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Study by electrical conductivity and infrared spectrometry of the thermal stability of defective iron spinels with aluminium and chromium

B. GILLOT, F. JEMMALI, M. LAARJ
Laboratoire de Recherches sur la Réactivité des Solides UA 23, Faculté des Sciences Mirande, BP 138, 21004 Dijon Cédex, France

F. CHASSAGNEUX
Laboratoire de Chimie Minérale, Université Claude Bernard, Lyon I, 43 Boulevard du 11 novembre 1918, 69621 Villeurbanne, France

A. ROUSSET
Laboratoire de Chimie des Matériaux Inorganiques, Université Paul Sabatier, Toulouse III, 118 route de Narbonne, 31062 Toulouse Cédex, France

Precipitation in defective chromium- or aluminium-substituted magnetites, $\gamma\text{-}(Fe^{3+}_{(8/3)-(8/9)x}M^{3+}_{(8/9)x}\square_{1/3})O_4^{2-}$ ($M^{3+} = Al^{3+}, Cr^{3+}$; $0 < x < 2$), and defective iron aluminium chromium spinels, $\gamma\text{-}(Fe^{3+}_{8/9}Al^{3+}_{(8/9)(2-x)}Cr^{3+}_{(8/9)x}\square_{1/3})O_4^{2-}$ has been investigated by electrical conductivity and infrared spectrometry in the temperature range 600 to 1200° C. For highly γ-Al-substituted magnetites and γ-iron aluminium chromium spinels the transformation of the spinel lattice into an α-rhombohedral lattice has been found to be preceded by the formation of an intermediate phase at about 900° C with a high alumina content, approximately identical to disordered $\gamma\text{-}Al_2O_3$. It is only at higher temperatures (>1100° C) that the formation of an α-rhombohedral phase is observed. In the case of γ-Cr-substituted magnetites, temperatures of only about 700° C are required for the transformation $\gamma \rightarrow \alpha$.

1. Introduction

The stability of defective γ-phases of spinel structure resulting from the low-temperature oxidation (about 450° C) of aluminium- or chromium-substituted magnetites, $(Fe^{2+}Fe^{3+}_{2-x}M^{3+}_x)O_4^{2-}$ ($0 < x < 2$; $M^{3+} = Al^{3+}, Cr^{3+}$), as well as solid solutions, $(Fe^{2+}Al^{3+}_{2-x}Cr^{3+}_x)O_4^{2-}$ ($0 < x < 2$), is above all governed by the aluminium or chromium substitution ratio x and the nature of the substituent [1, 2]. From differential thermal analysis (DTA) measurements [3] it has been shown that the phases that are richer in aluminium are the more stable since temperatures of about 900° C are required for the transformation of defective aluminium-substituted magnetites and 700° C for the transformation of defective chromium-substituted magnetites. In all cases those temperatures are far higher than those of the transformation $\gamma\text{-}Fe_2O_3 \rightarrow \alpha\text{-}Fe_2O_3$ for which the temperature is about 400° C.

For the temperatures considered and for sufficiently long reaction times, the structural change occurring when defective γ-phases undergo a thermal treatment eventually leads to a rhombohedral lattice which is stable at high temperature. However, it should be noticed that in the course of the precipitation of some systems, a number of intermediate phases may form; thus, for magnesium aluminates, the final stage ($\alpha\text{-}Al_2O_3$) is reached only after prior precipitation followed by the occurrence and the transformation of one or several monoclinic phases [4, 5]. For manganese aluminates, first a compound $\gamma\text{-}(MnAl)_2O_3$ forms with a distorted spinel structure [6], which gradually becomes $\gamma\text{-}Al_2O_3$ by diffusion of manganese ions out of the previous phase, and $\alpha\text{-}Al_2O_3$ in the final phase. In defective chromium-substituted magnetites with high chromium content, it is found [2] that, under given temperature and time conditions, an α-rhombohedral phase less rich in chromium than the initial product could be obtained by oxidizing iron chromite. For mixed ferrites, $MFe_2O_4\text{–}Fe_3O_4$ (M = Co, Zn), oxidation to $\alpha\text{-}Fe_2O_3$ may also be, in some cases, preceded by the formation of a defect cubic phase $\gamma\text{-}(MFe_2O_4\text{–}Fe_2O_3)$ [7, 8] if the crystals are sufficiently small.

In the present work, the structural changes occurring when defective aluminium- or chromium-substituted magnetites and iron chromium aluminate spinels undergo thermal treatment are followed using electrical conductivity and infrared spectroscopy in order to elucidate the phase change from a new point of view. Interest in these techniques has recently been shown for studying the phase transformation during heating of "cubic" iron sesquioxides, $\gamma\text{-}Fe_2O_3$, substituted by divalent ions such as Zn^{2+}, Co^{2+} and Mn^{2+} [9, 10].

