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CONTROL OF PURITY AND CRYSTALLINITY OF MVO_4 COMPOUNDS (M = Al, Cr, Fe, In, Y, Nd) BY DTA*

M. Touboul and *A. Popot*

LABORATOIRE DE CHIMIE STRUCTURALE DES MATÉRIAUX —
BAT. F, UNIVERSITÉ P. ET M. CURIE, 4, PLACE JUSSIEU 75230
PARIS CEDEX 05, FRANCE

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Two aqueous methods were followed for the synthesis of MVO_4 (M = trivalent element). The first, with vanadium pentoxide and M nitrate yielded crystalline $InVO_4$ III and amorphous $FeVO_4$. The second method, using ammonium metavanadate and M nitrate, led to amorphous compounds with M = In, Fe, Cr or Al, and semi-amorphous compounds with M = Nd or Y. The crystallinity and purity of these products were examined by DTA.

Starting with amorphous compounds, two irreversible effects appeared; the first, at about 100°, was endothermic and corresponded to a considerable loss of water; the second was exothermic and corresponded to the crystallization of the compounds in the temperature range from 250 to 550°. Only $InVO_4$ presented two more irreversible exothermic peaks, corresponding to allotropic transformations, as proved by the X-ray diagrams.

A reversible effect then appeared, showing an invariant equilibrium corresponding to a peritectic process for $InVO_4$ III, $FeVO_4$, $CrVO_4$ and $AlVO_4$ at 1134, 870 and 765°, respectively; these temperatures agreed with the known M_2O_3—V_2O_5 phase diagrams.

The DTA curves of the semi-amorphous Nd and Y compounds showed only a loss of water at about 100°; crystallization then occurred gradually during heating; X-ray analysis confirmed these results.

The dry preparation of orthovanadates MVO_4 and their ranges of existence in the M_2O_3—V_2O_5 phase diagrams have already been reported [1–4]. Recently, the wet synthesis of In orthovanadate and its thermal properties were published [5, 6]. In this paper, the DTA and TG results on some orthovanadates obtained from aqueous solution ($FeVO_4$, $CrVO_4$, $AlVO_4$, $InVO_4$, $NdVO_4$ and YVO_4) are described. These measurements allowed a good control of the purity and the crystallinity of the MVO_4 compounds.

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Experimental

DTA was carried out with a home-made apparatus [7]. Pt, 10% Rh–Pt thermocouples were used in the range 20–1200° and the reference material was magnesia (MgO). The measurement conditions were the same for all compounds: the sample weight was 2 g and the heating rate was 2 deg/min, temperatures above 100° were given at ±5°. The solid products were studied by X-ray analysis (Guinier–de Wolff camera, Cu K_α radiation), IR spectroscopy (Perkin–Elmer 580) and TG (Setaram G70). Vanadium was determined quantitatively by chemical analysis.

In order to prepare the orthovanadates, two different methods were used. In the first (A), an aqueous nitrate solution of M^{3+} was added to V_2O_5 dispersed in boiling water. In the second method (B), a solution of ammonium metavanadate was mixed with a solution of $M(NO_3)_3$. The resulting precipitate was dissolved in concentrated nitric acid. The addition of ammonia solution led to the precipitation of the sought orthovanadate [5].

Results

In a recent work [8] $GaVO_4 \cdot 3H_2O$ was reported to be obtained by keeping mixed solutions of gallium nitrate and sodium vanadate at suitable pH for three months at 20°. Its thermal properties have also been studied. When the aqueous methods A and B were used, $GaVO_4$ was not observed; we obtained only $Ga(OH)_3$ and V_2O_5 or $NH_4VO_3 \cdot H_2O$. Our study of the binary system Ga_2O_3—V_2O_5 confirmed the absence of $GaVO_4$ and showed only one effect at 670°, which corresponded to an eutectic process

$$\text{liq E} \rightleftarrows V_2O_5 + Ga_2O_3.$$

The orthovanadates we obtained by these two methods are given in Table 1.

1) *With method A,* only crystalline $InVO_4$ and amorphous $FeVO_4$ were obtained. The DTA curve of $FeVO_4$ showed an important endothermic effect characterizing the loss of water and then two phenomena: the first one, exothermic, at 421°, corresponded to crystallization, and the second, endothermic, at 870°, corresponded to the peritectic process liq P + $Fe_2O_3 \rightleftarrows FeVO_4$.

