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THERMAL STUDIES ON THE CUBIC SPINEL Fe_2MoO_4

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The cubic spinel Fe_2MoO_4 was studied in air by DTA, DTG, TG and X-ray in the temperature interval 298—1173 K. From these studies, it was concluded that above the Néel temperature Fe_2MoO_4 undergoes an irreversible crystalline phase transition from cubic to tetragonal at 623 K, where c/a is 1.022. Above 723 K, surface oxidation followed by bulk oxidation of the spinel occurs. At 948 K, after about half the total weight gain due to oxidation, a compound is formed which was confirmed by X-ray as ferrimolybdite, $Fe_2O_3 \cdot 3-4\ MoO_3$, indicating that in Fe_2MoO_4 the Mo^{4+} is more readily oxidized than the Fe^{2+}. Above 940 K, further oxidation of Fe^{2+} and Mo^{4+} into their respective oxide occurs. About 13 % of the MoO_3 vaporizes, and the rest melts at 1028 K.

Fe_2MoO_4 has Fe^{2+} and Mo^{4+} ions distributed among the octahedral and tetrahedral interstices of the cubic spinel lattice [1]. It is ferrimagnetic below 348 K and undergoes spin compensation at 160 K [2]. Neutron diffraction studies have shown that the spin arrangement is non-collinear below the compensation temperature, due to strong B-B interactions, i.e. strong magnetic interactions between $Fe^{2+}-Fe^{2+}$, $Mo^{4+}-Mo^{4+}$ and $Fe^{2+}-Mo^{4+}$ cations at the octahedral sites [3].

Both the cations in Fe_2MoO_4 are present in their lower valence states and are likely to be oxidized to Fe^{3+} and Mo^{6+} on heating in air. However, oxidation of the cations of this spinel will largely depend on the thermal stability of Fe_2MoO_4 in air. The present paper deals with the results of thermal studies on the cubic spinel Fe_2MoO_4 in air by DTA, TG, DTG and X-ray analysis.

Experimental

The compound was prepared by the method followed by Ghose *et al.* [3]. DTA, TG and DTG of powdered Fe_2MoO_4 were carried out in air, with a MOM derivatograph, from 298 K to 1173 K. The heating rate was 10°/min. Temperature calibration was performed with standard calcium oxalate and the baseline was determined in a blank run. The room temperature X-ray photographs were taken with a Philips X-ray unit (Model No. PW 1012/10), using CrK_α radiation (λ = 2.2890 Å). The high-temperature X-ray diffraction patterns were obtained using a Philips X-ray diffractometer with the MRC model X-86-N3 high-temperature attachment.

Results and discussion

DTA, TG and DTG curves are shown in the Fig. 1. Between 298 K and 1173 K, the DTA curve reveals several endothermic and exothermic changes. The TG and DTG curves indicate a continuous weight gain from 723 K onwards.

The first endothermic peak between 328 K and 368 K is in the region of the Néel temperature of Fe_2MoO_4, and probably manifests the magnetic change of Fe_2MoO_4. Such endothermic asymmetric DTA peaks have also been found in other spinels undergoing a second-order magnetic order-disorder transformation [4]. Hence, the first DTA peak may be due to the magnetic transformation of Fe_2MoO_4, which is further supported by the fact that there is no weight change accompanying this peak. The change seems to be around 333 K, but the exact Néel temperature is very difficult to locate from the broad and asymmetric nature of the peak.

