

Infrared Spectrum of Several Double Oxides with Corundum Structure Resulting from the Transformation of Lacunar γ Phases with a Spinel Structure

B. GILLOT AND F. BOUTON

Laboratoire de Recherches sur la Réactivité des Solides associé au CNRS, Faculté des Sciences Mirande, B.P. 138 21004 Dijon Cedex, France

AND F. CHASSAGNEUX

Laboratoire de Chimie Minérale, Université Claude Bernard, Lyon I, 43 boulevard du 11 Novembre 1918, 69621 Villeurbanne, France

AND A. ROUSSET

Laboratoire de Chimie des Matériaux Inorganiques, Université Paul Sabatier, Toulouse III, 118, route de Narbonne, 31000 Toulouse, France

Received July 24, 1979

When aluminum or chromium is substituted by Fe^{3+} ions in $\alpha\text{-Fe}_2\text{O}_3$, all the ir bands gradually shift toward high frequencies. Alternatively, for the α phases of type $(\text{Fe}_2\text{Cr}_{4-y}\text{Al}_y)\text{O}_9$ the transition occurs sharply for a composition y close to 2. For α phases substituted by $(\text{Fe}_{8-y}\text{Cr}_y)\text{O}_9$ -type chromium a linear variation of frequency with chromium content is observed. From ir data it has been shown that, under given temperature and time conditions, an α phase less rich in chromium than the initial product could be obtained by oxidizing iron chromite. The ir spectrum of the oxidation of pure magnetites the size of which is between 1400 and 15000 Å evolves versus the latter to yield either the $\gamma\text{-Fe}_2\text{O}_3$ or the $\alpha\text{-Fe}_2\text{O}_3$ phase which can be formed from $\gamma\text{-Fe}_2\text{O}_3$ or by direct oxidation of Fe_3O_4 .

Introduction

The stability of lacunar spinel γ phases resulting from the low-temperature oxidation (350°C) of Al- or Cr-substituted magnetites $(\text{Fe}^{2+}\text{Fe}_{\frac{3}{2}-x}^3M_x^{3+})\text{O}_4^{2-}$ ($0 < x < 2$; $M^{3+} = \text{Al}^{3+}, \text{Cr}^{3+}$) as well as solid solutions $(\text{Fe}^{2+}\text{Al}_{\frac{3}{2}-x}^3\text{Cr}_x^{3+})\text{O}_4^{2-}$ ($0 < x < 2$) (1-3) is above all governed by the Al or Cr substitution ratio x and the nature of the substituent (4, 5). All these lacunar spinels undergo crystal structure changes by rising temperature; in all cases it is the

transformation of a lattice of cubic symmetry into a rhombohedral lattice which is stable at high temperature. The phases that are richer in Al are the more stable since temperatures of about 900°C are required for the transformation $\gamma\text{-Fe}_2\text{Al}_4\text{O}_9 \rightarrow \alpha\text{-Fe}_2\text{Al}_4\text{O}_9$ and 700°C for the transformation $\gamma\text{-Fe}_2\text{Cr}_4\text{O}_9 \rightarrow \alpha\text{-Fe}_2\text{Cr}_4\text{O}_9$. In all cases those temperatures are far higher than those of the transformation $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ for which the temperature is about 400°C.

For the temperatures considered and for

sufficiently long oxidation times, the α -phase composition is the same as that of the γ phase. It has also been shown (6) that during the initial spinel oxidation, the passage of the intermediate γ phase is possible only if crystallite size is less than about 4000 Å. Above oxidation results directly in α phase. However, it should be noticed that during the oxidation of some systems of aluminates and ferrites—although a passage through one or several intermediate phases is also observed—the precipitation of corundum α -Al₂O₃ or hematite α -Fe₂O₃ is most often observed. Thus, for magnesium aluminates, the final stage is reached (α -Al₂O₃) only after prior precipitation followed by the occurrence and the transformation of one or several monoclinical phases (7, 8). For manganese aluminates first, a compound γ -(Mn,Al)₂O₃ forms with distorted spinel structure (9), which gradually becomes γ -Al₂O₃ by diffusion of manganese ions out of the previous phase, and α -Al₂O₃ in final phase. For mixed ferrites $M\text{Fe}_2\text{O}_4$ -Fe₃O₄ ($M = \text{Ni, Mg, Zn, Co}$) oxidation to α -Fe₂O₃ may also be, in some cases, preceded by the formation of a lacunar cubic phase γ -(Fe₂O₃)_{1-z}(MFe₂O₄)_z (10, 11) if the crystals are sufficiently small.

