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COMPARATIVE THERMAL TRANSFORMATIONS OF SYNTHETIC Fe-Mn GLYCERATE (ALKOXIDES)

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Synthetic iron-manganese glycerates with compositions corresponding to different molar ratios of Fe:Mn, contain large amounts of H_2O (up to 22%). Heating in air at ~270°C produces a hydrated, disordered Mn-ferrite structure (jacobsite), as shown by XRD and IR spectroscopy. At this temperature no alkoxide groups are detected. TG curves show 45.6% to ~54% weight losses at 290°C, with a sharp loss from 270° to 290°C for all samples, attributed mostly to the Curie transition of $MnFe_2O_4$. Further heating of each sample at ~670°C results in a well-crystallized hematite and variable amounts of bixbyite. At this stage no H_2O is left. Further calcination at ~1050°C gives qualitatively the same products as at 670°C. Colour changes occur during the heating process. In admixtures of goethite with $MnCO_3$ or pyrolusite the main difference from the counterpart alkoxide is shown after heating at 270°C, when the Fe-Mn mineral mixture produces mostly protohematite (disordered hematite) instead of disordered jacobsite resulting from the alkoxides.

Keywords: iron-manganese glycerates, metal-glycerate complexes, TG

Introduction

The preparation of metal–glycerate complexes as well as metal-substituted glycerate (i.e. Al-substituted iron alkoxide) has been reported [1, 2]. Recently a combined Fe-Mn glycerate has been synthesised by thermal reaction of glycerol (at ~265°C) with iron and manganese minerals, XRD patterns indicating formation of a crystalline, single-phase, mixed alkoxide [3]. The present paper describes structural and thermal properties of Fe-Mn glycerates heated at increasing temperatures and compares these with properties of equivalent admixtures of synthetic goethite with $MnCO_3$ or pyrolusite (β-MnO_2) submitted to the same heat treatments. When Fe-Mn alkoxides or counterpart admixtures of Fe and Mn starting materials are fired in air distinct products may result, characterized by changes in structure, particle size and colour. The nature of the resulting products depends on initial composition, granulometry and heating conditions of the starting materials. It is known that changes in particle size of Mn-ferrite may influence the pigmenting and magnetic properties of such materials [4]. X-ray

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powder diffraction (XRD), infrared absorption spectroscopy (IR) and thermogravimetric analysis (TG) have been used in this investigation.

Experimental

Synthetic iron-manganese glycerates prepared at different Fe:Mn molar ratios, namely 2:1, 1:1 and 4:1 [3], were gradually and progressively heated in a furnace at 270°, 670° and 1050°C. In addition, 2:1 mixtures of goethite mixed mechanically with $MnCO_3$ or with finely divided pyrolusite, keeping the Fe:Mn ratio at ~2:1, were submitted to the same heating programme. After each heating interval, the products were examined by XRD using a Philips 1730 diffractometer and by IR spectroscopy using a Perkin Elmer 283 spectrophotometer. Identical instrumental settings were employed for examination of each product. Surface areas (BET) of starting materials and heated products were determined with a Quantachrome apparatus. The Fe-Mn glycerates (alkoxides) were submitted to TG, carried out on 7.5 mg samples in a Dupont model TG 951, in flowing air, from room temperature to ~1000°C, at a heating rate of 10 deg·min^{-1}. Weight losses at 105°C were determined separately by heating each sample for 16 hours.

