Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 1073–1080

SYNTHESIS AND PROPERTIES OF SOLID SOLUTIONS IN THE $FeVMoO_7$–$CrVMoO_7$ SYSTEM

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Abstract

X-ray phase analysis (XRD), differential thermal analysis (DTA) and IR spectroscopy have shown that continuous substitution solid solutionsin are formed in the $FeVMoO_7$–$CrVMoO_7$ system. With increasing the degree of Cr^{3+} ion incorporation into the $FeVMoO_7$ structure, a crystal lattice contraction of the $Fe_{1-x}Cr_xVMoO_7$ solid solution arise. Elevation of temperature of its incongruent melting and gradual shifting of the corresponding IR absorption bands towards higher wavenumbers have been noticed, as well. The solid product of incongruent melting for $x\leq0.5$ is the $Fe_{4-y}Cr_yV_2Mo_3O_{20}$ solid solutions phase, whereas for $x>0.5$ $Fe_{2-z}Cr_z(MoO_4)_3$ and $Fe_{2-u}Cr_uO_3$ solid solutions.

Keywords: DTA, $Fe_{1-x}Cr_xVMoO_7$ solid solutions, IR, XRD

Introduction

A literature scan has shown that phases of a $MVMoO_7$ type are built in the three-component oxide systems, M_2O_3–V_2O_5–MoO_3, where *M*=Al, Cr or Fe [1–6].

The compound $AlVMoO_7$ crystallises in an orthorhombic system (space group Pmcn, *Z*=4) [1] whereas $FeVMoO_7$ and $CrVMoO_7$ are isostructural and crystallise in a triclimic system (space group $P\bar{1}$, *Z*=2) [7].

Studies on the $FeVMoO_7$–$AlVMoO_7$ system have led to the conclusion that a solid solution of a $Fe_{1-x}Al_xVMoO_7$ type, holding the $FeVMoO_7$ structure, occurs in the system. Despite essential differences noticed in the internal structure of $FeVMoO_7$ and $AlVMoO_7$, the solubility of $AlVMoO_7$ in $FeVMoO_7$ is high and reach *x*=0.5 [8].

As for the $FeVMoO_7$–$CrVMoO_7$ system, one can expect that the isostructural character of $MVMoO_7$ phases and approximate values of Fe^{3+} and Cr^{3+} radii will cause the formation of continuous substitution solid solutions. In view of the fact that the phase relations have not been investigated yet, it has been deemed advisable to undertake works on the resolution of this problem.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

The following reagents were used in the experiments: an analytically pure Fe_2O_3 (POCH, Glivice, Poland), a 98+% Cr_2O_3 (Aldrich, Germany), an analytically pure V_2O_5 (POCH, Glivice, Poland), a pure MoO_3 (POCH, Glivice, Poland) and phases, $FeVMoO_7$ and $CrVMoO_7$ prepared by the procedures given in works [2, 3].

DTA measurements were made using a derivatograph (MOM, Hungary). Samples of 500 mg placed in quartz crucibles were heated in air, at a rate of 10 deg min^{-1} and within the temperature range of 293–1273 K. The accuracy of reading the temperatures characteristic of the effects recorded on the DTA curves for the preparations at an equilibrium state was determined to be equal to ±5 deg, as it was established by repeated DTA examinations of the same sample.

The phase composition of the samples was defined by X-ray phase analysis with the aid of a diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, Russia) using CoK_{α}/Fe radiation.

IR spectra were recorded using a spectrometer of a SPECORD M 80 type (Carl Zeiss, Jena, Germany). A technique of pressing pastilles with KBr was applied. The samples were mixed with KBr at a mass ratio of 1:300. IR spectra were recorded over a wavenumber range of 1400–250 cm^{-1}.