The temperature of the latter phenomenon was the same as that observed in the phase diagram Fe_2O_3—V_2O_5 [1]. The systems Fe_2O_3—V_2O_5, Cr_2O_3—V_2O_5 [2], Al_2O_3—V_2O_5 [1, 3] and In_2O_3—V_2O_5 [5] presented the same aspect: a peritectic

Table 1 Physical aspect, nature and crystallinity of products obtained by methods A and B

		$InVO_4$	$FeVO_4$	$CrVO_4$	$AlVO_4$	$NdVO_4$	YVO_4
A	Physical aspect	yellow grains	brown viscous mixture	black mixture	orange grains		
	X-ray	crystalline $InVO_4$ III	amorphous	$V_2O_5 + Cr_2O_3$	V_2O_5	V_2O_5	V_2O_5
B	Physical aspect	yellow blocks	viscous brown	dark brown mixture	orange	very fine grains violet	white
	X-ray	amorphous	amorphous	amorphous	amorphous	semi-amorphous	semi-amorphous
	Water* content	$InVO_4 \cdot 2.6H_2O$	$FeVO_4 \cdot 3H_2O$	$CrVO_4 \cdot 3.2H_2O$	$AlVO_4 \cdot 3.3H_2O$	$NdVO_4 \cdot 1.6H_2O$	$YVO_4 \cdot 2H_2O$

* The water content was measured by TG on several preparations.

process for MVO_4 and an eutectic process between MVO_4 and V_2O_5; for example, Fig. 1 shows the In_2O_3—V_2O_5 diagram, where the orthovanadate was the same phase as that obtained in the aqueous method A ($InVO_4$ III).

2) *With method B,* the orthovanadates were obtained with different degrees of crystallinity.

The temperatures of the thermal effects which appeared in the DTA heating curves of the orthovanadates obtained by method B are given in Table 2.

a) $InVO_4$ [5] (Fig. 2)

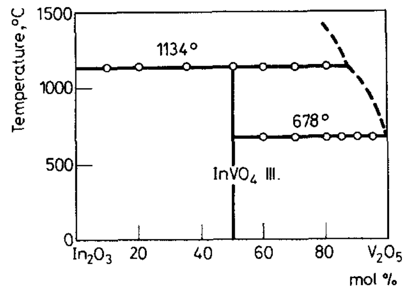

Fig. 1 Phase diagram of In_2O_3—V_2O_5 binary system

Table 2 DTA results on orthovanadates synthetized by method B

MVO_4	$InVO_4$	$FeVO_4$	$CrVO_4$	$AlVO_4$	$NdVO_4$	YVO_4
	100° endothermic	100° endothermic 330° exothermic	100° endothermic	100° endothermic	100° endothermic	100° endothermic
DTA	541° exothermic	410° exothermic	430° exothermic	266° exothermic		
increasing temperature	682° and 716° exothermic					
	1134° endothermic	870° endothermic	880° endothermic	765° endothermic		

Five thermal phenomena appeared: an appreciable effect at 100° showing the loss of water, followed by three exothermic effects, at 541, 682 and 716°, and an endothermic one at 1134°. The DTA was interrupted at 300, 541 and 716°, respectively, to permit examination of the powders by X-ray diffraction.

The compound obtained between 100 and 541° was amorphous. The product formed above 541° was crystalline and was identified as $InVO_4$. The effects at 682 and 716° corresponded to allotropic transformations. Above 716°, the product was $InVO_4$ III and was the same compound as described above (method A and In_2O_3—V_2O_5 diagram). All these effects were irreversible. The reversible phenomenon at 1134° related to the peritectic process

$$InVO_4\ III \rightleftarrows liq\, P + In_2O_3.$$

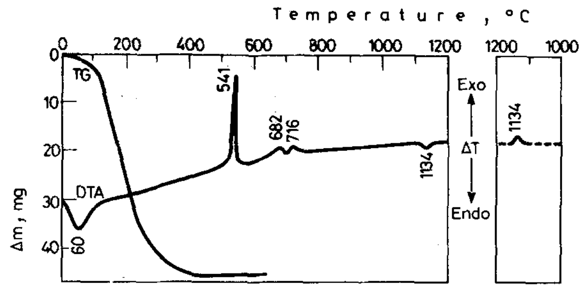

Fig. 2 DTA and TG curves of $InVO_4 \cdot 2.6H_2O$

b) $CrVO_4$ and $AlVO_4$ (Fig. 3)

