mm s^{-1}, i.e. very near to that observed in this work. In effect, the X-ray diffraction spectrum (see Fig. 3a) of the sample at 500 °C shows two very large broad peaks indicating that the formation of the spinel phase has started.

The Mössbauer spectrum for the sample heated at 600 °C (Fig. 2c) clearly shows an increase in the intensity of the α-Fe_2O_3 sextet relative to that of the central doublet. This is in agreement with the X-ray diffraction spectrum (see Fig. 3b) showing the presence of both α-Fe_2O_3 and $CdFe_2O_4$. Further small absorption peaks appear in the spectrum. Their position corresponds to the $SrFe_{12}O_{19}$ Mössbauer spectrum showing that, even at such low temperatures, the formation of the M-phase has already started. The spectrum for the same sample measured at $T = 78$ K (Fig. 4a) still shows the central doublet. At 4.2 K its intensity is greatly reduced.

On heating the coprecipitated samples above 600 °C the rate of formation of $SrFe_{12}O_{19}$ increases. At $T_h = 1000$ °C the only phases present in the sample are $SrFe_{12}O_{19}$ and $CdFe_2O_4$ as shown in Fig. 3c. The Mössbauer spectrum shows the typical pattern of the M-type structure superimposed onto a quadrupole doublet attributable to the cadmium–spinel compound (Fig. 4b). The ratio of the areas submitted by these two subspectra turns out to be approximately 3. This value, assuming the hypothesis of the same Mössbauer recoilless fraction for the above two compounds, is what one would expect from the stoichiometric amount of iron in the two phases. In fact, chemically the W-hexaferrite can be thought as: W = M + 2S (i.e. $SrCd_2Fe_{16}O_{27} = SrFe_{12}O_{19} + 2\,CdFe_2O_4$). The same value (≈ 3) for the ratio between the subspectra has been obtained from the Mössbauer spectrum measured at 78 K. The absence of the α-Fe_2O_3 phase as been proved by the Mössbauer spectrum measured at 500 °C, i.e. above the Curie temperature of $SrFe_{12}O_{19}$ ($T_C = 450$ °C) but below the Néel temperature of α-Fe_2O_3 ($T_N = 678$ °C). Indeed, in this spectrum (Fig. 5a) the sextet due to α-Fe_2O_3 is absent. The same behaviour has been observed in the sample heated at 1100 °C.

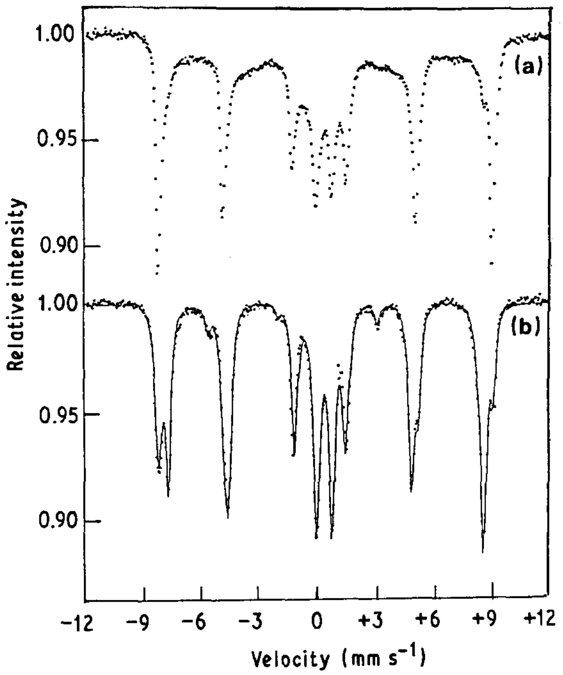

Figure 4 Mössbauer spectra measured at 78 K for samples heated at (a) 600 and (b) 1000 °C.