Following results by spectrometry for Al- or Cr-substituted magnetites and γ lacunar spinels (12) it was worthwhile to further investigate the α phases precisely resulting from transformation by raising the temperature of these γ lacunar phases and hence to see whether composition is not changed during precipitation.

Samples—Experimental

The techniques of preparation and characterization (TDA, X-ray analysis, specific area, chemical analysis, morphology) have already been quoted in Refs. (1-3). The products oxidized into γ phase of same composition and morphology as initial products are those obtained by oxidation

kinetic studies in thermobalance, i.e., under conditions such that the spinel structure is preserved (oxidation temperature less than 350°C and oxygen pressure 12 Torr). In all cases X-ray analysis has confirmed this structure so long as crystallites are sufficiently small (<4000 Å). The transformation into the α phase is simply achieved by heating, with air, to temperatures slightly above those of occurrence of the second exothermic phenomenon elsewhere exhibited by TDA (4, 5).

In the case of pure magnetites and to bring to its end a previous study (6) the crystallites were made to vary from 1400 to 15,000 Å so as to obtain not only the γ but also the rhombohedral α phase during oxidation. The magnetites termed (C), (D), (E), and (F) were 1400, 6000, and 15,000 Å, respectively. For magnetites (D), (E), and (F) the partial oxidation ratios θ ($0 < \theta < 1$) obtained in thermobalance (6) were also considered.

The spectra were recorded with a Beckman IR 4250 spectrometer over the range 1100-200 cm⁻¹. About 1 mg of sample was mixed and ground with 200 mg CsI before being pelleted under 160 bars.

Results and Discussion

1. Infrared Spectrum Evolution with Crystallite Size during Oxidation of Pure Magnetite

Earlier studies on the kinetics of oxidation in thermobalance have shown that this kinetics differs with the size of crystallites (6). The ir spectra of partially ($\theta < 1$) or totally oxidized ($\theta = 1$) products (Fig. 1) exhibit only the γ -Fe₂O₃ phase for crystals less than 5000 Å (magnetite C), and the rhombohedral α phase for crystals more than 10,000 Å (magnetite F); the large number of absorption bands for γ -Fe₂O₃ (C) results from a vacancy ordering on octahedral sites (4).

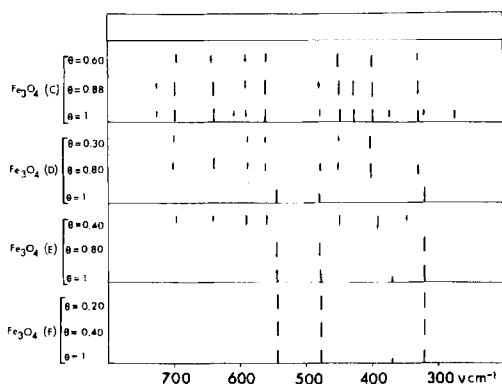


FIG. 1. Evolution of magnetite ir spectrum for different sizes during oxidation.

For sizes of intermediate crystallites Fe_3O_4 (D) and Fe_3O_4 (E) first the γ phase occurred during oxidation, then the α phase at the end of the reaction. For instance, for crystallites about 6000 \AA (Fe_3O_4 (D)) the ir spectrum shows that the γ phase remains until a conversion extent $\theta = 0.8$; beyond the rhombohedral α phase occurs. For Fe_3O_4 (F) the γ phase disappears much earlier, i.e., since, when $\theta > 0.40$, only the α phase occurs.

The results obtained by ir spectrometry thus confirm a previous study in thermogravimetry and X-ray analysis (6). Both phases γ and α do not seem to be able to coexist, the γ phase being transformed into the α phase as soon as stresses occur in the grain bulk.