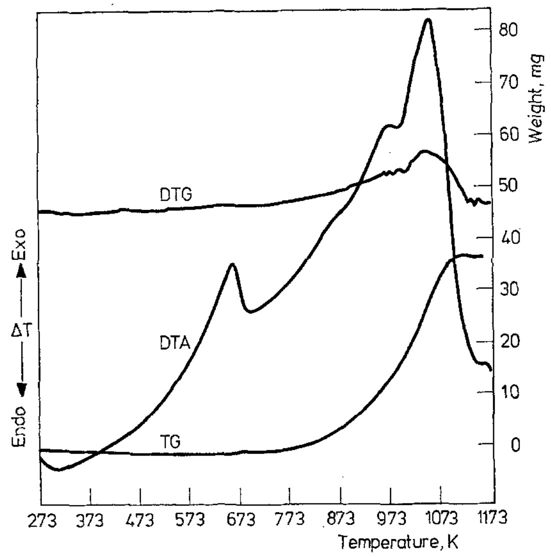

Fig. 1. Thermal curves of the cubic spinel Fe_2MoO_4

Following the magnetic transformation, there is a sharp exothermic DTA peak at 623 K, which is again unaccompanied by any weight change. This peak could be due either to a phase change or to decomposition of Fe_2MoO_4 into its respective oxides, i.e. $Fe_2MoO_4 \rightarrow 2\ FeO + MoO_2$. Neither process involves weight change, but in the former case X-ray should show a single phase compound, and in the latter case lines of both monoclinic MoO_2 and cubic FeO should be observed. The high-temperature X-ray diffractograph at 763 K has shown conclusively that only one phase is present at this temperature; it is still a spinel, but instead of the original cubic structure, it has a tetragonal structure with $c/a = 1.022$. Hence, it is apparent that the exothermic peak at 623 K is due not to the decomposition of Fe_2MoO_4, but to the cubic → tetragonal phase transition of the spinel. Such phase transitions have been observed in other spinels containing Fe^{2+} ions, e.g. $FeCr_2O_4$ [5] and FeV_2O_4 [6], due to the Jahn–Teller effect. However, this phase transition was not found to be reversible, as no peak was observed in the DTA curve at 623 K when the sample was cooled from 773 K to room temperature. This is because cubic Fe_2MoO_4 is the high-temperature stable phase, and so the tetragonal → cubic phase transition temperature is expected to be higher than the cubic → tetragonal phase transition temperature, as has been observed in $CuFe_2O_4$ [7]. Unfortunately, the tetragonal → cubic phase transition could not be detected due to oxidation of Fe_2MoO_4 above 773 K, as shown by the increase in weight in the TG curve.

Above 723 K, the compound starts gaining weight very slowly and there is also an onset of a large DTA peak. The slope of the DTA peak changes around 850 K and above 948 K an endothermic peak appears. Following this peak, there is a very rapid weight gain, as well as completion of the large exothermic DTA peak.

These results indicate that above 723 K the compound is undergoing a number of thermal changes; from the nature of the weight gain, as well as the DTA and DTG peaks, it seems that above 723 K surface oxidation occurs, and hence the weight gain is very slow. Above 850 K, the weight gain is probably not due to surface oxidation alone, as indicated by the change in the slope of the TG curve. It may be possible that after a certain amount of surface oxidation bulk oxidation sets in, whereby the slope of the TG curve increases. With increasing amounts of surface and bulk oxidation, the spinel phase is liable to become unstable, resulting in disintegration of the spinel lattice. Thus, the endothermic DTA peak at 948 K could be due to this disintegration. On examination of the powder X-ray photograph of the compound heated to 940 K, a large number of lines were observed, in contrast to the few lines of the spinel lattice. Some of the lines could be identified with those of FeO and α-Fe_2O_3, but the majority of the lines were not due to any of the single oxides of molybdenum or iron. However, the lines could be identified with those of orthorhombic iron(III)molybdite, $Fe_2O_3 \cdot 3-4\,MoO_3$, heated to 1323 K [8]. Thus, instead of disintegrating into the respective oxides, Fe_2MoO_4 is converted into orthorhombic iron(III)molybdite on being heated in air. The TG curve shows that for 0.360 g of Fe_2MoO_4, the total weight gain is 0.0395 g. However, the weight gain is only 0.018 g when iron(III)-molybdite is formed. Hence, it appears that during the oxidation of Fe_2MoO_4, Mo^{4+} is oxidized more readily than Fe^{2+}, and around 940 K 66% of the Mo^{4+} and 19% of the Fe^{2+} are oxidized.

After the formation of iron(III)molybdite, the iron oxide is present as a separate phase, as shown by X-ray, and some MoO_2 is also present; these are then oxidized. For complete oxidation of Fe^{2+} and Mo^{4+} in 0.360 g of Fe_2MoO_4, the total weight gain should be 0.0424 g, whereas the actual weight gain is only 0.0395 g. The difference of 0.0029 g seems to be due to vaporization of MoO_3 which is formed above 940 K. Thus, about 13.5% of the MoO_3 formed is vaporized. Above 1028 K, the sample was found as a molten mass and the sharp exothermic peak at 1028 K may be due to melting. Of the three components present at this temperature, ferrimolybdite and Fe_2O_3 are stable, but the melting point of pure MoO_3 is slightly above this temperature, i.e. 1068 K. However, in the presence of other components, the melting point is expected to be lowered and thus the DTA peak at 1028 K could be due to the melting of the MoO_3 formed.