Results and discussion

Comparative gradual heating of starting materials in the furnace

Figure 1a shows the X-ray powder patterns of a 2:1 Fe-Mn glycerate, which agrees with that of a single-phase mixed alkoxide. Previous studies of this alkoxide suggested that structural changes occured at about 270° and 670°C [3]. Figures 1b, c and d show XRD patterns of the 2:1 Fe-Mn glycerate after successive heating, in air, at 270°, 670° and 1050°C, respectively. IR spectra of the same products are given in Fig. 2, which show OH absorption bands (at 3400 and 1600 cm^{-1}) of the alkoxide after heating at 270°C but not at higher temperatures; the organic groups of the alkoxide appear to have been removed during the first heating stage (Fig. 2a and b). Other structural developments during heating are seen in the 1200 to 250 cm^{-1} region. XRD and IR spectroscopy results indicate that after heating at 270°C the alkoxide is transformed into a disordered Mn-ferrite structure (jacobsite) with high water content. XRD shows that further heating at 670° and 1050°C resulted in well crystallized hematite and variable amounts of bixbyite, Mn_2O_3. The IR spectra show no OH groups remaining after heating at 670°C (Fig. 2c). The IR spectrum after heating at 1050°C (not shown in the figure) is similar to that at 670°C, but the absorption bands are less intense. The olive-grayish colour of the starting alkoxide became dark-reddish after heating at 270°C and very dusky-red after 1050°C.

Table 1 lists the thermal transformation products of Fe-Mn alkoxides from mixtures of starting materials in different proportions. The table shows that,

qualitatively, the same products are obtained after each heating interval, regardless of the initial Fe:Mn ratio in the alkoxide. Bixbyite is not detected by XRD