2. Infrared Spectrum of α Rhombohedral Phases Obtained during Transformation of γ Lacunar Phases of Type $(Fe_{6-y}^{3+}M_y^{3+})O_9^{2-}$ and $(Fe_2^{3+}Cr_{4-y}^{3+}Al_y^{3+})O_9^{2-}$

Whereas the ir spectra of $\alpha-Fe_2O_3$, $\alpha-Al_2O_3$, and $\alpha-Cr_2O_3$ phases have already been published for those structures of corundum type (13, 14) no data are available in the literature on mixed phases of type $\alpha-(Fe_{6-y}M_y)O_9$ and $\alpha-(Fe_2Cr_{4-y}Al_y)O_9$. Also, whereas Raman and ir spectra are totally available for $\alpha-Al_2O_3$ and only partially for $\alpha-Cr_2O_3$ and $\alpha-Fe_2O_3$ nothing satisfactory

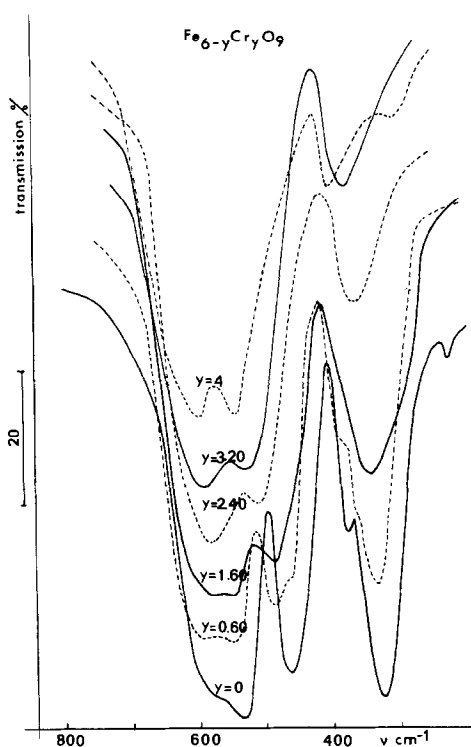


FIG. 2. Infrared spectra of solid solutions $\alpha-(Fe_{6-y}Cr_y)O_9$.

has been assigned for the vibrations of those structures.

(a) Infrared spectrum of phases $\alpha-(Fe_{6-y}M_y)O_9$ ($M^{3+} = Al^{3+}, Cr^{3+}; 0 < y < 4$). Figures 2 and 3 relate to α phases

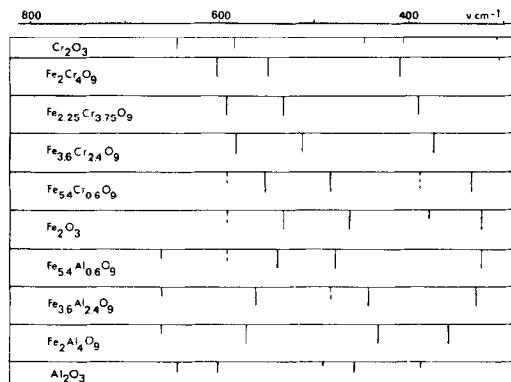


FIG. 3. Vibrational behavior. Evolution of absorption bands for solid solutions $\alpha-(Fe_{6-y}Cr_y)O_9$ and $\alpha-(Fe_{6-y}Al_y)O_9$.

obtained by transformation, between 400 and 700°C, of Cr-substituted γ phases and, between 400 and 900°C, of Al-substituted γ phases. A regular evolution of the spectra is noticed when passing on the one hand from α -Fe₂O₃ to α -FeCr₄O₉ and, on the other, from α -Fe₂O₃ to α -FeAl₄O₉, substitution by chromium or aluminum causing all the bands to shift toward high frequencies. Figure 4 contains the position of the absorption bands of the α phases whose composition changes from that of α -Fe₂O₃ to that of α -FeCr₄O₉, the chromium composition variation being the ordinate. The bands move linearly with chromium content. In addition it has been established that by extending the dotted lines in Fig. 4 until the composition of α -Cr₂O₃ ($y = 6$) the following values are obtained for the three sharpest absorption bands of this compound: 639, 582, and 440 cm⁻¹, which are very close to the values reported by Preudhomme (14), which are 643, 583, and 444 cm⁻¹; respectively. For the α phases whose composition varies from α -Fe₂O₃ to α -Al₂O₃ and passing through α -Fe₂Al₄O₉ the previous relation between band position and aluminum content is far less evident. Indeed, if considering as previously the linear relation for the highest-frequency band of α -Fe₂O₃ passing through every