Thus, it may be concluded from DTA, DTG, TG and X-ray studies that cubic Fe_2MoO_4 is chemically stable in air up to 723 K, although it undergoes magnetic and crystalline phase transitions around 350 K and 623 K, respectively. Chemical instability is caused by surface and bulk oxidation, which leads to the formation of ferrimolybdite, $Fe_2O_3 \cdot 3-4\,MoO_3$ at 940 K, followed by further oxidation to Fe_2O_3 and MoO_3. A part of the latter volatilizes and it finally melts at 1028 K.

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References

1. Y. D. Kozmanov and L. M. Sorokin, Tr. Ural'sk. Politekhn. Inst. (1961) 154; through R. W. G. Wyckoff: Crystal Structures (Interscience Publishers, N. Y. 1965) 2nd ed., Vol. 3, p. 79.
2. M. Abe, M. Kawachi and S. Nomura, J. Phys. Soc. Japan, 31 (1971) 940.
3. J. Ghose, N. N. Greenwood, G. C. Hallam and D. A. Read, J. Sol. State Chem., 11 (1974) 239.
4. S. L. Blum, A. E. Palandino and L. G. Rubin, Am. Ceram. Soc. Bull., 36 (1957) 175.
5. E. R. Whipple and A. Wold, J. Inorg. Nucl. Chem., 24 (1962) 23.
6. D. B. Rogers, R. J. Arnott, A. Wold and J. B. Goodenough, J. Phys. Chem. Solids, 24 (1963) 347.
7. H. Ohnishi and T. Teranishi, J. Phys. Soc. Japan, 16 (1961) 35.
8. P. F. Kerr, A. W. Thomas and A. M. Langer, Am. Min., 48 (1963) 14.

Zusammenfassung — Das kubische Spinell Fe_2MoO_4 wurde in Luft im Temperaturbereich von 298 bis 1173 K durch DTA, DTG, TG und Röntgen untersucht. Aus diesen Studien wurde gefolgert, daß oberhalb der Neel Temperature ein irreversibler kristalliner Phasenübergang des Fe_2MoO_4 aus der kubischen in die tetragonale Form bei 623 K stattfindet, wobei $c/a = 1.022$ beträgt. Oberhalb von 725 K findet eine Oberflächenoxidierung des Spinels statt, der eine allgemeine Oxidation folgt. Bei 948 K, nachdem etwa die Hälfte der infolge der Oxidation auftretenden Gewichtszunahme erfolgte, wird eine durch Röntgen als Ferrimolybdit bestätigte Verbindung gebildet ($Fe_2O_3 \cdot 3-4\,MoO_3$), welche zeigt, daß in Fe_2MoO_4 das Mo^{4+} leichter oxidiert wird als das Fe^{2+}. Oberhalb von 940 K erfolgt eine weitere Oxidation von Fe^{2+} und Mo^{4+} zu ihren entsprechenden Oxiden. Etwa 13% des MoO_3 verdampft und das übrige schmilzt bei 1028 K.

Резюме — С помощью ДТА, ДТГ, ТГ и рентгенографии изучена шпинель Fe_2MoO_4 кубической структуры в интервале температур 298—1173 К и в атмосфере воздуха. Сделано заключение, что выше температуры Нееля Fe_2MoO_4 подвергается при 623 К необратимому фазовому переходу от кубической до тетрагональной структуры, для которой отношение параметров c/a составляет 1.022. Выше 723 К, вслед за окислением поверхности, следует окисление во всем объеме. В результате окисление происходит увеличение общего веса почти наполовину и при 948 К образуется соединение $Fe_2O_3 \cdot 3$—$4MoO_3$, подтвержденное рентгеноструктурных анализом. Это свидетельствует о том, что в Fe_2MoO_4 ион Mo^{4+} более легко окисляется, чем ион Fe^{2+}. Выше 940 К происходит дальнейшее окисление ионов Fe^{2+} и Mo^{4+} до соответствующих окислов. Около 13% MoO_3 испаряется, а остаток плавится при 1028 К.