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TABLE I Sample characteristics for defective $\gamma\text{-}(\mathrm{Fe}^{3+}_{(8/3)-(8/9)x}\mathrm{M}^{3+}_{(8/9)x}\square_{1/3})\mathrm{O}_4^{2-}$ after oxidation of initial phases at 500° C

Compound	Particle size (nm)	Lattice parameter (nm)
$\mathrm{M}^{3+} = \mathrm{Cr}^{3+}$		
$x = 0.27$	48	0.8335
$x = 0.75$	30	0.8319
$x = 1.20$	78	0.8298
$x = 1.60$	80	0.8276
$x = 2$	50	0.8262
$\mathrm{M}^{3+} = \mathrm{Al}^{3+}$		
$x = 0.27$	29	0.8290
$x = 1.20$	30	0.8178
$x = 1.60$	40	0.8117
$x = 2$	35	0.8060

TABLE II Sample characteristics for defective $\gamma\text{-}(\mathrm{Fe}^{3+}_{8/9}\mathrm{Al}^{3+}_{(8/9)(2-x)}\mathrm{Cr}^{3+}_{(8/9)x}\square_{1/3})\mathrm{O}_4^{2-}$ after oxidation of initial phases at 600° C

x	Particle size (nm)	Lattice parameter (nm)
0.05	43	0.8063
0.20	35	0.8082
0.40	31	0.8105
0.80	42	0.8150
1	35	0.8167
1.20	39	0.8186
1.50	41	0.8220
1.80	51	0.8267

2. Experimental procedure

The techniques of preparation and characterization (DTA, X-ray analysis, specific area, chemical analysis, morphology) of aluminium- or chromium-substituted magnetites, $(\mathrm{Fe}^{2+}\mathrm{Fe}^{3+}_{2-x}\mathrm{M}^{3+}_x)\mathrm{O}_4^{2-}$ ($\mathrm{M}^{3+} = \mathrm{Al}^{3+}, \mathrm{Cr}^{3+}$) and solid solutions, $(\mathrm{Fe}^{2+}\mathrm{Al}^{3+}_{2-x}\mathrm{Cr}^{3+}_x)\mathrm{O}_4^{2-}$, have already been given elsewhere [11–13]. When the crystallite size is less than about 200 nm, defective γ-phases with a spinel structure can be obtained by the oxidation of initial spinels in the temperature range 300 to 600° C according to the reactions

$$2[(\mathrm{Fe}^{2+}\mathrm{Fe}^{3+}_{2-x}\mathrm{M}^{3+}_x)\mathrm{O}_4^{2-}] + \tfrac{1}{2}\mathrm{O}_2 \rightarrow \gamma\text{-}(\mathrm{Fe}^{3+}_{6-2x}\mathrm{M}^{3+}_{2x})\mathrm{O}_9^{2-}$$

and

$$2[(\mathrm{Fe}^{2+}\mathrm{Al}^{3+}_{2-x}\mathrm{Cr}^{3+}_x)]\mathrm{O}_4^{2-}$$
$$+ \tfrac{1}{2}\mathrm{O}_2 \rightarrow \gamma\text{-}(\mathrm{Fe}^{3+}_2\mathrm{Al}^{3+}_{4-2x}\mathrm{Cr}^{3+}_{2x})\mathrm{O}_9^{2-}$$

The formulae of these oxidized compounds can be structurally represented as follows:

$$(\mathrm{Fe}^{3+}_{(8/3)-(8/9)x}\mathrm{M}^{3+}_{(8/9)x}\square_{1/3})\mathrm{O}_4^{2-}$$

and

$$(\mathrm{Fe}^{3+}_{8/9}\mathrm{Al}^{3+}_{(8/9)(2-x)}\mathrm{Cr}^{3+}_{(8/9)x}\square_{1/3})\mathrm{O}_4^{2-}$$

where □ is the vacant lattice site. The morphology of these defect spinels is similar to that of the initial phases; in particular, the size of the crystallites (Tables I and II) is almost the same. X-ray crystallographic analysis, performed from diagrams obtained in a vacuum with Cr$K\alpha$ monochromatized radiation, shows that the samples exhibit only the spinel phase. Lattice parameters are listed in Tables I and II.

The electrical properties of time–temperature transformation of defective γ-phases was followed by measuring the d.c. electrical conductivity. The measuring device and the operating conditions have already been reported [14]. The samples were oxidized isothermally in the cell at 500° C for 12 h in air followed by rapid cooling, during which the initial phase was transformed to γ-phase. The samples thus obtained were heated in air at a constant rate of 1.5° C min^{-1} from 500 to 1000° C. The phases present in the course of the precipitation were investigated by infrared spectroscopy from samples rapidly cooled from various temperatures in the cell. The spectra were measured at room temperature using a Perkin-Elmer Model 580B double-beam spectrophotometer over the range 1000 to 200 cm^{-1}. About 1 mg of the sample was mixed and ground with 200 mg of CsI before being pelleted under 160 bar pressure.

