

*Short Communications*

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**THERMAL TREATMENTS OF Fe–Mn ALKOXIDE  
OF GLYCEROL  
Infrared absorption and emission spectroscopy**

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**Abstract**

Synthetic Fe–Mn alkoxide of glycerol samples are submitted to controlled heating conditions and examined by IR absorption spectroscopy. On the other hand, the same sample is studied by infrared emission spectroscopy (IRES), upon heating *in situ* from 100 to 600°C. The spectral techniques employed in this contribution, especially IRES, show that as a result of the thermal treatments ferromagnetic oxides (manganese ferrite) are formed between 350 and 400°C. Some further spectral changes are seen at higher temperatures.

**Keywords:** *in situ* infrared emission spectroscopy, iron-manganese alkoxide of glycerol, thermal treatments

**Introduction**

Crystalline, monophasic multimetal alkoxides of glycerol have been prepared by a thermal reaction between glycerol and mixtures of goethite,  $\alpha$ -FeOOH (as source of iron)+manganese oxide or manganese carbonate [1] and between glycerol and mixtures of goethite+cobalt carbonate [2]. The general formula calculated for these heterometal alkoxides is  $(C_3H_5O_2)_nA_xB_y$ , where  $A=Fe$ ,  $B=Mn$  or  $Co$ ,  $n$  may be 4 or 5 and the  $x/y$  ratios correspond approximately to the  $A/B$  ratios in the initial mixtures. Controlled heating of multimetal alkoxides is one of the methods to form these kind of multimetal ferromagnetic oxides and related products [3, 4]. The properties of the

ferromagnetic oxides, which have inverse spinel structures, are improved in comparison to similar products obtained by classical ceramic methods. Synthetic Fe–Mn alkoxides with variable Fe:Mn ratios and resulting thermoproducts have been characterised by surface and chemical analysis, X-ray diffraction (XRD), infrared absorption spectroscopy (IR) and by thermogravimetry (TG) [1, 3], the latter methods indicating that the transition of the alkoxides into correspondent oxides took place at about 300°C, in air.

In the present contribution we study the samples heated in the furnace until about 290°C, both in air and in nitrogen atmospheres, by IR absorption spectroscopy. As more information is needed on the characteristics of the products resulting in the intermediate stages of heating, we use in this contribution *in situ* emission infrared analysis (IRES) in various stages of heating the Fe–Mn alkoxide sample. As the IR absorption or transmittance examination in this case can give only a limited information on the heating process, the employment of the IRES *in situ* method may improve that information.

The IRES technique has been successfully employed in many fields where low transmitting, opaque solids or thin films on opaque substrates are formed or destroyed during experimental treatments and where the transmittance technique can be a limiting factor [5].

## Experimental

### *Materials*

Iron-manganese alkoxides of glycerol were synthesized by the reaction of powdered mixtures of synthetic goethite+manganese carbonate with glycerol at reflux temperature [1]. The amounts of the mixture components were calculated to correspond to a Fe:Mn stoichiometric ratio=2:1. The resulting products were heated in a controlled furnace at about 290°C (for 8 h) in air. The same products were also heated in the furnace at 290°C in a dynamic nitrogen atmosphere.

### *Instrumentation*

The alkoxide of glycerol sample and the solids resulting from the controlled heatings in the furnace were examined by infrared absorption spectroscopy (0.25% CsI disks) using a Perkin Elmer 283 spectrophotometer in the spectral range 4000–200 cm<sup>-1</sup>.

The Fe–Mn alkoxide was also investigated by means of the infrared emission spectroscopy (IRES) method, where the alkoxide powder was progressively heated at different temperatures, *in situ*, employing a FT-IR Nicolet Nexus instrument, with a MCT detector and an IRES attachment. Spectra were calculated using an Omnic 5.1 program and transformed by a Spectracalc software package Grams.