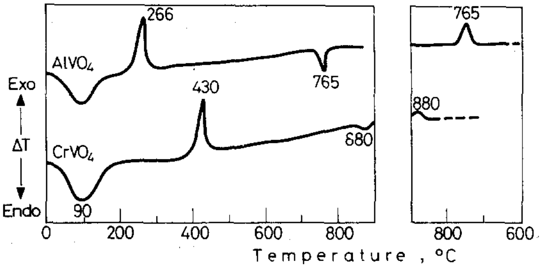

Fig. 3 DTA curve of $AlVO_4 \cdot 3.3H_2O$ and $CrVO_4 \cdot 3.2H_2O$

The DTA curves of Al orthovanadate and Cr orthovanadate showed an endothermic effect at 100°, corresponding to the loss of water. Exothermic and endothermic effects appeared at 266 and 765° for $AlVO_4$ and at 430 and 880° for $CrVO_4$. The first effect corresponded to the crystallization of these compounds. The highest temperature effect was characteristic of the equilibra liq $P+Al_2O_3 \rightleftarrows AlVO_4$ and liq $P+Cr_2O_3 \rightleftarrows CrVO_4$, which were found in the respective phase diagrams Al_2O_3—V_2O_5 [1, 3] and Cr_2O_3—V_2O_5 [2].

c) $FeVO_4$ (Fig. 4)

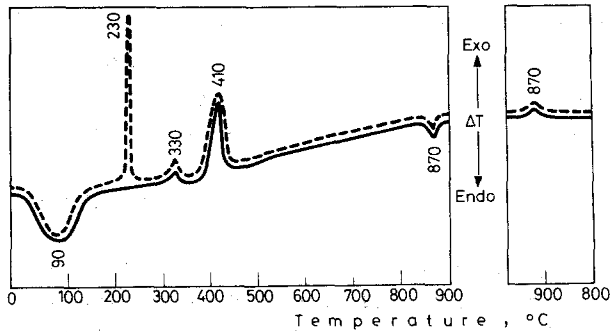

Fig. 4 DTA curve of $FeVO_4 \cdot 3H_2O$
DTA curve of impure $FeVO_4 \cdot 3H_2O$ (dotted line)

The DTA curve of Fe orthovanadate showed effects similar to those found for $AlVO_4$ and $CrVO_4$. The temperatures of these two phenomena were 410 and 870°, respectively. However, at 330°, an additional small exothermic effect appeared, which will be discussed below.

d) $NdVO_4$ and YVO_4

For these rare earth orthovanadates, only an endothermic effect appeared near 100°, relating to the loss of water. Since the melting points of these compounds are above 1200°, they were not studied further.

Discussion

1) The DTA for all the amorphous orthovanadates showed two similar initial effects: the loss of water and compound crystallization. As mentioned above, for the amorphous $FeVO_4$ (method B) an additional exothermic phenomenon occurred at 330°, before the crystallization. The hypothesis of a vitreous transformation could not be made because of its endothermic nature. This effect was attributed to a modification of the amorphous phase.

2) The DTA also allowed examinations of the purity of each of the orthovanadates obtained by methods A and B. An excess of V_2O_5 could be detected by a new endothermic effect relating to the eutectic equilibrium liq E $\rightleftarrows MVO_4 + V_2O_5$. The temperatures of this phenomenon were 678, 635, 665, 652 and 675° for $InVO_4$, $FeVO_4$, $CrVO_4$, $AlVO_4$ and YVO_4, respectively.

Only when method B was used did a very exothermic sharp effect appear between 230 and 260° (Fig. 4 for $FeVO_4$). As this phenomenon disappeared when more water was used during the preparation, an ammonium salt seemed to be obtained. A gravimetric study showed the presence of NH_3. This exothermic phenomenon corresponded to the decomposition of NH_4NO_3 [9]. The thermal effect intensities of the V_2O_5 or ammonium nitrate impurities were proportional to their amount in the sample.

3) The crystalline orthovanadates MVO_4 have already been studied by IR spectroscopy. Their infrared spectra [10–12] showed the characteristic absorption bands of the VO_4 and MO_6 polyhedra. The vibration ranges of all of the orthovanadates were similar. In order to compare with the published results, an infrared study of the same amorphous compounds was performed. The difference between the two spectra was the typical broadening of the bands and a decrease in their intensity at the crystalline-amorphous phase transition.