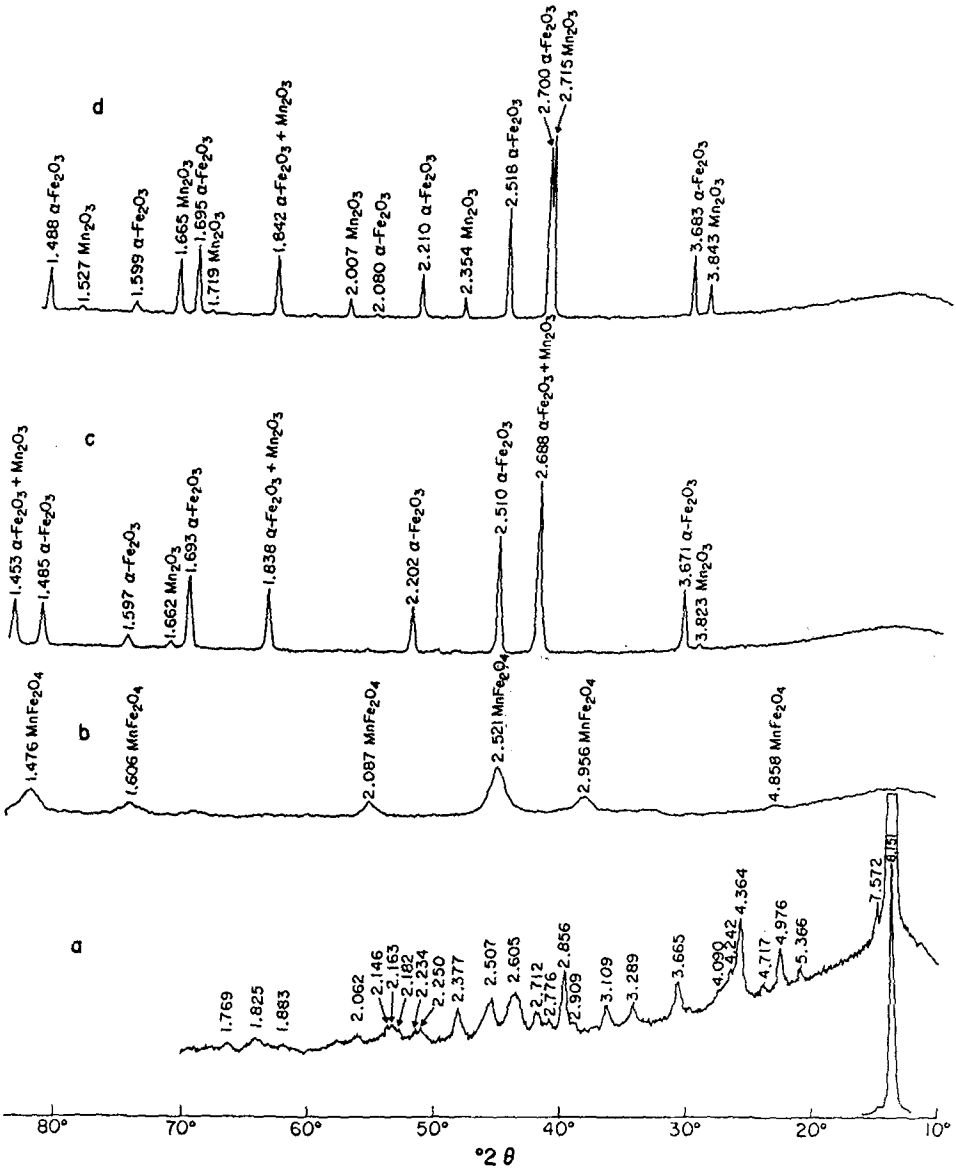

Fig. 1 X-ray diffraction patterns (random powders) of: a) Fe-Mn glycerate (2:1); b) sample a) heated at 270°C; c) sample b) heated at 670°C; d) sample c) heated at 1050°C. Spacings in Å FeK_α radiation

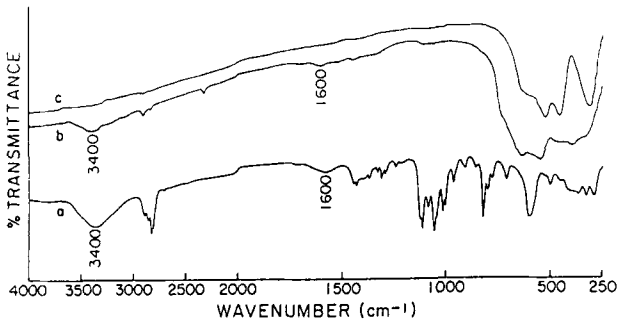

Fig. 2 IR absorption spectra (0.25% CsI disks) of: a) Fe-Mn glycerate (2:1); b) sample a) heated at 270°C; c) sample b) heated at 670°C

Table 1 Products obtained by gradual heating of Fe-Mn alkoxides and mixtures of goethite + Mn minerals

Starting materials			Products		
			270°C	670°C	1050°C
Alkoxides		From			
50%		50%	$MnFe_2O_4$*	α–Fe_2O_3 +	α–Fe_2O_3 +
$MnCO_3$	+	α–FeOOH		Mn_2O_3	Mn_2O_3
Alkoxides		From			
20%		80%	$MnFe_2O_4$*	α–Fe_2O_3	α–Fe_2O_3
$MnCO_3$	+	α–FeOOH			
Alkoxides		From			
35%		65%	$MnFe_2O_4$*	α–Fe_2O_3 +	α–Fe_2O_3 +
$MnCO_3$	+	α–FeOOH		Mn_2O_3	Mn_2O_3
or					
β–MnO_2					
35%		65%	α–Fe_2O_3*	α–Fe_2O_3 +	α–Fe_2O_3 +
$MnCO_3$	+	α–FeOOH		Mn_2O_3	Mn_2O_3 +
					Mn_3O_4
35%		65%	α–Fe_2O_3 +	α–Fe_2O_3 +	α–Fe_2O_3 +
β–MnO_2	+	α–FeOOH	β–MnO_2	Mn_2O_3	$MnFe_2O_4$

*HOH-containing structures

after >670°C in the alkoxide prepared from 20% $MnCO_3$ + 80% goethite, because of the small amount of Mn mineral in the composition of the starting material. Table 1 also gives the thermal transformations of admixtures of goethite with $MnCO_3$ or pyrolusite. The main difference from the counterpart alkoxide is shown after heating at 270°C, when the Fe-Mn mineral admixtures produce mostly protohematite (disordered hematite) instead of the disordered jacobsite resulting from Fe-Mn alkoxides heated at this temperature. Protohematite was partly characterized by a sharp decrease in relative intensities of the strong hematite peak at ~2.70 Å and by peak broadenings [5]. Protohematite is further crystallized to hematite by heating at 670°C. There is also some difference after heating at 1050°C when, beside hematite and bixbyite resulting from alkoxides, small amounts of Mn_3O_4 or (anhydrous) $MnFe_2O_4$ are eventually formed from the admixtures.

