

Synthesis of AlVMoO_7

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Abstract

Studies on the mechanism of reaction leading to AlVMoO_7 have been made using X-ray diffraction and infrared spectroscopy. The XRD study of the process was carried out in a high-temperature X-ray attachment. The AlVMoO_7 phase can be synthesized by two methods. The investigations lead to the conclusion that both reactions run through a stage in which $\text{Al}_2(\text{MoO}_4)_3$ is involved. The IR spectra of the AlVMoO_7 and of samples after selected stages of the synthesis reaction are given. The diffraction pattern of AlVMoO_7 was indexed. The phase crystallizes in an orthorhombic system with the unit cell parameters: $a=0.53826(11)$ nm, $b=0.81771(11)$ nm, $c=1.27493(20)$ nm.

Keywords: AlVMoO_7 ; IR; Mechanism of reaction; Solid state reaction; XRD

1. Introduction

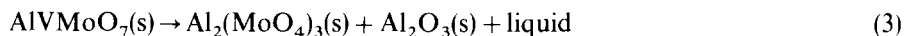
Study of the three-component system, Al_2O_3 – V_2O_5 – MoO_3 has proved that a hitherto unknown compound AlVMoO_7 occurs in the system [1]. The compound was obtained by two methods: (i) Reaction between the oxides in the solid state



(ii) Reaction of aluminium orthovanadate with molybdenum(VI) oxide



AlVMoO_7 is a yellow-green solid which melts incongruently at 963 ± 10 K according to [2]



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This publication presents the results of investigations carried out to measure the basic crystallographic parameters of AlVMoO_7 and to refine the mechanism of its synthesis. The main research techniques used were X-ray diffraction and IR spectroscopy, applied to the two methods of preparation of AlVMoO_7 . Both reactions take place in the solid state without mass change. Thus, it was believed that these analytical techniques would provide an in-depth knowledge of the process.

2. Experimental

In order to determine the precise positions of the diffraction lines characteristic of AlVMoO_7 , an internal reference standard, $\alpha\text{-Al}_2\text{O}_3$, was used. The indexing was performed using the program INDEXING [3], an integral part of the software package DHN-PDS.

The samples selected for monitoring the process of synthesis of the AlVMoO_7 phase were prepared from the reagents in proportions correlating with the composition of AlVMoO_7 . The reagents were homogenized by grinding three times for 15 min in an agate grinder. The reaction mixture was heated in a high-temperature X-ray attachment UVD-2000 (Bourestnik, Sankt-Petersburg, Russia) linked with an HZG-4/A2 diffractometer. When the temperature for the measurement had been reached and remained constant, the X-ray diffraction patterns of the samples were taken in situ and then used to establish the coexisting phases. The studies of reactivity were carried out at 673–873 K in 50° intervals. The degree of conversion was derived from the relation

$$\alpha = 1 - \frac{J_{060}^{\tau}}{J_{060}^0} \quad (4)$$

where J_{060}^{τ} is the intensity of the reflection (060) of MoO_3 after the time τ of the process, and J_{060}^0 is the intensity of the reflection (060) before the start of the synthesis.

The first materials to be investigated by IR spectroscopy were the reagents used in the syntheses of AlVMoO_7 by both methods, and $\text{Al}_2(\text{MoO}_4)_3$, which was considered to be the intermediate product of the reactions. To confirm the course of the reactions in the two methods, two samples were prepared for each case, with $\alpha \approx 0.5$ and $\alpha \approx 1$, respectively.

The measurement was made using a SPECORD M 80 spectrometer (Carl-Zeiss-Jena). The IR spectra were taken using the halide disc technique. The samples were mixed with KBr in a weight ratio of 1:300 and then pressed to pellets. The measurement was made in the frequency region 1400–300 cm^{-1} . The IR spectra were considered as a means for establishing the coexisting phases in the samples. The presence or absence of absorptions characteristic of the compounds that might appear during synthesis of AlVMoO_7 was taken into account.

3. Results and discussion

3.1. Indexing

Forty-five successive reflections in the range $2\theta = 10\text{--}61^\circ$ (Co K α) (Table 1) were taken for indexing. A number of solutions were considered of which the primitive orthorhombic unit cell was the best. The parameters of the unit cell refined by the method of least-squares are: $a = 0.53826(11)$ nm, $b = 0.81771(11)$ nm, $c = 1.27493(20)$ nm.