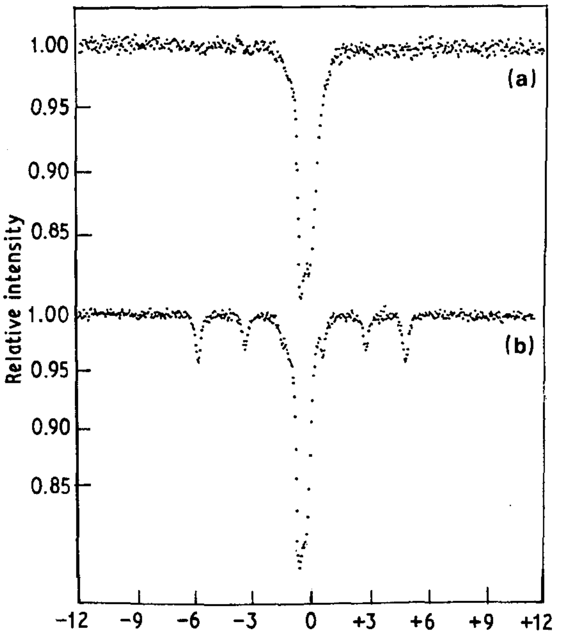

Figure 5 Mössbauer spectra measured at 500 °C for the sample heated at (a) 1000, and (b) 1200 °C.

The absence of α-Fe_2O_3 in the samples heated at 1000 and 1100 °C demonstrates that the reactions leading to the phases which are precursors of the W-compound have already ended.

From the above data one may conclude that up to the annealing temperature $T_h = 1100\,°C$ the main steps of the phase formation in the Cd_2-W system are analogous to those of other W-compounds: (i) dehydration of the hydroxide complexes and formation of α-Fe_2O_3 compound for $T_h < 500$–$600\,°C$; (ii) reaction of α-Fe_2O_3 with strontium and cadmium atoms giving rise to $SrFe_{12}O_{19}$ and $CdFe_2O_4$ for 500–$600 < T_h < 1000\,°C$. At 1000 and 1100 °C, the relative amounts of these two phases are in agreement with what one expects from the stoichiometry of the starting composition.

At $T_h > 1100\,°C$, the phase formation processes in cadmium-containing compounds differ from those of other W hexaferrites. In fact, as previously has been verified for the zinc, nickel, cobalt W-ferrites [9–11], above 1100 °C a solid state reaction between the hexagonal M-phase and the corresponding spinel compound occurs, leading to the formation of the W-hexaferrite.

In contrast, in samples containing cadmium, the formation of the W-structure does not take place. This fact is confirmed both by X-ray diffraction and Mössbauer analysis. The Mössbauer spectrum measured at room temperature for a sample heated at 1200 °C is shown in Fig. 6. It can be seen that the central doublet due to $CdFe_2O_4$ is absent. The spectrum can be interpreted as the superposition of two contributions due to a M-type hexagonal structure and α-Fe_2O_3. The relative amount of α-Fe_2O_3 present in the sample can be estimated from a spectrum measured at 500 °C, i.e. above the T_C of the M-phase. In this spectrum the area submitted by the α-Fe_2O_3 sextet is clearly distinguishable from the central component (see Fig. 5b). The relative amount of iron in α-Fe_2O_3 is $\approx 33\%$ in agreement with that expected under the hypothesis of decomposition of the cadmium-spinel phase

$$CdFe_2O_4 \rightarrow \alpha\text{-}Fe_2O_3 + CdO(?) \qquad (1)$$

A microanalysis performed by SEM revealed the presence of a significant amount of cadmium in the sample; unfortunately it was not possible to determine its actual chemical status and amount.

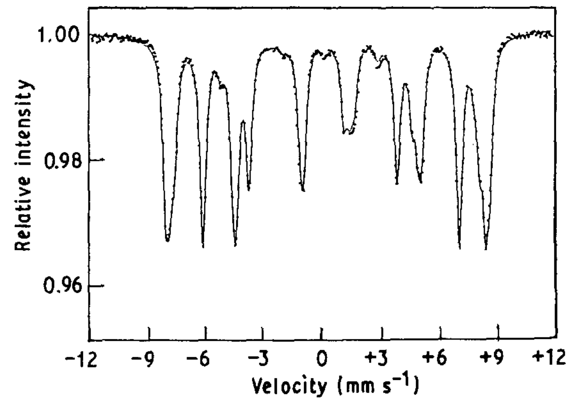

Figure 6 Room-temperature Mössbauer spectrum for a sample heated at 1200 °C.