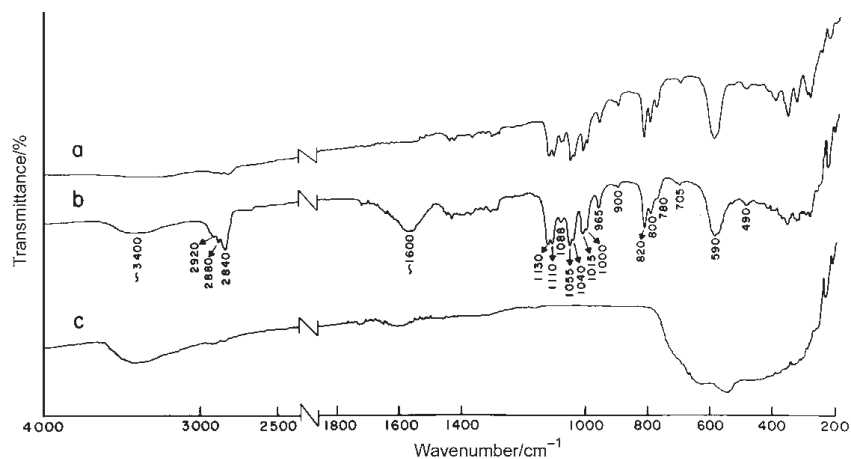
## Results and discussion

The thermal treatments of synthetic Fe-Mn alkoxide samples (Fe:Mn ratio 2:1) heated in a furnace at different temperatures, in air, were investigated by XRD, TG, sorptometry and IR spectroscopy [3]. Although this study revealed many interesting aspects of the resulting products, it could not disclose the precise range of formation of ferromagnetic oxides in these heating conditions.

In the present spectroscopic study, the alkoxide samples were comparatively heated at about 290°C in the furnace, both in air and in nitrogen atmospheres and examined by IR absorption spectroscopy. On the other hand, infrared emission spectroscopy spectra were recorded, while heating *in situ*, the alkoxide powder between 100 and 600°C.

### *Infrared absorption spectroscopy*

In Fig. 1 the IR absorption spectra of the Fe-Mn alkoxide of glycerol heated at about 290°C in nitrogen and in air atmospheres are displayed. Figure 1b shows that the alkoxide sample heated in a nitrogen atmosphere does not form a new structure, giving the same band positions as those shown by the initial alkoxide sample (Fig. 1a). Some bands are more enhanced in the sample heated in nitrogen atmosphere, as i.e. the 2840, 2880 and 2920  $\text{cm}^{-1}$  peaks, attributed to the stretching CH vibrations of the alkoxy groups as well as the broad bands at about 3400 and 1600  $\text{cm}^{-1}$ , assigned to the stretching and deformation vibrations, respectively, of HOH (Fig. 1b). The bands recorded in this spectrum are characteristic of the Fe-Mn alkoxide and have been partially discussed in an earlier work [1]. The spectrum of the sample heated at 290°C, in air, is shown in Fig. 1c. As expected from XRD and other results, in these thermal conditions the structure of the Fe-Mn alkoxide of glycerol is changed, as no peaks due to the alkoxy groups are detected



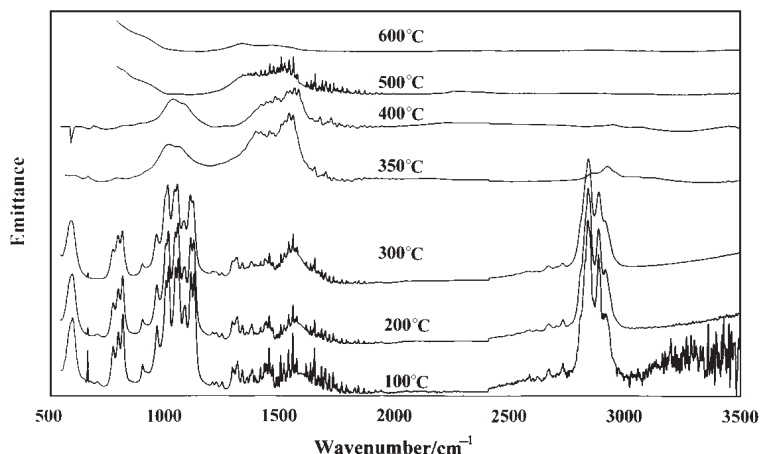
**Fig. 1** Infrared adsorption spectra of a – Fe-Mn alkoxide of glycerol; b – sample heated at 290°C in  $\text{N}_2$  atmosphere; c – sample heated in air at 290°C