For the experiments 7 samples with contents corresponding to 10, 30, 40, 50, 60, 70 and 90 mol% of $CrVMoO_7$ in mixtures with $FeVMoO_7$ were prepared. The samples were synthesized from oxides: Cr_2O_3, Fe_2O_3, V_2O_5 and MoO_3. For the comparative purpose there were also prepared 3 samples comprising 30, 50 and 70 mol% of $CrVMoO_7$ in mixtures with $FeVMoO_7$, both the phases being pure $MVMoO_7$ phases.

Weighed in suitable proportions preparations were homogenized and calcinated at 873, 923 and 953 K in 24 h cycles. After each of the heating cycles the samples were triturated and analysed by XRD.When the diffraction patterns taken after two consequent heating cycles were identical both with respect to the positions and to the intensities of the recorded diffraction lines, it was assumed that the samples reached an equilibrium state. The procedure of heating samples was then finished and on the last heating cycle the samples were investigated, apart from XRD measurement, by means of the DTA method and IR spectroscopy.

Results and discussion

The diffraction patterns of preparations obtained both from the oxides and from previously prepared $FeVMoO_7$ and $CrVMoO_7$ showed, on the last heating cycles, the presence of the set of diffraction lines that were shifted towards higher diffraction angles (2θ) in comparison to the set of the lines characteristic of the $FeVMoO_7$ compound. In comparison to the diffraction pattern of $CrVMoO_7$, these lines were shifted towards smaller angles, so they corresponded to bigger d values. Based on the obtained diffraction patterns, it can be concluded that in the $FeVMoO_7$–$CrVMoO_7$ system continuous solid solutions are formed and their general formula can be written both as $Fe_{1-x}Cr_xVMoO_7$ and as $Cr_{1-x}Fe_xVMoO_7$. In order to depict the changes of selected properties of the formed solid solutions, their formula was always written as $Fe_{1-x}Cr_xVMoO_7$. The analysis of the diffraction patterns of the obtained $Fe_{1-x}Cr_xVMoO_7$ solid solutions proved that with increasing x – the interplanar distances (*d*), characteristic of these solutions, decreased in comparison to pure $FeVMoO_7$ and approached to the values characteristic of $CrVMoO_7$.

When the initial reactants for the formation of $Fe_{1-x}Cr_xVMoO_7$ were the oxides: Fe_2O_3, Cr_2O_3, V_2O_5, and MoO_3, the synthesis of the solutions occurred very quickly. The diffraction patterns of the preparations on the first cycle of heating already, i.e. at 873 K for 24 h, revealed apart from little intensity reflections characteristic of the initial reactants – only the set of lines characteristic of the solid solution. The second cycle of heating at the same temperature yielded all monophase preparations, i.e. the solid solutions of $Fe_{1-x}Cr_xVMoO_7$ type.

In case of previously obtained compounds $FeVMoO_7$ and $CrVMoO_7$ taken as reactants in the investigated system, the degree of conversion of the reactants into the solid solutions was significantly lower than in case of the synthesis from the oxides at the same temperature. Therefore the preparations obtained from the $MVMoO_7$ phases required an additional sintering at temperatures higher than 873, i.e. at 923 and 953 K.

Figure 1 presents, apart from a fragment of a diffraction pattern of an equimolar mixture of $FeVMoO_7$ and $CrVMoO_7$ (curve a), fragments of the diffraction patterns of this sample after selected heating cycles (curves b and c) as well as a diffraction pattern of a monophase sample containing only $Fe_{0.5}Cr_{0.5}VMoO_7$ (curve d).