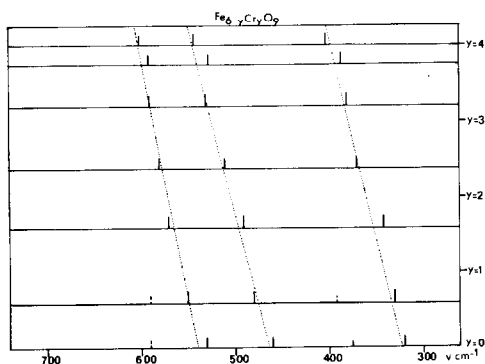


FIG. 4. Displacement of the absorption bands of solid solutions α -(Fe_{6-y}Cr_y)O₉ versus chromium content.

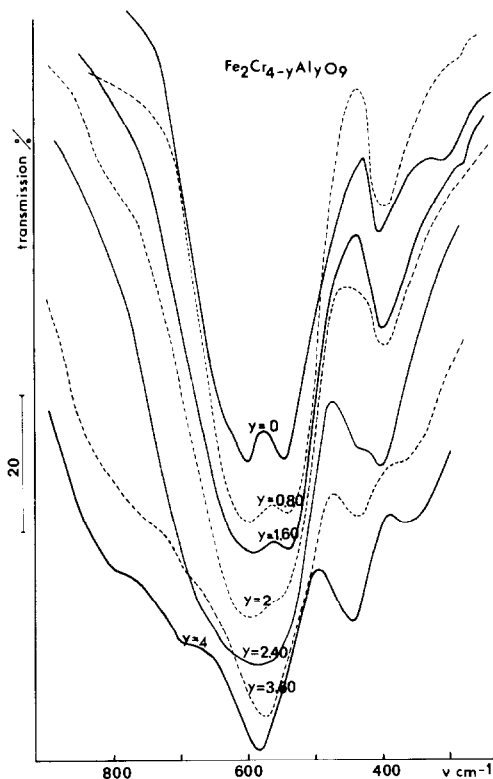


FIG. 5. Infrared spectra of solid solutions α -(Fe₂Cr_{4-y}Al_y)O₉.

intermediate composition, 596 cm⁻¹ is obtained for the α -Al₂O₃ band, a value which is more in agreement with that of the second band frequency of high intensity reported by Preudhomme (602 cm⁻¹) than with that of the first band (645 cm⁻¹). This frequency difference, when light atoms such as aluminum are substituted by heavier atoms like chromium or iron, seems to be rather common since Preudhomme and Tarte (15) and the authors (12) had already observed such an anomaly for spinel solid solutions of type M Cr₂O₄- M Al₂O₄ ($M = \text{Fe, Zn, Cd, Co}$). This anomaly is shown still better in the case of solid solutions which are studied below.

(b) Infrared spectrum of phases α -(Fe₂³⁺+Al_y³⁺+Cr_{4-y}³⁺)O₉²⁻ ($0 < y < 4$). Figures 5 and 6

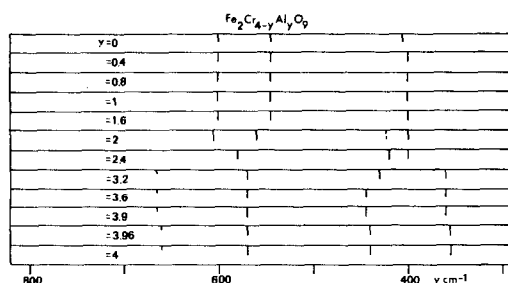
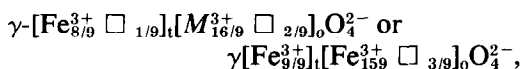


FIG. 6. Vibrational behavior. Evolution of absorption bands for solid solutions $\alpha\text{-(Fe}_2\text{Cr}_{4-y}\text{Al}_y\text{O}_9\text{)}$.

show, respectively, the ir spectrum and the position of the absorption bands of α phases obtained by the transformation, between 700 and 900°C, of the chromium- and aluminum-substituted γ phases. The spectra obtained look like that of either $\alpha\text{-FeAl}_4\text{O}_9$ or $\alpha\text{-FeCr}_4\text{O}_9$ depending on whether the phase is richer in aluminum than in chromium or inversely. The spectrum of $\text{Fe}_2\text{Al}_{2.4}\text{Cr}_{1.6}\text{O}_9$ is intermediate.