3. Results and discussion

3.1. Stability of defective chromium- or aluminium-substituted magnetites

A plot of log σ against $1/T$ (Figs 1 and 2) shows the dependence of substitution extent x when the samples were heated in air at a constant rate. In all cases a break is observed. For temperatures lower than this break (Line AB), the electrical conductivity increases with increase in temperature according to the negative temperature coefficient of defective γ-phases. The increase in σ is then followed by a discontinuity (Line BD) which can be regarded as being caused by the phase change, for example of a lattice of cubic symmetry (γ-phase) to a rhombohedral lattice (α-phase) which is stable at high temperature (Line DE). The effect of substitution extent x on temperature transformation can be directly investigated by evaluating the temperatures T_B and T_D of the beginning and end of

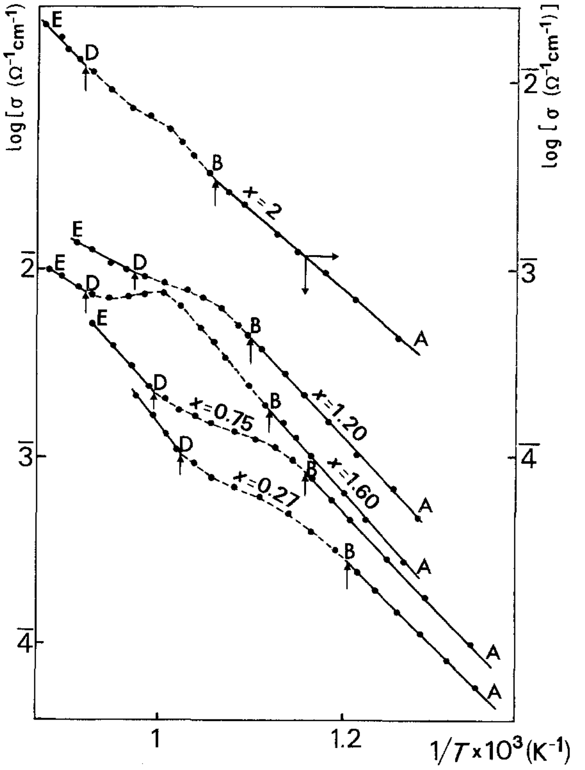

Figure 1 Behaviour of electrical conductivity with temperature during the transformation of defective chromium-substituted magnetites, $\gamma\text{-}(\mathrm{Fe}^{3+}_{(8/3)-(8/9)x}\mathrm{Cr}^{3+}_{(8/9)x}\square_{1/3})\mathrm{O}_4^{2-}$.

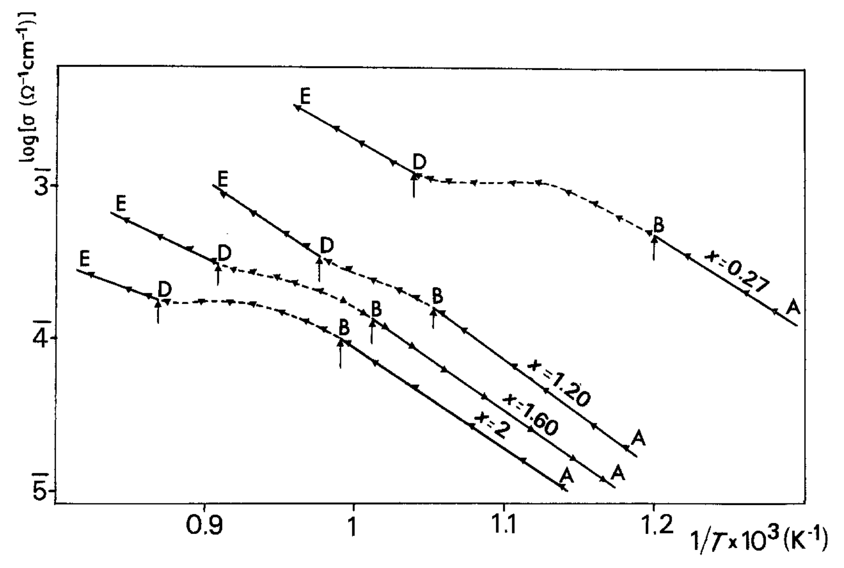

Figure 2 Behaviour of electrical conductivity with temperature during the transformation of defective aluminium-substituted magnetites, $\gamma\text{-}(\mathrm{Fe}^{3+}_{(8/3)-(8/9)x}\mathrm{Al}^{3+}_{(8/9)x}\square_{1/3})\mathrm{O}_4^{2-}$.

each discontinuity and the average temperature $T_M = (T_B + T_D)/2$ (Table III). For these defective γ-phases a shift of T_M toward higher temperatures was observed with increase of substitution extent. It is obvious from Table III and Fig. 3 that the stabilization of defect spinel is more pronounced for defective aluminium-substituted magnetites than for defective chromium-substituted magnetites, particularly when the substitution extent becomes large ($x > 1.20$). It may also be noted that the conductivity in the γ-phase region (at 560° C) of highly aluminium-substituted magnetites (Fig. 4) is smaller than that of highly chromium-substituted magnetites by about two orders of magnitude.