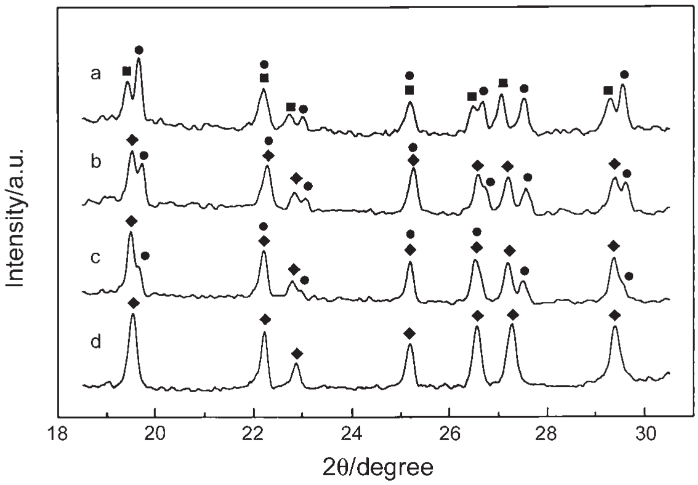

Fig. 1 The changes in powder diffraction patterns on selected stages of the $Fe_{1-x}Cr_xVMoO_7$ (◆) synthesis reaction from $FeVMoO_7$ (■) and $CrVMoO_7$ (●) in their equimolar mixture; a – initial mixture of $FeVMoO_7$ and $CrVMoO_7$; b – after heating at 873 K(2×24 h); c – after additional heating at 923 K(2×24 h); d – after additional heating at 953 K(2×24 h), pure $Fe_{0.5}Cr_{0.5}VMoO_7$

The analysis of these diffraction patterns allows a statement: with the progress in the occurring reaction the angular positions of the reflections, characteristic of the pure $CrVMoO_7$ phase in the initial samples, did not change (*d* is constant), but their intensity successively decreased. On the other hand, the diffraction reflections characteristic initially of $FeVMoO_7$ increased their intensity and, what is more, they moved towards higher angles 2θ (*d* decreased). Such changes were also observed in case of the remaining preparations obtained from $FeVMoO_7$ and $CrVMoO_7$. These facts suggest that in case of the synthesis from the $MVMoO_7$ compounds the Cr^{3+} ions insert themselves in the crystal lattice of $FeVMoO_7$.

Based on X-ray diffraction patterns of the $Fe_{1-x}Cr_xVMoO_7$ solid solitions for x=0.3, 0.5 and 0.7 parameters and volumes of their unit cells were calculated by using program INDEXING. Table 1 shows parameters and volumes of the unit cells of pure $FeVMoO_7$ [9] and $CrVMoO_7$ [7] phases as well as those of solid solutions for x=0.3, 0.5 and 0.7. The data in Table 1 point to the fact that with the increasing degree of incorporation of Cr^{3+} ions in the place of Fe^{3+} ions the contraction of the crystal lattice and consequential decrease in the unit cell volumes take place.

Table 1 Unit cell parameters and volumes for the $FeVMoO_7$ (x=0) and $CrVMoO_7$ (x=1.0) phases and $Fe_{1-x}Cr_xVMoO_7$ solid solutions

x	a/nm	b/nm	c/nm	α/°	β/°	γ/°	V/nm^3
0.0	0.5573(2)	0.6674(2)	0.7906(3)	96.19(2)	90.31(3)	101.30(3)	0.2866
0.3	0.5559(1)	0.6650(1)	0.7897(2)	96.16(2)	90.21(2)	101.47(2)	0.2843
0.5	0.5540(2)	0.6630(1)	0.7891(3)	96.11(2)	90.09(2)	101.64(2)	0.2822
0.7	0.5537(1)	0.6613(1)	0.7878(2)	96.14(2)	89.95(2)	101.75(2)	0.2808
1.0	0.5527(1)	0.6582(1)	0.7865(1)	96.19(1)	89.87(1)	102.01(1)	0.2782

Pure $CrVMoO_7$ and $FeVMoO_7$ phases as well as the solid solutions of $Fe_{1-x}Cr_xVMoO_7$ where x=0.1, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.9 were investigated by using the DTA method.