Table 2 TG weight losses and surface areas (S_o) shown by alkoxides prepared from goethite + $MnCO_3$ in different proportions

Fe:Mn molar ratios in alkoxides	Temperature/ °C	Weight loss/ %	S_o / $m^2 \cdot g^{-1}$
	105*	11.38	26.0
	270	12.93	26.0
2:1	290	45.58	
	670	44.22	<1
	1050	42.86	<1
	105*	20.00	21.5
	270	26.00	23.0
1:1	290	54.67	
	670	53.33	<1
	1050	52.00	<1
	105*	22.30	27.0
	270	25.68	28.0
4:1	~290	54.73	
	670	53.38	<1
	1050	52.03	<1

* Determined by heating at 105°C for 16 h

The X-ray results for admixtures of goethite with pyrolusite and with $MnCO_3$ heated at 270°C are shown in Fig. 3a and 3b respectively and in Table 1. When pyrolusite is present in the initial admixture, most of this pyrolusite remains after heating at 270°C, whereas goethite is transformed into protohematite at this

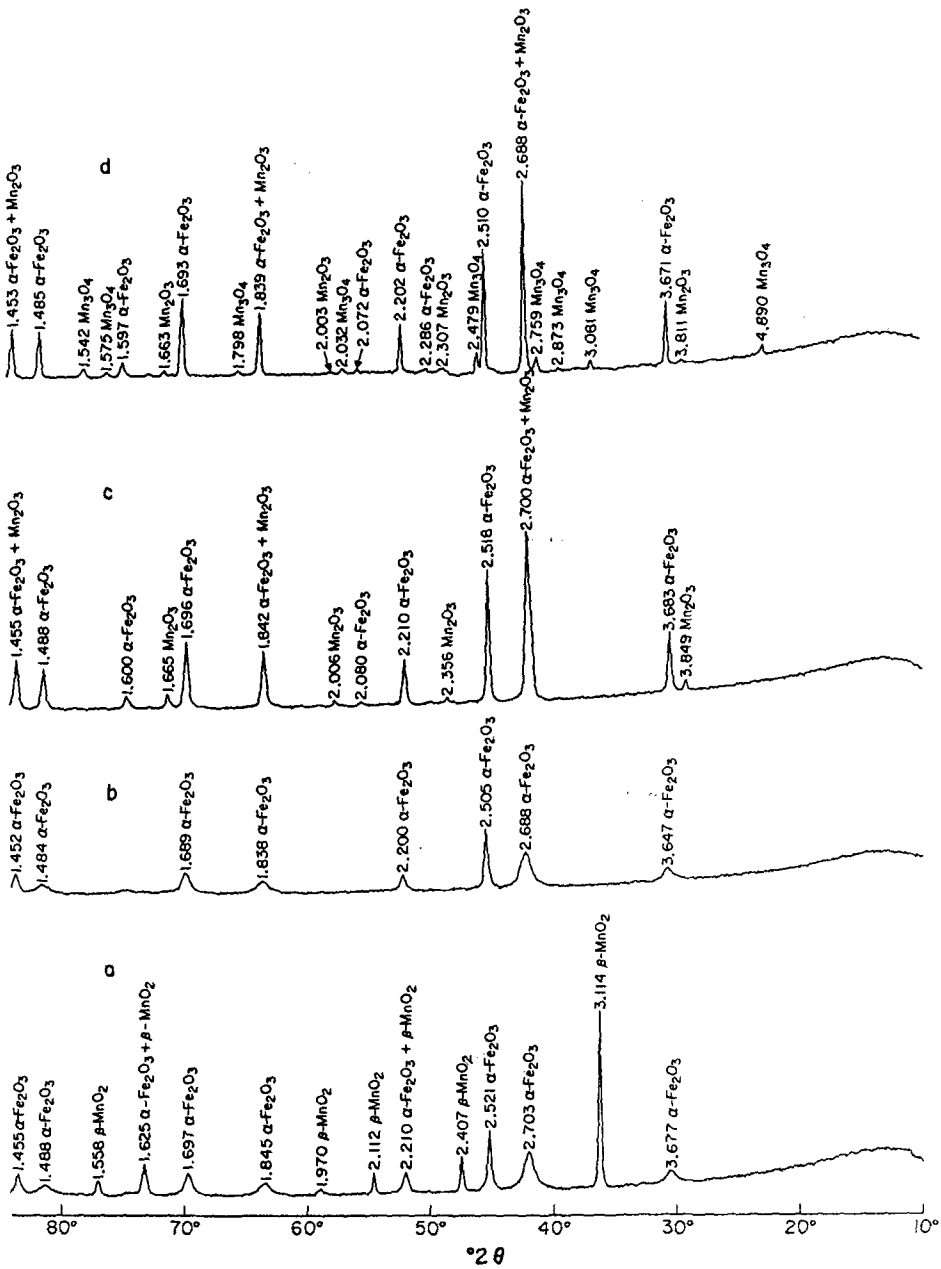

Fig. 3 X-ray diffraction patterns of admixtures of: a) goethite + pyrolusite (2:1 ratio) heated at 270°C; b) goethite + $MnCO_3$ (2:1 ratio) heated at 270°C; c) sample b) heated at 670°C; d) sample c) heated at 1050°C

temperature. Otherwise, when crystalline $MnCO_3$ is a component of the initial admixture, only protohematite is detected after heating at 270°C, as shown by XRD and IR spectroscopy. This means that most of the manganese carbonate (35% $MnCO_3$) of the starting admixture is decomposed into a non-crystalline phase. The nature of the products obtained at 270°C (Table 1) and related phases are being further investigated. The products obtained after heating admixtures of goethite with Mn minerals at higher temperatures, especially at 1050°C, depend not only on the initial composition of the admixtures but also on the heating conditions.