in the spectrum (Fig. 1c). In agreement with the XRD results which indicated the formation of a disordered manganese ferrite structure, the spectrum in Fig. 1c suggests a spinel structure, which is characterized by a broad band centered around  $550\text{ cm}^{-1}$  [6]. The absorption bands at about  $3400$  and  $1600\text{ cm}^{-1}$  due to water, persist after heating the alkoxy samples at  $290^\circ\text{C}$ . The nature of this water present in multimetal alkoxydes of glycerol will be further investigated.

As expected, no formation of ferromagnetic oxide (spinel structures) is observed on heating the alkoxy in the furnace at  $290^\circ\text{C}$  in nitrogen, because in an inert atmosphere there is no oxidation of the organic (alkoxy) groups.

#### *Infrared emission spectroscopy*

Figure 2 exhibits the IRES spectra ( $3500\text{--}500\text{ cm}^{-1}$ ) of the Fe-Mn alkoxy sample, heated *in situ* between  $100$  and  $600^\circ\text{C}$ . No satisfactory spectrum can be discerned below  $100^\circ\text{C}$  employing this technique. No big difference is observed in the peak positions and emittances of the spectra recorded between  $100$  and  $300^\circ$ . Between  $300$  and  $350^\circ$  there is a strong decrease in the intensities of all the Fe-Mn alkoxy peaks. The spectrum recorded at  $350^\circ\text{C}$  shows significant differences in comparison to the spectra recorded at lower temperatures, indicating important structural changes in the metallic alkoxy. A former study of the Fe-Mn alkoxy indicated that a major TG mass loss occurred between  $270$  and  $290^\circ\text{C}$ , attributed to the Curie transition temperature and coinciding with the formation of a  $\text{MnFe}_2\text{O}_4$  (spinel) structure [3]. The present IRES study reveals that the CH bands are missing after  $350^\circ\text{C}$ , thus the formation range of ferromagnetic oxide is between  $350$  and  $400^\circ\text{C}$ . The strong band at  $600\text{ cm}^{-1}$ , characteristic of metallic oxidation states in the alkoxy [1], is not detected after heating at  $350^\circ\text{C}$ . Beside the disappearance of the sharp peaks around  $2900\text{ cm}^{-1}$  attributed to CH vibrations there is a decrease in the intensities of the sharp peaks around  $1000\text{ cm}^{-1}$ , ascribed to metal-oxygen-carbon vibra-



**Fig. 2** Infrared emission spectra of Fe-Mn alkoxy of glycerol at different temperatures

tions [7]. The latter are resolved into two small, broad bands at about 1015 and 1090  $\text{cm}^{-1}$  after heating at 350°C.

Further spectral changes are seen in the spectra recorded at higher temperatures. The IRES spectrum recorded at 600°C shows no initial peaks of the alkoxide nor of the intermediary heating products (Fig. 2). The rotational bands of water, especially those appearing around 1600  $\text{cm}^{-1}$  (OH deformation) are present in all the spectra recorded below 600°C. The actual IRES results are supplementary to an earlier work based on XRD and IR absorption spectroscopy, which reported the formation of ferromagnetic oxides (manganese ferrites) after heating in air Fe-Mn alkoxides at about 670°C [3].

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