According to the literature data, the $FeVMoO_7$ compound melts incongruently at 953 K and the solid product of melting is $Fe_4V_2Mo_3O_{20}$ [3]. $Fe_4V_2Mo_3O_{20}$ is the other compound, apart from $FeVMoO_7$, crystallising in the Fe_2O_3–V_2O_5–MoO_3 system. It melts at 1033 K depositing two solid products: $Fe_2(MoO_4)_3$ and Fe_2O_3 [10]. On the other hand, $CrVMoO_7$ is the only compound formed in the Cr_2O_3–V_2O_5–MoO_3 system, melting incongruently at 1093 K [2]. The solid product of melting $CrVMoO_7$ is Cr_2O_3. Our investigations conducted at present and concerning a four-component system of Fe_2O_3–Cr_2O_3–V_2O_5–MoO_3 imply among others that in this system $Fe_{4-y}Cr_yV_2Mo_3O_{20}$ type phases are formed [11, 12]. In the phases of this type the Cr^{3+} ions are inserted in the crystal lattice of $Fe_4V_2Mo_3O_{20}$ in the sites of the Fe^{3+} ions. These are solutions of limited solubility because, among others in the Cr_2O_3–V_2O_5–MoO_3 system, there exists no compound of $Cr_4V_2Mo_3O_{20}$ [11, 12].

Figure 2 shows some DTA curves of the samples $Fe_{0.9}Cr_{0.1}VMoO_7$ (curve a) and $Fe_{0.3}Cr_{0.7}VMoO_7$ (curve b).

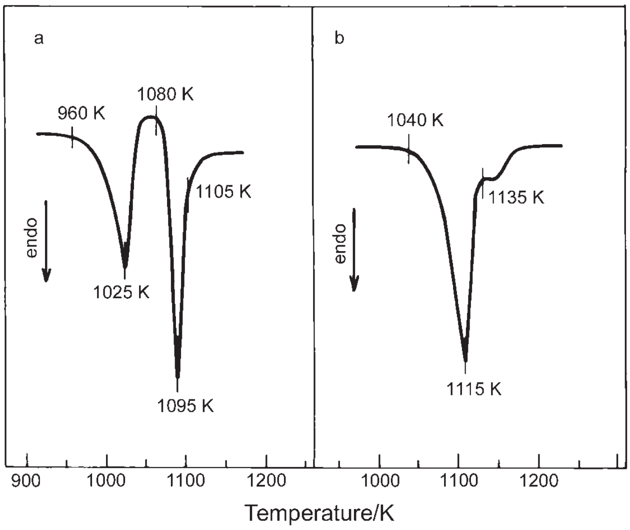

Fig. 2 The DTA curves of a – $Fe_{0.9}Cr_{0.1}VMoO_7$; b – $Fe_{0.3}Cr_{0.7}VMoO_7$

DTA curves obtained in this work for the solid solutions of $Fe_{1-x}Cr_xVMoO_7$ where $0.1 \leq x \leq 0.9$ revealed the presence of two endothermic effects. With increasing x the onset temperature both of the first and the other effect increased. The first endothermic effect for $x=0.1$ had its onset at 960 K, for $x=0.3$ – at 978 K, for $x=0.4$ – at 988 K, for $x=0.5$ – at 1003 K, for $x=0.6$ – at 1018 K, for $x=0.7$ at 1038 K, and for $x=0.9$ – at 1073 K. Thus, it can be concluded that the onset temperature of the first effect was always higher than the melting temperature of $FeVMoO_7$ and lower than the melting temperature of $CrVMoO_7$ [2, 3]. The other endothermic effect recorded on the DTA curves of the $Fe_{1-x}Cr_xVMoO_7$ phases, which suggested their incongruent melting, had its onset at 1080 K for $x=0.1$. With increasing x the temperature of this effect increased reaching 1150 K for $x=0.9$.

In order to determine the way of melting the solid solutions of $Fe_{1-x}Cr_xVMoO_7$, all the obtained monophase preparations of $0.1 \leq x \leq 0.9$ were additionally heated for 1–3 h at the temperatures of the extremum of the first endothermic effect recorded on their DTA curves, i.e. at the temperatures ranging from 1025 K for $x=0.1$ to 1120 K for $x=0.9$.