3. Discussion

An earlier paper (16) showed that the process proposed by Kachi *et al.* (17) for the restacking of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ may be assumed valid for all substituted magnetites. If the beginning of that process does not involve vacancies (applicable to Fe_3O_4 as well as $\gamma\text{-Fe}_2\text{O}_3$), on the contrary the final process consisting of transforming the "kagome" lattices formed at the beginning of the transformation into the "honeycomb" lattices of the final rhombohedral phase must take those vacancies into account. Indeed one-ninth of the lattice points must be occupied by vacancies of structural formulas:



depending on whether the vacancies are distributed between the tetrahedral and octahedral sites (e.g., $\gamma\text{-(Fe}_{1/3}^{3+}\text{M}_{2/3}^{3+})_2\text{O}_3^{2-}$) or are all on octahedral sites (e.g., $\gamma\text{-Fe}_2\text{O}_3$). Under these conditions some metallic ions will

cooperatively migrate to neighboring positions and the "honeycomb" configuration is set up. Let us notice, however, that the corundum structure is a distorted form of the idealized arrangement of hexagonally close-packed O^{2-} ions with M^{3+} ions regularly distributed in two-thirds of the octahedral holes. Thus, it may be regarded as a structure of linked MO_6 octahedra (Fig. 7a). If attention is focused on anions these lie on twofold axes coordinated by four cations in a distorted tetrahedron (Fig. 7b) so that it may be predicted that one direction of displacement of the oxygens (d_2) must be less restrained than either the other perpendicular displacement (d_1) or the axial displacement (a). One vibration involving (d_2) is predicted to appear in each of the A_{2u} , E_u , and E_g modes, these being already identified at frequencies between 400 and 450 cm^{-1} in Al_2O_3 and Cr_2O_3 , decreasing to around 300 cm^{-1} in Fe_2O_3 (18). In $\alpha\text{-(Fe}_{6-y}\text{M}_y\text{O}_9\text{)}$ -type compounds this vibration occurs between 300 and 420 cm^{-1} , and between 350 and 420 cm^{-1} for $\alpha\text{-(Fe}_2\text{Al}_y\text{Cr}_{4-y}\text{O}_9\text{)}$ -type compounds. As for higher-frequency bands (perpendicular displacement d_1 and axial displacement a), which must necessarily be assigned to the vibrations of the octahedra lattice of MO_6 type, they are found in the same absorption range (550–650 cm^{-1}) as the high-frequency bands of normal II–III spinels and are in

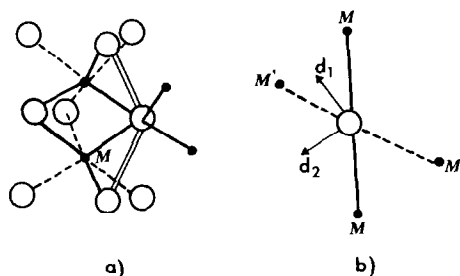


FIG. 7. Corundum structure. (a) Coordination of M^{3+} . (b) Coordination of O^{2-} : taking O as lying on the plane of the paper, R lies above and R' below the plane; the twofold axis through oxygen is perpendicular to the plane. Displacement d_1 is stronger than d_2 .

very good agreement with the absorption ranges of several groups of "condensed" octahedra (this notation has been reported by Tarte (19) and corresponds to coordinated groups interlinked by common oxygen atoms to form chains, sheets, or tridimensional networks) reported by Preudhomme and Tarte (15). This correspondence is well illustrated in Fig. 8 showing an easy comparison of the absorption range for different condensed octahedra $M^{III}O_6$ in nonspinel compounds and those for spinel compounds, γ lacunar phases, and the corresponding rhombohedral phases. This confirms earlier results (12) where the two, sharp high-frequency bands ν_1 and ν_2 of the initial and oxidized spinels had been attributed to the vibrations of octahedral groups. In addition, the comparison of the above results for solid solutions rich in iron with those for slightly aluminum- or chromium-substituted magnetites is also interesting—in both cases, the higher frequencies are about 100 cm^{-1} less as similar frequencies of aluminum- or chromium-rich compounds. Figure 8 shows that in all cases the lower frequencies are related to the FeO_6 groups, those low frequencies probably resulting from a weakening in the cation–oxygen bond.