Thermogravimetric analysis of Fe-Mn alkoxides

The TG curve of the 2:1 Fe-Mn glycerate (Fig. 4) shows three main weight losses, at about 100°, 270° and 290°C. The 12.93% weight loss at 270°C represents removal of organic groups from the glycerate and a partial dehydroxylation. Once disordered jacobsite has been formed, the sharp loss from 270° to 290°C is attributed to transition at the Curie temperature, which is also shown by $MnFe_2O_4$ prepared by standard ceramic techniques [6]. At 290°C the Tg curve indicates a 45.58% total weight loss. Thereafter, small relative weight gains, namely to 44.22% and 42.86% are observed at 670° and ~1000°C respectively (Fig. 4). Weight losses of the 2:1 Fe-Mn alkoxide together with weight losses of the 1:1 and 4:1 glycerates are listed in Table 2. The latter two Fe-Mn alkoxide preparations both show a similar trend on heating to the 2:1 Fe-Mn alkoxide, but they give higher values at all temperatures. The weight losses at 105°C listed in this table were determined separately, by heating for 16 hours. These weight losses, varying from 11.38% to 22%, represent less tightly bonded HOH groups, as IR spectra (employing water-free CsI as matrix) of samples heated at 105°C (and at 270°C) still show the 3400 and 1600 cm^{-1} bands in the structure of each Fe-Mn alkoxide.