After this additional heating the preparations were rapidly quenched to ambient temperature, ground and XRD investigated. The phase analysis of the obtained preparations for $x \leq 0.5$ showed that they contained apart from the phases having crystallised from the liquid (e.g. $V_2O_{5(s.s.)}$) also a phase identified on the base of our other investigations as $Fe_{4-y}Cr_yV_2Mo_3O_{20}$ solid solution phase. The diffraction lines characteristic of $Fe_4V_2Mo_3O_{20}$ were shifted towards higher angles which is an additional proof that the crystal lattice of this compound contains inserted Cr^{3+} ions. This shift of the diffraction lines increased with the increasing x in the initial samples, which suggested that in the solid product of melting $Fe_{1-x}Cr_xVMoO_7$ solid solutions the degree of Cr^{3+} ions insertion into the crystal lattice of $Fe_4V_2Mo_3O_{20}$ also increases reaching its maximal value at $x=0.5$. The onset temperature of the other endothermic effect recorded on the DTA curves of $Fe_{1-x}Cr_xVMoO_7$ for $x\leq0.5$, i.e. 1080 K ($x=0.1$), 1100 K ($x=0.3$), 1105 K ($x=0.4$) and 1115 K ($x=0.5$), increases with increasing x and is always higher than the melting temperature of $Fe_4V_2Mo_3O_{20}$. This is an additional support to the fact that the solid product of melting the investigated solutions for $x\leq0.5$ is the $Fe_{4-y}Cr_yV_2Mo_3O_{20}$ solid solution phase. The curve (a) presented in Fig. 2 is a DTA curve of $Fe_{0.9}Cr_{0.1}VMoO_7$, i.e. a solid solution representing the composition range of $0.1\leq x\leq0.5$. Based on the results obtained in this part of the research, it can be concluded that the first endothermic effect recorded on the DTA curves of the $Fe_{1-x}Cr_xVMoO_7$ preparation for $0.1\leq x\leq0.5$ is caused by incongruent melting of these phases, whereas the other is related to melting $Fe_{4-y}Cr_yV_2Mo_3O_{20}$ (Fig. 2, curve a). A small shoulder recorded at the higher temperatures side on the second effect for $x=0.1$, 1105 K, is probably due to melting the melting's products of $Fe_{4-y}Cr_yV_2Mo_3O_{20}$ [12].

The interpretation of the DTA curves and the determination of solid products of melting solid solutions of $Fe_{1-x}Cr_xVMoO_7$, for $x>0.5$, were carried out in an analogous way as in case of $x\leq0.5$. X-ray phase analysis of melted $Fe_{1-x}Cr_xVMoO_7$ solid solutions for $x>0.5$ has shown that the solid products of their melting are two phases. On the basis of the literature data, it was found that the first phase was a solid solution involving $Fe_2(MoO_4)_3$ and $Cr_2(MoO_4)_3$, i.e. $Fe_{2-z}Cr_z(MoO_4)_3$ [13], whereas the other phase was a solid solution of $Fe_{2-u}Cr_uO_3$ type [14–16]. Curve (b) in Fig. 2 is the DTA curve of $Fe_{0.3}Cr_{0.7}VMoO_7$, i.e. of the solid solution representing this range of x. The first endothermic effect with its onset temperature at 1040 K is due to incongruent melting of the solution, while the other with its onset at 1135 K can be ascribed to melting $Fe_{2-z}Cr_z(MoO_4)_3$. No effect was recorded that would correspond to melting $Fe_{2-u}Cr_uO_3$, because the DTA investigation was performed up to 1273 K. Such phases melt in the temperature range ca 1800–2500 K [15].

Solid solutions with different compositions, were examined by IR spectroscopy. Figure 3 shows IR spectra of the $FeVMoO_7$ phase (curve a), of the $Fe_{0.5}Cr_{0.5}VMoO_7$ solid solution (curve b) and of the $CrVMoO_7$ phase (curve c). The spectra are distinguished by a very similar distribution of their absorption bands.