It has also been reported (18) that vibrations involving cations moving relative to each other (absorption bands occur for low-

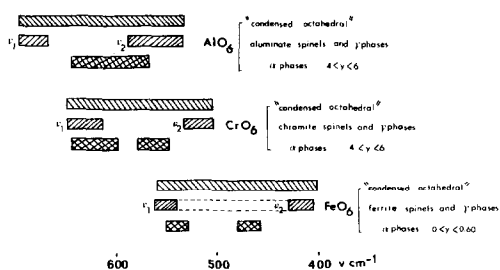


FIG. 8. Analogy between absorption ranges of AlO_6 , CrO_6 , and FeO_6 of "condensed" octahedra in nonspinel compounds and frequencies ν_1 and ν_2 for spinels, lacunar phases, and rhombohedral α phases.

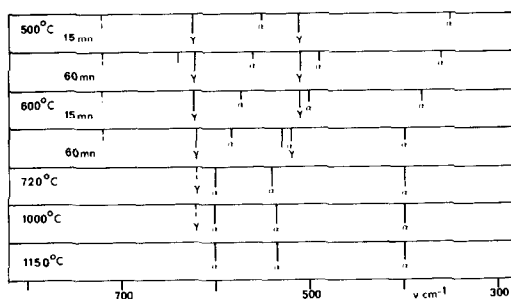


FIG. 9. Identification of α and γ phases of oxidized iron chromite for various times and temperatures.

est frequencies) show the expected drop in frequency from Al to Cr. The decrease in all vibrations of Fe_2O_3 compared with those of Cr_2O_3 is a common feature of ferric compounds.

4. Evolution of the IR Spectrum of $\gamma-(Fe^{3+}Cr_4^{3+}O_9^{2-})$ under Different Treatment Conditions

It has been shown above that the sharpest three bands of α phases whose composition changes from $\alpha-Fe_2O_3$ to $\alpha-FeCr_4O_9$ move linearly with Cr content. Thus, when the spectrum of an unknown, $\alpha-Fe_{6-y}Cr_yO_9$ -type product is available, the latter may be identified referring to Fig. 4. This identification is made easier due to the fact that γ phases only yield two absorption bands, situated in the range $500\text{--}600\text{ cm}^{-1}$ (as for spinels), thus largely different from the third absorption band of α phases which is situated around 400 cm^{-1} .

Figure 9 shows the evolution of the absorption bands of $\alpha-Fe_2Cr_4O_9$, which is obtained for various times and transformation temperatures of $\gamma-Fe_2Cr_4O_9$. For transformation temperatures not exceeding 600°C the γ -phase bands are observed and, by comparison with Fig. 4, the bands of an α phase, the composition of which evolves. We thus pass from the composition of $\alpha-(Fe_{4.4}Cr_{1.6}O_9)$ (transformation for 15 min at 500°C) to that of $\alpha-(Fe_4Cr_2O_9)$ (transformation for 60 min at 500°C), then that of $\alpha-$

($\text{Fe}_3\text{Cr}_3\text{O}_9$) (transformation for 15 min at 600°C), and finally that of $\alpha\text{-Fe}_2\text{Cr}_4\text{O}_9$ from 600°C for 1 hr. For temperatures above 600°C the bands corresponding to phase $\alpha\text{-}(\text{Fe}_2\text{Cr}_4\text{O}_9)$ are observed with only traces of γ .

This information conforms to that obtained in X-ray analysis (F. Chassagneux, private communication). The α phase thus occurs with a composition less rich in chromium than the initial product; then as temperature rises and transformation time increases, this α phase is enriched in chromium to yield finally $\alpha\text{-}(\text{Fe}_2\text{Cr}_4\text{O}_9)$ which is that of the compound corresponding to the initial phase. Hence it must be concluded that meanwhile the Cr content of the γ phase evolves inversely.

