

# Characterization of the High Temperature Form of $\text{Fe}_2(\text{MoO}_4)_3$

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Ferric molybdate in its high temperature orthorhombic phase has been characterized by conductometric and thermogravimetric measurements.

In the temperature range 793–973 K the compound can exist with  $\text{O}_2$  and  $\text{MoO}_3$  deficiencies. Defect models are proposed which can explain the experimental results: while a majority defect pair constituted by  $(V_{\text{O}}^{2+}, e')$  seems to be valid at  $T = 793$  K, two majority defect pairs  $(V_{\text{O}}^{2+}, e'; V_{\text{Mo}}^{6+}, V_{\text{O}}^{2+})$  are taken as possible at  $T = 873$  K.

## Introduction

Our interest in the formation mechanism of divalent and trivalent metal molybdates and tungstates is a few years old [1]. These investigations require the knowledge of the transport properties and consequently of the defect chemistry of these compounds.

Little is known till now on the point defects of divalent molybdates and tungstates (recent information is restricted to  $\text{CaWO}_4$  [2],  $\text{CaMoO}_4$  [3] and  $\text{PbMoO}_4$ - $\text{PbWO}_4$  [4]) while no literature information exists on trivalent compounds. Among the latter  $\text{Fe}_2(\text{MoO}_4)_3$  looks as particularly interesting owing to peculiar physico-chemical properties [5] not found in any other trivalent molybdate or tungstate.

The kinetics of the  $\text{Fe}_2(\text{MoO}_4)_3$  solid state formation reaction from the constituent oxides was already studied [6]. The object of this work is the characterization of  $\text{Fe}_2(\text{MoO}_4)_3$  in its high temperature ( $T > 786$  K) [7] orthorhombic phase [8] in order to propose defect models which might account for the observed properties.

An experimental approach was achieved through electrical conductimetry, thermogravimetry and optical microscopy in the temperature range 793–973 K.

## Experimental

### a) Products

Alfa Inorganics 99.9%  $\text{Fe}_2\text{O}_3$  and Koch-Light 99.9%  $\text{MoO}_3$  were used. These oxides were mixed in the ratios  $1\text{Fe}_2\text{O}_3/3(1+\gamma)\text{MoO}_3$  with  $\gamma$  ranging between 0 and 0.1. Near to the stoichiometric composition ( $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3$ )  $\gamma$  was changed in steps of 0.001. The mixtures so obtained were sealed in quartz tubes and kept in a furnace at 950 K for one week, then grinded and finally annealed at the same temperature, again in sealed quartz tubes, for another week.

Ferric molybdate was also prepared by keeping the  $\gamma = 0$  sample in a sealed quartz tube at 950 K in the presence of  $\text{MoO}_3$  vapours for one week. Care was taken to prevent  $\text{MoO}_3$  condensation on the compound when the tube was withdrawn from the furnace.

The samples so prepared will be denoted as S.

### b) Apparatuses and Procedures

TG isothermal measurements (Thermogravimetric Analyzer Du Pont mod. 950) were performed on S type and  $\gamma > 0$  samples ( $\cong 50$  mgr) at different oxygen partial pressures and for  $793 < T < 973$  K.

Conductivity measurements in the frequency range 1–20 kHz were performed in the same temperature range and with oxygen partial pressures ranging between  $10^{-4}$  and 1 atm. A home-made three electrodes quartz cell in connection with a Wayne-Kerr bridge mod. B 301, with a H.P. 3312 A signal source, and with a G.R. 1332 A null detector was used. The samples were in the form of pellets ( $\varnothing = 8$  mm, thickness ranging between 1 and 5 mm) obtained by pressing ( $10^3$  kg/cm<sup>2</sup>) powders prepared

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as described. A platinum film was evaporated on the pellets to form electrodes.

After each change in the oxygen partial pressure about forty hours elapsed before measurements to allow equilibrium to be attained.

## Results and Discussion

Preliminary microscopic observations of  $\gamma \geq 0$  samples were performed to verify if there is any solubility of  $\text{MoO}_3$  in  $\text{Fe}_2(\text{MoO}_4)_3$  (excess  $\text{MoO}_3$  being identifiable under polarized light owing to its transparency in these conditions).