IR spectrum of the $Fe_{0.5}Cr_{0.5}VMoO_7$ solid solution (Fig. 3, curve b) contains absorption bands with their maxima lying at 954, 895, 840, 714, 524 and 400 cm^{-1}, respectively. A broad, intensive band spreading over the range of 1100–650 cm^{-1} has its maximum at 954 cm^{-1} and two shoulders at 966 and 980 cm^{-1}. At this wavenumber range one can expect the occurrence of stretching vibrations in VO_4 and MoO_4 tetrahedra [7, 17, 18]. A shoulder at 980 cm^{-1} is most probably related with stretching vibrations of the shortest Mo–O linkage, having a character of double bond [7, 17]. Bands lying within the wavenumber range of 650–250 cm^{-1} may be related with the stretching vibrations in FeO_6 or CrO_6 octahedra and with the bending vibrations in VO_4 and MoO_4 tetrahedra. They may also have a mixed character [7, 17, 18].

A series of IR spectra characteristic of solid solutions of a $Fe_{1-x}Cr_xVMoO_7$ type with different compositions (x) have shown that with the increase in the degree of the

Cr^{3+} ion incorporation into the $FeVMoO_7$ lattice, a shift in the position of absorption bands towards higher wave numbers takes place.

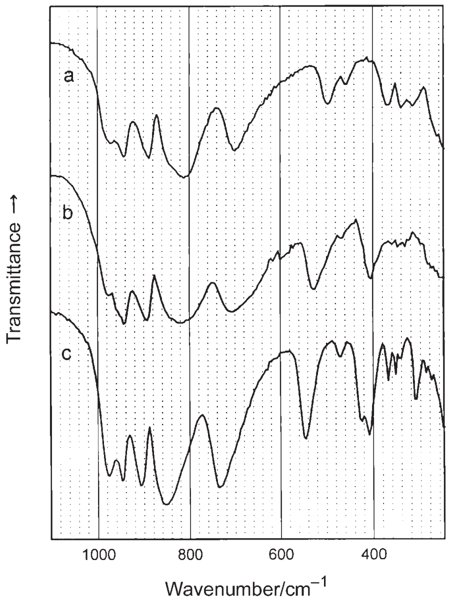

Fig. 3 IR spectra of a – $FeVMoO_7$; b – $Fe_{0.5}Cr_{0.5}VMoO_7$; c – $CrVMoO_7$

The change in the contents of samples exerts a strong impact on the position of absorption bands lying at 496 and 368 cm^{-1} of IR spectrum of the pure $FeVMoO_7$ phase (Fig. 3, curves a, b, c). The bands can most possibly be attributed to the stretching vibrations existing in CrO_6 and FeO_6.

Conclusions

1. Some continuous substitution solid solutions of a $Fe_{1-x}Cr_xVMoO_7$ type are formed in the $FeVMoO_7$–$CrVMoO_7$ system.
2. With increasing x in the $Fe_{1-x}Cr_xVMoO_7$ there takes place contraction in the crystal lattice of the arising solid solutions, measured in terms of decreasing volumes of unit cells and shift in the position of IR absorption bands towards higher wave numbers.
3. Solid $Fe_{1-x}Cr_xVMoO_7$ solutions melt incongruently. The melting temperature is increasing with the increase in the $CrVMoO_7$ content of initial mixtures and is within the range of 960–1073 K.
4. The solid products of incongruent melting of $Fe_{1-x}Cr_xVMoO_7$ solid solution for $x \leq 0.5$ is the $Fe_{4-y}Cr_yV_2Mo_3O_{20}$ solid solution phase, and for $x>0.5$, two solid solutions, i.e. $Fe_{2-z}Cr_z(MoO_4)_3$ and $Fe_{2-u}Cr_uO_3$.

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