The phase changes described here have also been demonstrated in studies of infrared (IR) spectra as well as by X-ray diffraction. Fig. 5 shows the evolution with temperature of the IR spectrum, and Fig. 6 represents the vibrational behaviour during the transformation for chromium-substituted magnetite with $x = 1.60$. It is thus possible to evaluate a transition average temperature. For this purpose, we can for example refer to the temperature at which the 495 cm^{-1} band of the γ-phase disappears (at about 680° C) and to the temperature at which the 400 and 530 cm^{-1} bands of the α-phase are observed (at about 730° C). Thus, for this composition, one temperature of about 705° C appears reasonable to characterize the transformation. Comparison of this temperature with that determined previously from electrical measurements (715° C) reveals good agreement between the two methods of determining the transition temperature. Moreover, for these chromium-substituted compounds, the evolution of absorption band positions with the chromium content of partially or totally transformed phases confirms that α-rhombohedral phases are directly obtained [2] without the formation of an intermediate phase. Indeed, these bands are in very good agreement with the absorption ranges of groups of "condensed" octahedra and must be assigned to the vibrations of octahedral lattices of $\mathrm{CrO_6}$ and $\mathrm{FeO_6}$ [15].

On the other hand, in the case of defective highly aluminium-substituted magnetites, the IR spectrum in

TABLE III Evolution of the transformation temperature for defective $\gamma\text{-}(\mathrm{Fe}^{3+}_{(8/3)-(8/9)x}\mathrm{M}^{3+}_{(8/9)x}\square_{1/3})\mathrm{O}_4^{2-}$

Compound	T_B (°C)	T_D (°C)	$T_M = (T_B + T_D)/2$ (°C)
$M^{3+} = Cr^{3+}$			
$x = 0.27$	560	690	625
$x = 0.75$	593	727	660
$x = 1.20$	635	761	698
$x = 1.60$	625	800	712
$x = 2$	670	800	735
$M^{3+} = Al^{3+}$			
$x = 0.27$	560	692	626
$x = 1.20$	678	751	715
$x = 1.60$	715	825	770
$x = 2$	740	876	807

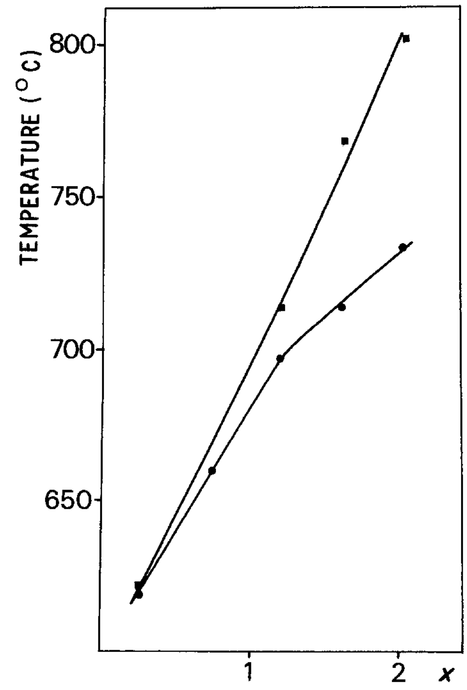

Figure 3 Variation of T_M with composition x for defective (●) chromium- and (■) aluminium-substituted magnetites.

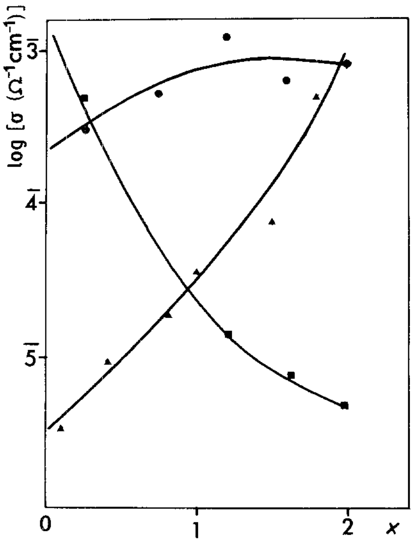

Figure 4 Variation of log σ with composition x for different γ-phases at 560° C: (●) Cr, (■) Al, (▲) Al + Cr.