Free  $\text{MoO}_3$  was always found when  $\gamma > 0$  while it was absent when  $\gamma = 0$ . Moreover X-ray measurements on  $\text{Fe}_2(\text{MoO}_4)_3$  samples [7] showed that the lattice constants are independent of the  $\gamma$  value, so confirming that no detectable solubility of  $\text{MoO}_3$  in  $\text{Fe}_2(\text{MoO}_4)_3$  exists.

### Thermogravimetric Measurements

A weight decrease due to  $\text{MoO}_3$  loss was always observed when operating with both the S and the  $\gamma > 0$  samples: in the latter case the decrease was slightly larger than expected from stoichiometry, the "excess decrease" being, at any temperature, in good agreement with the overall weight decrease measured on the S type samples at the same temperature. The time required to reach weight constancy depended on temperature and ranged between 250 min ( $T = 843$  K) and 30 min ( $T = 973$  K). In Fig. 1 the percent weight decrease is reported vs temperature for S type samples:  $\text{MoO}_3$  sublimation is apparently not detectable for  $T < 820$  K.

A deficiency of  $\text{MoO}_3$  in  $\text{Fe}_2(\text{MoO}_4)_3$  seems to be consistent also with X-ray thermal expansion measurements [7], which showed that the lattice con-

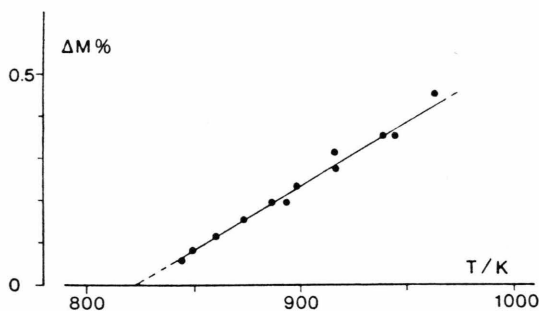


Fig. 1.  $\text{MoO}_3$  loss: percent weight decrease of  $\text{Fe}_2(\text{MoO}_4)_3$  as a function of temperature.

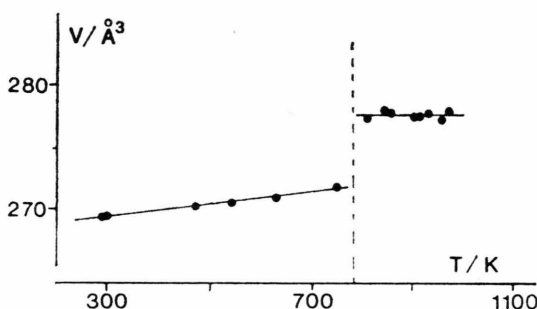


Fig. 2. Molecular volume of  $\text{Fe}_2(\text{MoO}_4)_3$  as a function of temperature. The volume of the low temperature monoclinic phase ( $T < 786$ ) has been reported for comparison.

stants **b** and **c** present an increase while **a** diminishes on increasing temperature, thus leading to a nearly constant value of the molecular volume in a large temperature range as shown in Figure 2.

For temperatures higher than 973 K it was not possible to attain constant weight: microscopic observation of the thermogravimetric specimens heated at  $T > 973$  K gave evidence for free  $\text{Fe}_2\text{O}_3$ , so showing that the compound partly decomposes at these temperatures (it cannot be excluded that a contribution to the overall weight decrease might be due to  $\text{MoO}_3$  loss through compound decomposition also at temperatures lower than 973 K).

Thermogravimetric measurements were also performed on S type samples at different oxygen partial pressures and at a temperature (793 K) at which a  $\text{MoO}_3$  loss can be excluded: the weight decrease observed in the isotherms at low oxygen partial pressures ( $p_{\text{O}_2} = 10^{-5}$  atm) was equal to the weight increase recorded at the same temperature when the surrounding atmosphere became air ( $p_{\text{O}_2} = 0.2$  atm), so showing that not only  $\text{MoO}_3$  but also  $\text{O}_2$  deficiencies can be present in ferric molybdate.

### Electrical Conductivity Measurements

Preliminary isothermal measurements of  $\sigma$  vs  $p_{\text{O}_2}$  were performed in the frequency range 1–20 kHz. It was observed that the conductivity values are scarcely dependent on frequency and that anyhow the slope of the straight-line  $\log \sigma$  vs  $\log p_{\text{O}_2}$  is independent on frequency. Figure 3 reports two isotherms  $\log \sigma$  vs  $\log p_{\text{O}_2}$  obtained at 793 and 973 K (frequency 1592 Hz); the slopes are respectively  $-1/6$  and  $-1/6.5$ .