Table 2 also gives the surface areas (BET) of the three Fe:Mn alkoxides after each heating stage. For any alkoxide the initial surface area does not change until

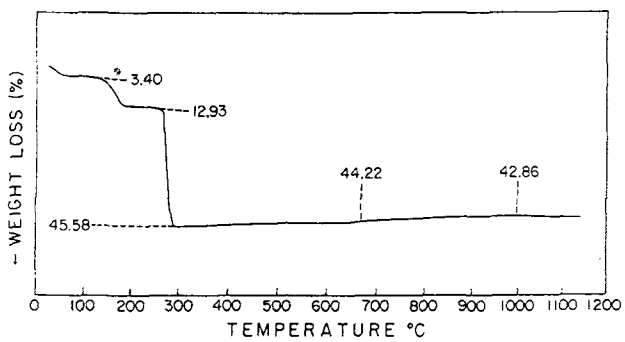

Fig. 4 TG curve (in flowing air) of Fe-Mn glycerate (2:1) prepared from goethite + $MnCO_3$

270°C. On further heating 670° and 1050°C, when OH groups are removed, the surface areas drop sharply (from > 20 to <1 m^2/g) indicating a particle-size increase during the structural transformations taking place at high temperature.

Conclusions

a) A disordered spinel structure, $MnFe_2O_4$, is invariably produced by heating any Fe-Mn glycerate in air at 270°C.

b) Fe-Mn glycerates contain large amounts of water (up to 22%). The OH groups are partially retained after heating at 270°C but are completely removed at 670°C, when Mn ferrite is transformed into bixbyite and hematite.

c) TG results show large weight losses between 270° and 290°C for all alkoxides, which are attributed to the Curie transition of $MnFe_2O_4$.

d) When admixtures of goethite with $MnCO_3$ and with pyrolusite are heated at 270°C, the resulting products are protohematite (disordered hematite) and protohematite + pyrolusite, respectively, instead of the disordered jacobsite structure obtained from Fe-Mn alkoxides heated at this temperature.

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References

1 E. W. Radoslovich, M. Raupach, P. G. Slade and R. M. Taylor, Aust. J. Chem., 23 (1970) 1963.
2 E. Mendelovici, A. Sagarzazu and R. Villalba, Thermochim. Acta, 107 (1986) 75.
3 E. Mendelovici, R. Villalba and A. Sagarzazu, J. Mater. Sci. Lett. 9 (1990) 28.
4 M. A. Denecke, W. GunBer, G. Buxbaum and P. Kuske, Mat. Res. Bull., 27 (1992) 507.
5 Sh. Yariv and E. Mendelovici, Applied Spectroscopy, 33 (1979) 410.
6 J. H. Boy and G. P. Wirtz, in L. C. Dufour et al. (eds.), Surfaces and Interfaces of Ceramic Materials, Kluwer Academic Publishers, 1989, p.691.

Zusammenfassung — Synthetische Eisen-Manganglycerate mit Zusammensetzungen mit unterschiedlichen Fe:Mn-Verhältnissen enthalten eine große Menge Wasser (bis 22 %). Wie Röntgendiffraktion und IR-Spektroskopie zeigen, entsteht beim Erhitzen an Luft bei etwa 270°C eine hydratierte, fehlgeordnete Mn-Ferrit-Struktur (Jacobsit). Bei dieser Temperatur werden keine Alkoxidgruppen festgestellt. Die TG-Kurven zeigen einen 45.6-54%-igen Gewichtsverlust bei 290°C, mit einem scharfen Verlustpeak zwischen 270° und 290°C für alle Proben, meist charakterisiert durch eine Curie-Umwandlung von $MnFe_2O_4$. Ein weiteres Erhitzen aller Proben ergibt bei etwa 670°C gutkristallisiertes Hämatit und verschiedene Mengen Bixbyit. An dieser Stelle wird kein Wasser zurückgelassen. Ein weiteres Kalzinieren bei etwa 1050°C liefert qualitativ die gleichen Produkte wie bei 670°C. Während des Erhitzungsvorganges verändern sich die Farben. In Gemischen von Goethit mit $MnCO_3$ oder Pyrolusit zeigt sich der Hauptunterschied nach Erhitzen bei 270°C, wenn das Fe-Mn-Mineralgemisch anstelle des fehlgeordneten Jacobsit hauptsächlich Protohämatit (fehlgeordnetes Hämatit) ergibt.