The presence of a small amount of W-phase was detected by X-ray analysis in the sample heated at 1300 °C. Unfortunately, the close resemblance of the Mössbauer spectra of M- and W-hexaferrites does not allow one to distinguish a small amount of W-phase and thus to confirm the X-ray data. However, from the Mössbauer spectrum of the same sample measured at 500 °C, it was found, following the same procedure described above, that the relative percentage of iron belonging to α-Fe_2O_3 decreased to 22%. The relative decrease of α-Fe_2O_3 content in the sample is also revealed by X-ray diffraction showing a remarkable decrease in the relative intensities of the α-Fe_2O_3 peaks (see Fig. 3e). The difference with respect to the sample heated at 1200 °C is probably due to the fact that part of the iron may give rise to $SrFe_{18}O_{27}$ (Fe_2-W). The formation of a small quantity of W-phase could explain the increase of the saturation magnetization observed in the sample heated at 1300 °C (see Table III).

4. Conclusion

The problem of the preparation of cadmium-containing W-type hexagonal ferrites still remains open. The following main points can be made.

TABLE III Values of $\sigma_{s,\,i}H_c$, T_C and H_a for cadmium-containing W-ferrite, obtained by heating the coprecipitated powder at different temperatures (T_h) for 6 h

T_h (°C)	σ_s (e.m.u g^{-1})	$_iH_c$ (O_e)	T_C (°C)	H_a (kOe)
600	5.5	0		
900	33.9	5330	450	17
1100	44.4	2770	450	
1200	55.5	1245	460	
1300	63.3	100	460	14.1–18.5
1375	77.7	100	([a])	

[a] Three magnetic phases with $T_C = 460$, 500 and 550 °C, respectively.

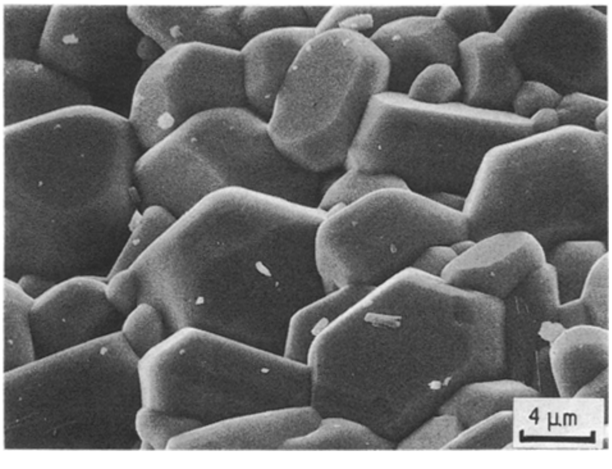

Figure 7 Scanning electron micrograph of cadmium-containing W-ferrite sample. The coprecipitated powder was pressed and heated at 1300 °C for 6 h.

1. Up to annealing temperatures of about 1100 °C, the phase formation processes in samples with composition $SrCd_2Fe_{16}O_{27}$ are very close to those of W-compounds containing other divalent metallic ions: the formation of $SrFe_{12}O_{19}$ ferrite and $CdFe_2O_4$ spinel compound occurs.

2. At higher annealing temperatures the solid state reaction between the M-type hexagonal and the cadmium-spinel phases does not take place: the $CdFe_2O_4$ compound decomposes to form a residual amount of α-Fe_2O_3.

3. The ${}_iH_c$ value decreases abruptly due to a large grain size (> 15 μm, see Fig. 7) after heat treatments at $T_h > 1250$ °C for 6 h.

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