For what concerns the isotherm at 793 K, thermogravimetric measurements showed that a  $\text{MoO}_3$

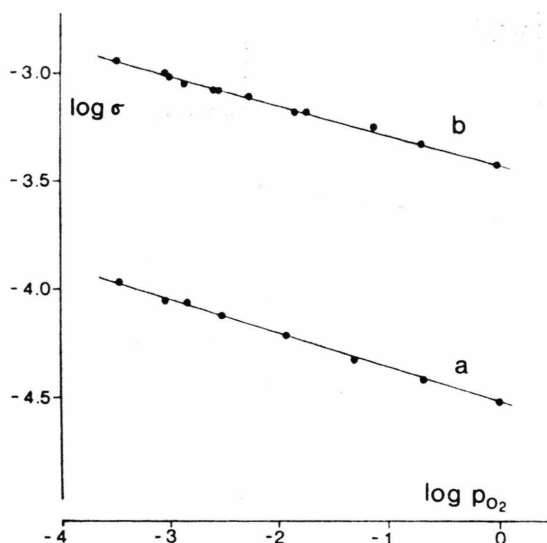
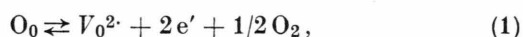


Fig. 3. Electrical conductivity ( $\text{ohm}^{-1} \text{cm}^{-1}$ ) of  $\text{Fe}_2(\text{MoO}_4)_3$  as a function of the oxygen partial pressure:

a)  $T = 793 \text{ K}$ , b)  $T = 873 \text{ K}$ .

loss may be excluded while an oxygen loss may be present at this temperature.

If the oxygen deficiency is assumed to be equivalent to a majority defect pair constituted by oxygen vacancies and free electrons generated through the crystal-gas equilibrium



then the approximated electroneutrality condition

$$2(V_{\text{O}}^{2\cdot}) \cong (e') \quad (2)$$

is valid, and from (1) and (2) it is easily seen that

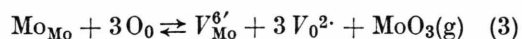
$$d \log(e') = -1/6 d \log p_{\text{O}_2}.$$

Consequently the slope of the experimental straight-line  $\log \sigma$  vs  $\log p_{\text{O}_2}$  is equal to that provided by this model. (Ferric molybdate has an electronic

transference number  $t_e > 0.95$  in the temperature range 773–973 K [9]).

In the isotherm  $\log \sigma$  vs  $\log p_{\text{O}_2}$  at 873 K, a  $\text{MoO}_3$  deficiency must be taken into account according to Figure 1.

This deficiency might be assumed to be equivalent to a majority defect pair constituted by oxygen and molybdenum vacancies generated by the crystal-gas equilibrium



with the approximated electroneutrality condition

$$3(V_{\text{Mo}}^{3\cdot}) \cong (V_{\text{O}}^{2\cdot}), \quad (4)$$

and with the concentration of oxygen and molybdenum vacancies practically independent of  $p_{\text{O}_2}$ . From (1) it is easily seen that for this case  $d \log(e') = -1/4 d \log p_{\text{O}_2}$ . Petrov and Kofstad [3] found this model valid in the case of  $\text{CaMoO}_4$ .

As in the present study the measurements gave  $d \log(e') = -1/6.5 d \log p_{\text{O}_2}$ , it may be concluded that this model cannot be applied to  $\text{Fe}_2(\text{MoO}_4)_3$ .

The observed dependence of  $\log \sigma$  on  $\log p_{\text{O}_2}$  can be explained on the basis of two hypotheses:

a) also at 873 K the majority defect pair is constituted by oxygen vacancies and free electrons generated by equilibrium (1),

b) the defect generation due to internal equilibria cannot be disregarded with respect to that due to  $\text{MoO}_3$  and oxygen losses.

In this case, by applying the Schmalzried-Wagner theory [10] as indicated by Rigdon and Grace [2] to all possible types of fully ionized defects, it can be shown that only the majority defect pair constituted by oxygen and molybdenum vacancies ( $d \log(e') = -5/32 d \log p_{\text{O}_2}$ ) is consistent with the experimental slope value.

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