Conclusion

Using two aqueous methods, orthovanadates with different degrees of crystallinity were obtained. Method A led to crystalline $InVO_4$ III and amorphous $FeVO_4$. For all the compounds obtained by method B, the DTA began with an appreciable loss of water near 100°, followed for amorphous $InVO_4$, $FeVO_4$, $CrVO_4$ and $AlVO_4$ by their crystallization at 541, 410, 430 and 266, respectively. With $FeVO_4$, an additional effect at 330° has been attributed to a transformation of the amorphous phase. Only $InVO_4$ showed two irreversible allotropic phenomena, at 682 and 716°, characterized by the scheme $InVO_4\ I \xrightarrow{682^\circ} InVO_4\ II \xrightarrow{716^\circ} InVO_4\ III$. $InVO_4$, $FeVO_4$, $CrVO_4$ and $AlVO_4$ presented their peritectic equilibrium liq $P+M_2O_3 \rightleftarrows MVO_4$ at 1134, 870, 880 and 765°, respectively, in accordance with the known M_2O_3—V_2O_5 phase diagrams. The rare earth orthovanadates YVO_4 and $NdVO_4$ were obtained in the semi-amorphous state and became crystalline with increasing temperature. The purities of the orthovanadates were controlled by thermal analysis and these compounds were examined by X-ray diffraction and IR spectroscopy.

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Zusammenfassung — MVO_4^- (M = dreiwertiges Element) wurde nach zwei Methoden in wässrigem Medium dargestellt. Die erste, bei der von Vanadinpentoxid und dem Nitrat von M ausgegangen wird, ergibt kristallines $InVO_4$ III und amorphes $FeVO_4$. Die zweite, von Ammoniummetavanadat und dem Nitrat von M ausgehende Methode ergibt amorphe Produkte für M = In, Fe, Cr oder Al und halbamorphe für M = Nd oder Y. Kristallinität und Reinheit dieser Produkte wurden mittels DTA untersucht. Bei den amorphen Verbindungen treten zwei irreversible Effekte in Erscheinung, nämlich bei etwa 100° ein durch Abgabe einer beträchtlichen Wassermenge bedingter endothermer Effekt und ein exothermer im Temperaturbereich von 250–550°, der der Kristallisation der Verbindungen zuzuschreiben ist. Nur $InVO_4$ zeigt zwei weitere irreversible exotherme Effekte, die auf allotropische Umwandlungen zurückzuführen sind, wie durch röntgendiffraktometrie gezeigt werden konnte. Danach tritt ein reversibler Effekt ein, der ein invariantes Gleichgewicht eines peritektischen Prozesses für $InVO_4$ III, $FeVO_4$, $CrVO_4$ und $AlVO_4$ bei 1134, 870, 880 bzw. 765° anzeigt. Diese Temperaturen stimmen mit den bekannten Phasendiagrammen von M_2O_3—V_2O_5 überein. Die DTA-Kurven der halbamorphen Nd- und Y-Verbindung lassen nur den Wasserverlust bei 100° erkennen, die Kristallisation erfolgt dann nach und nach während des Aufheizvorganges, wie dusch Röntgenanalyse gezeigt werden konnte.

Резюме — Для синтеза в водной среде соединений MVO_4 (M — трехвалентных металл) были использованы два метода. В первом методе, при взаимодействии пятиокиси ванадия и нитратов индия и железа, получался кристаллический $InVO_4$ и аморфный $FeVO_4$. Во втором методе, взаимодействие метаванадата аммония и нитратов индия, железа, хрома и алюминия приводило к образованию аморфных соединений, тогда как аналогичное взаимодействие с нитратами неодима и иттрия — к полуаморфным соединениям. Чистота и кристалличность полученных соединений была изучена методом ДТА. В случае аморфных соединений наблюдались два термических эффекта: первый из них при температуре 100° являлся эндотермическим и соответствовал потере значительного количества воды, а второй, наблюдавшийся в области температур 250–550°, являлся эксотермическим и соответствовал кристаллизации этих соединений. Только для соединения $InVO_4$ наблюдалось больше эксотермических пиков, обусловленных, как показано их рентгенограммами, аллотропными превращениями. Для соединений $InVO_4$, $FeVO_4$, $CrVO_4$ и $AlVO_4$ при температурах, соответственно, 1134, 870, 880 и 765°, наблюдался обратимый эффект, относящийся к перитектическому процессу для этих соединений. Указанные температуры согласуются с известными, установленными на основе фазовых диаграмм систем M_2O_3—V_2O_5. ДТА-кривые полуаморфных соединений неодима и иттрия показали только потерю воды при 100°. Фазовый анализ этих соединений показал их постепенную кристаллизацию в процессе нагрева.