the discontinuity region is more complex since a band at about 800 cm^{-1} appears during transformation, indicating the presence of "isolated" AlO_4 groups [16]. This is illustrated in Fig. 7, where the evolution of the IR spectrum for the defective γ-$(Fe^{3+}_{8/9}Al^{3+}_{16/9}\square_{1/3})O_4^{2-}$ phase ($x = 2$) is presented during thermal treatment. The spectrum of the partially transformed sample (800° C) closely resembles that of pure disordered γ-Al_2O_3 [17] (compare Fig. 7, Curve (a)). It is only at higher temperature (> 1100° C) that the spectrum is characteristic of a rhombohedral phase [17] (compare Fig. 7, Curve (c)).

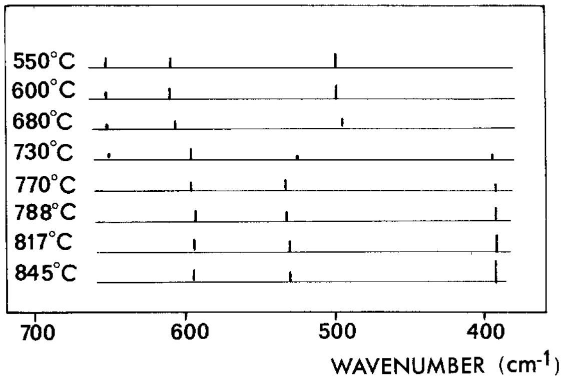

Figure 6 Vibrational behaviour. Evolution of absorption bands with temperature for defective chromium-substituted magnetite with $x = 1.60$.

In order to confirm this behaviour, we have also studied the structural changes of defective iron chromium aluminate spinels.

3.2. Stability of defective iron chromium aluminate spinels

The behaviour of electrical conductivity near the transformation temperature is shown in Fig. 8. In all cases a discontinuity is observed but a maximum of conductivity (Point C) is noted in this region. Table IV gives the temperatures T_B, T_C and T_D of each discontinuity and Fig. 9 shows the effect of composition variable x on the changes of T_B, T_C and T_D. The transformation temperature decreases with x and exhibits one maximum for about $x = 0.8$. Fig. 4 also shows that the conductivity σ progressively decreased when Cr^{3+} is

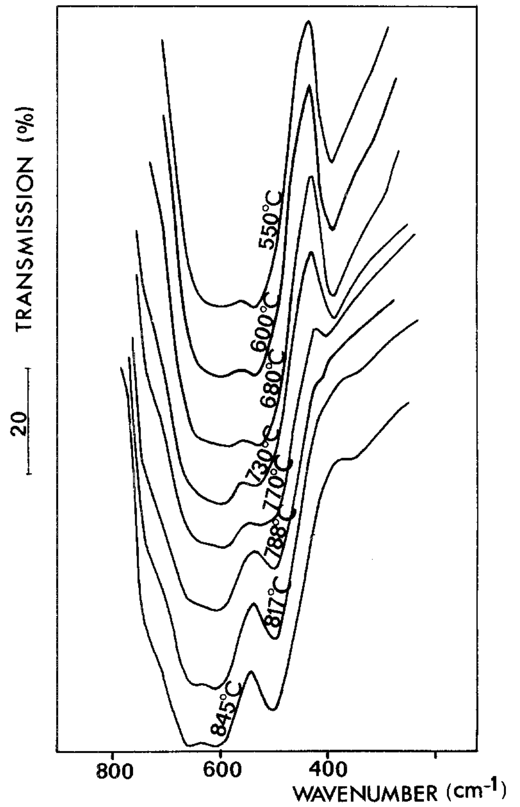

Figure 5 Evolution with temperature of the IR spectrum of the defective chromium-substituted magnetite of composition $x = 1.60$.