Conclusion

The ir investigation, in the range $800\text{--}200\text{ cm}^{-1}$, already carried out for Al- and Cr-substituted magnetites as well as the lacunar γ phases has been extended to the α rhombohedral phases from which they derive by high-temperature transformation. All bands shift toward high frequencies when Al or Cr is substituted by iron in $\alpha\text{-Fe}_2\text{O}_3$. Concerning the α phases substituted by Al and Cr and the α phases strongly substituted by Al or Cr, both sharp bands in the range $550\text{--}650\text{ cm}^{-1}$ (which must necessarily be assigned to the vibrations of the octahedra lattice) recall, in their profile and their position, both high-frequency bands of normal spinels II–III. The analogy is also valid for α phases slightly substituted to Al or Cr for which, as for slightly substituted spinels (inverse spinels II–III), a decrease of about 100 cm^{-1} in frequency is observed with far more diffuse bands.

The ir spectra of the α phases substituted by Cr are particularly interesting. As the shift of the bands is regular with Cr content it has been possible, by comparison, to identify rapidly an unknown product. It has

thus been shown that under given time and temperature conditions, the composition of the α phase may be different from that of the γ phase from which it is derived with, in particular, a Cr content less than that of the initial phase. Such a behavior, if it exists, is more difficult to show by ir for similar compounds substituted by Al because of a greater inaccuracy in the determination of the position of the absorption bands and a lack of linearity between those bands' position and the Al content.

Finally in the case of magnetite oxidation (size between 1400 and $15,000\text{ \AA}$) ir spectrometry proved an interesting method to identify the phases present. This method had already proved useful to solve problems such as ordering or lack of ordering of vacancies in γ phases (12).

References

1. B. GILLOT, J. TYRANOWICZ, AND A. ROUSSET, *Mater. Res. Bull.* **10**, 775 (1975).
2. B. GILLOT, J. F. FERRIOT, G. DUPRE, AND A. ROUSSET, *Mater. Res. Bull.* **11**, 843 (1976).
3. B. GILLOT, F. BOUTON, F. CHASSAGNEUX, AND A. ROUSSET, *Ann. Chim. Fr.* **4**, 115 (1975).
4. A. ROUSSET, J. PÄRIS, AND P. MOLLARD, *Ann. Chim. Fr.* **7**, 119 (1972).
5. F. CHASSAGNEUX AND A. ROUSSET, *J. Solid State Chem.* **16**, 161 (1976).
6. B. GILLOT, A. ROUSSET, AND G. DUPRE, *J. Solid State Chem.* **25**, 263 (1978).
7. H. SAAFELD AND H. JAGODZINSKI, *Z. Kristallogr.* **109**, 87 (1957).
8. M. H. LEWIS, *Phil. Mag.* **20**, 985 (1969).
9. E. H. L. J. DEKKER, AND G. D. RIECK, *Rev. Int. Hautes Temp. Refract.* **11**, 187 (1974).
10. T. YAMAGUCHI AND T. KIMURA, *J. Amer. Ceram. Soc.* **59**, 333 (1976).
11. A. ROUSSET, P. MOLLARD, AND A. GIRAUD, *C.R. Acad. Sci. Paris* **275**, 709 (1972).
12. B. GILLOT, F. BOUTON, J. F. FERRIOT, F. CHASSAGNEUX, AND A. ROUSSET, *J. Solid State Chem.* **21**, 375 (1977).
13. S. P. S. PORTO AND R. S. KRISHNAN, *J. Chem. Phys.* **47**, 1009 (1967).
14. J. PREUDHOMME, Thèse, Liège (1970).
15. J. PREUDHOMME AND P. TARTE, *Spectrochim. Acta Part A* **27**, 1817 (1971).

16. B. GILLOT, *Mater. Res. Bull.* **13**, 783 (1978).
17. S. KACHI, K. MOMIYAMA, AND S. SHIMIZU, *J. Phys. Soc. Japan* **18**, 106 (1963).
18. V. C. FARMER, "The Infrared Spectra of Minerals," London (1974).
19. P. TARTE, *Spectrochim. Acta Part A* **23**, 2127 (1967).