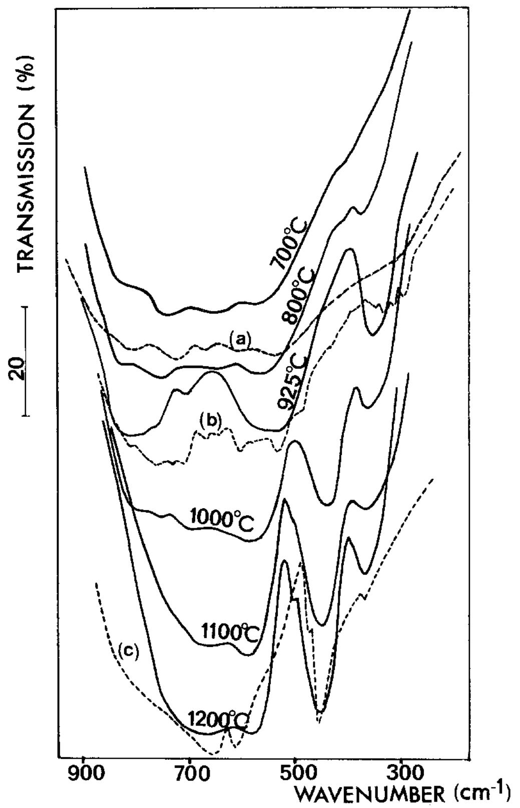

Figure 7 Evolution with temperature of the IR spectrum of defective γ-$(Fe^{3+}_{8/9}Al^{3+}_{16/9}\square_{1/3})O_4^{2-}$ phase. Curve (a): disordered γ-Al_2O_3; Curve (b): ordered γ-Al_2O_3; Curve (c): α-Al_2O_3.

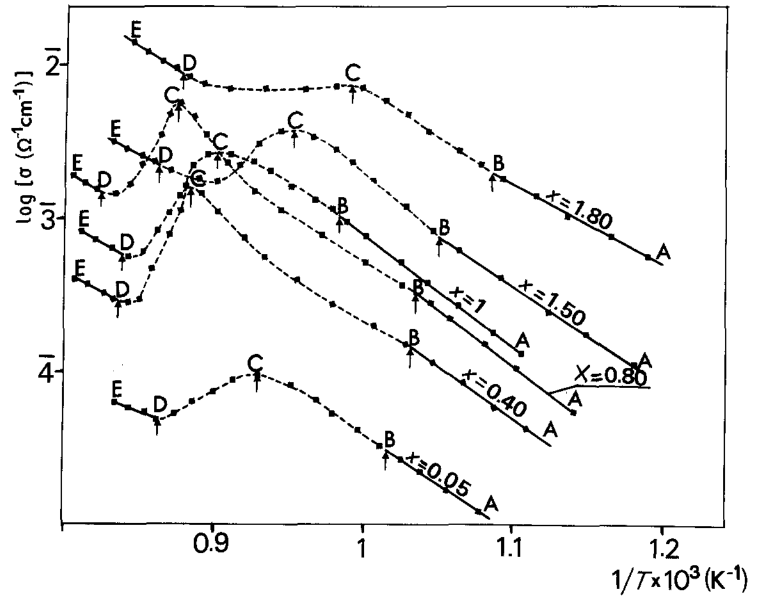

Figure 8 Behaviour of electrical conductivity with temperature during the transformation of defective iron chromium aluminate spinels, $\gamma\text{-}(\mathrm{Fe}^{3+}_{8/9}\,\mathrm{Al}^{3+}_{(8/9)(2-x)}\mathrm{Cr}^{3+}_{(8/9)x}\square_{1/3})\mathrm{O}_4^{2-}$.

substituted by Al^{3+}. It is, therefore, easy to understand that such difference in σ between chromium compounds and aluminium compounds would induce substantial modifications by the formation of oxides such as γ-Al_2O_3, which has a very low conductivity compared with chromium-rich spinels. This corresponds closely to the change of electrical behaviour with aluminium concentration observed in Fig. 8 in the discontinuity region, when the conductivity falls strongly with temperature in the concentration region $0.4 < x < 1.2$. This result provides clear evidence of the formation of a second phase in which the aluminium content is high.

Turning to the IR spectral data, a study of the effect of aluminium concentration on the absorption band profile as a function of temperature (Fig. 10) shows that the 800 cm^{-1} absorption peak becomes more and more intense as the concentration of aluminium increases. This band, assigned to an "isolated" AlO_4 group [16], might be attributed to the presence of aluminium on the tetrahedral sites of the spinel lattice. Since for defective iron chromium aluminium spinels the Al^{3+} ions are on octahedral positions [13], it can be assumed that after heat treatment at about 900° C, γ-Al_2O_3 should act as an independent second phase. The oxygen sublattice is continuous between the γ-Al_2O_3 and the spinel matrix, which are presumably coherent and only involve cation redistribution. This compound has a metastable spinel structure with a large number of vacancies in the cation sublattice [18, 19] as indicated by the structural formula $(\mathrm{Al}\square_x)[\mathrm{Al}_{5/3}\square_{(1/3)-x}]\mathrm{O}_4^{2-}$ (square brackets denote octahedral sites). The distribution of the vacancies among the octahedral and tetrahedral positions is disordered, although not purely random.

The infrared spectrum of γ-Al_2O_3 possesses one very broad band (850 to 500 cm^{-1}) at low temperature, characteristic of a disordered phase (Fig. 7, Curve (a)) which becomes better defined when heated at 950° C for 24 h (Fig. 7, Curve (b)). This fine structure corresponds to an ordering of the vacant sites in the γ-phase (i.e. the δ-phase) [17].

The change in IR spectrum with increasing Al_2O_3 concentration and after heating at 1200° C is given in Fig. 11. For all samples it can be assumed, on the basis of the evolution of absorption bands, that the

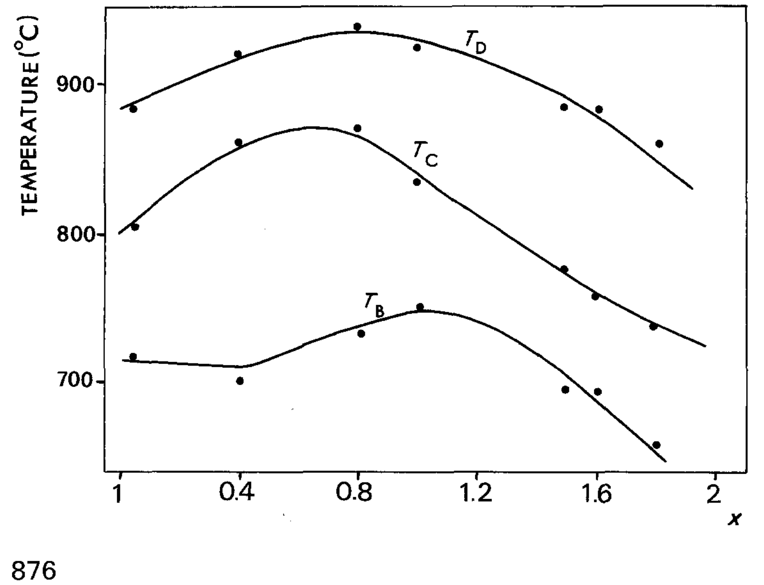

Figure 9 Variation of T_B, T_C and T_D with composition x for iron chromium aluminate spinels.

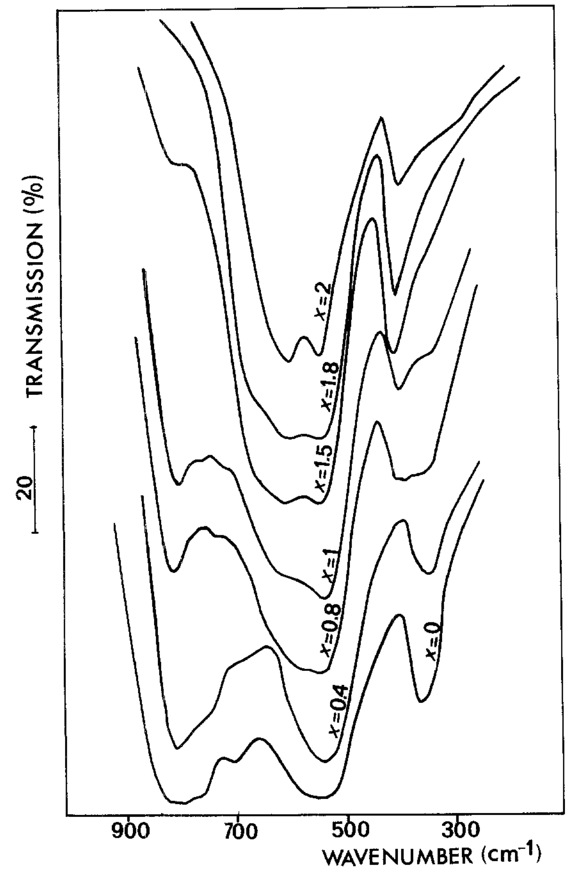

Figure 10 Evolution with composition x of the IR spectrum of iron chromium aluminate spinels in the discontinuity region (temperature 900° C).

rhombohedral α-phase occurs for all compositions [2]. Comparison of the spectra with α-Cr_2O_3 and α-Al_2O_3 (Fig. 11) shows that the bands shift to lower frequencies when the composition varies from α-Cr_2O_3 to α-$Fe_2Cr_4O_9$ or from α-Al_2O_3 to α-$Fe_2Al_4O_9$, which is a common feature of ferric compounds [15]. For α-$(Fe_2Al_{4-x}Cr_{2x})O_9$ rhombohedral phases, the spectra obtained look like that of either α-$Fe_2Cr_4O_9$ or α-$Fe_2Al_4O_9$ depending respectively on whether the phase is richer in chromium than in aluminium or

TABLE IV Evolution of the transformation temperature for defective γ-$(Fe^{3+}_{8/9}\,Al^{3+}_{(8/9)(2-x)}Cr^{3+}_{(8/9)x}\square_{1/3})O_4^{2-}$

x	T_B (° C)	T_D (° C)	T_C (° C)
0.05	720	885	805
0.40	700	920	860
0.80	735	940	870
1	750	930	836
1.50	694	885	775
1.80	650	860	740

conversely. The spectrum of α-$(Fe_2Cr_{1.6}Al_{2.4})O_9$ is intermediate.

4. Conclusion

In conclusion it can be said that the presence of Al^{3+} in the precipitate from defective iron spinels explains the occurrence of a spinel-type intermediate as well as the absence of intermediate compounds in the precipitate from defective chromium–iron spinels. The formation of γ-Al_2O_3 during the thermal treatment might account for the strong decrease of conductivity in the discontinuity region and of the absorption band at about 800 cm^{-1} for defective Al–Cr–Fe spinels. The transition to γ-Al_2O_3, though gradual, also explains the transformation of these defective phases into α-phases at temperature considerably higher than those containing only iron and chromium where direct precipitation is observed.

References

1. B. GILLOT, F. BOUTON, J. F. FERRIOT, F. CHASSAGNEUX and A. ROUSSET, *J. Solid State Chem.* **21** (1977) 375.
2. B. GILLOT, F. BOUTON, F. CHASSAGNEUX and A. ROUSSET, *ibid.* **33** (1980) 245.
3. F. CHASSAGNEUX, PhD thesis, University of Lyon (1981).
4. H. SAAFELD and J. JAGODZINSKI, *Z. Kristallogr.* **109** (1957) 87.
5. M. H. LEWIS, *Phil. Mag.* **20** (1969) 985.
6. E. H. L. J. DEKKER and G. D. RIECK, *Rev. Int. Hautes Temp. Refract.* **11** (1974) 187.

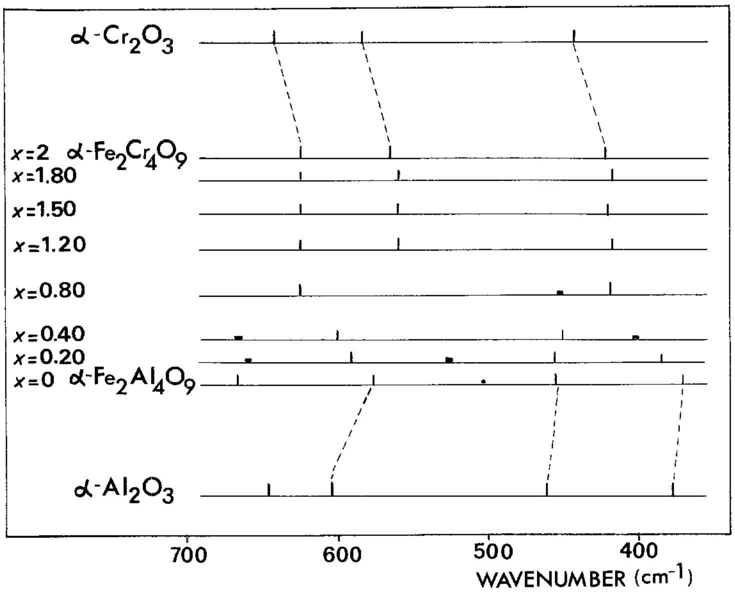

Figure 11 Vibrational behaviour of α-$(Fe_2Al_{4-2x}Cr_{2x})O_4$ rhombohedral phase after heating at 1200° C. The absorption band positions of α-Cr_2O_3 and α-Al_2O_3 are given for comparison.

7. T. YAMAGUCHI and T. KIMURA, *J. Amer. Ceram. Soc.* **59** (1976) 333.
8. A. ROUSSET, P. MOLLARD and A. GIRAUD, *C.R. Acad. Sci. Paris* **275** (1972) 709.
9. B. GILLOT, R. M. BENLOUCIF and F. JEMMALI, *J. Mater. Sci.* **19** (1984) 3806.
10. B. GILLOT, F. JEMMALI and A. ROUSSET, *J. Solid State Chem.* **50** (1983) 138.
11. A. ROUSSET, J. PARIS and P. GERMI, *Ann. Chim. Fr.* **7** (1972) 57.
12. A. ROUSSET and J. PARIS, *Bull. Soc. Chim. Fr.* (1972) 3729.
13. F. CHASSAGNEUX and A. ROUSSET, *J. Solid State Chem.* **16** (1976) 161.
14. B. GILLOT and J. F. FERRIOT, *J. Phys. Chem. Solids* **37** (1976) 857.
15. J. PREUDHOMME and P. TARTE, *Spectrochim. Acta* **A27** (1971) 1817.
16. P. TARTE, *ibid.* **A23** (1967) 2127.
17. M. I. BARATON and P. QUINTARD, *J. Molec. Struct.* **79** (1982) 337.
18. B. C. LIPPENS and J. H. DE BOER, *Acta Crystallogr.* **17** (1964) 1312.
19. V. A. USKAKOV and E. M. MOROZ, *React. Kinet. Catal. Lett.* **34** (1984) 113.

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