The figures of merit for the solution are: $F(20) = 56.33(0.0101, 35)$ and $F(45) = 37.18(0.0151, 80)$. $F(N)$ were calculated according to the formula [4]

$$F(N) = \frac{N}{N_{\text{poss}} \langle |\Delta(2\theta)| \rangle}$$

and given as

$$F(N) = X(\langle |\Delta(2\theta)| \rangle, N_{\text{poss}}) \quad (5)$$

where N is the number of observed lines, N_{poss} is the number of possible diffraction lines up to the N th observed line, $\langle |\Delta(2\theta)| \rangle$ is the average absolute discrepancy between the observed and calculated 2θ values, and X is the value of $F(N)$. The calculated volume of the unit cell V is 0.5611 nm^3 .

The density of AlVMoO_7 measured by the method described in Ref. [5] was $3.38 \pm 0.05 \text{ g/cm}^3$. The calculated density for four particles in the cell was also 3.38 g/cm^3 .

3.2. IR spectrum of AlVMoO_7

The IR spectra of V_2O_5 , Al_2O_3 , MoO_3 , AlVO_4 and $\text{Al}_2(\text{MoO}_4)_3$ were in agreement with the literature data [6–11].

Fig. 1 shows the IR spectra of AlVO_4 (curve a), $\text{Al}_2(\text{MoO}_4)_3$ (curve b) and AlVMoO_7 (curve c). The IR spectrum of AlVMoO_7 contains a broad band in the range $1100\text{--}990 \text{ cm}^{-1}$ and sharp peaks at 1040 , 1020 and 1004 cm^{-1} which can probably be assigned to the stretching mode of the $\text{M}=\text{O}$ bonds; the 1020 cm^{-1} band may be due to the $\text{V}=\text{O}$ bond and the 1004 cm^{-1} band to the $\text{Mo}=\text{O}$ bond. The positions of these bands are similar to those of the corresponding absorption bands in the IR spectra of V_2O_5 and MoO_3 [6, 8].

Another broad band in the $990\text{--}800 \text{ cm}^{-1}$ region, with a peak at 908 cm^{-1} and two shoulders on the side of the band lying at 980 and 944 cm^{-1} , as well as a sharp band with a 784 cm^{-1} peak, could be assigned to the stretching vibrations of $\text{M}\text{--}\text{O}\text{--}\text{M}'$ bonds in tetrahedra of VO_4 , MoO_4 or AlO_4 [9–12]. Within this frequency region, there may be a stretching mode in the $\text{M}\text{--}\text{O}\text{--}\text{M}'$ bridge-linking polyhedra [12].

The broad, intensive band with its maximum at 592 cm^{-1} may be developed by the stretching vibration of the $\text{O}\text{--}\text{Al}\text{--}\text{O}$ bonds in the AlO_6 octahedra [9, 10, 12]. The broad band with a number of sharp peaks at 440 , 402 , 370 , 336 and 300 cm^{-1} may represent the deformation mode of the $\text{M}\text{--}\text{O}\text{--}\text{M}'$ or $\text{O}\text{--}\text{M}\text{--}\text{O}$ bonds in polyhedra of MoO_4 , VO_4 , AlO_4 or AlO_6 . It may also be of mixed character.

Table 1
The results of indexing the AlVMoO₇ X-ray powder diffraction pattern

No.	h k l	d_0/nm	d_c/nm	$I/I_0 \%$
1	0 1 1	0.68942	0.68831	3
2	0 0 2	0.63762	0.63746	8
3	0 1 2	0.50254	0.50275	2
4	1 1 0	0.44936	0.44960	61
5	1 1 1	0.42391	0.42400	100
6	1 0 2	0.41065	0.41126	14
7	0 2 0	0.40905	0.40886	15
8	0 2 1	0.38938	0.38933	6
9	0 1 3	0.37686	0.37709	89
10	1 1 2	0.36743	0.36741	7
11	0 0 4	0.31873	0.31873	14
12	1 2 1	0.31553	0.31546	60
13	1 1 3	0.30880	0.30884	12
14	0 1 4	0.29701	0.29697	1
15	1 2 2	0.28982	0.28995	66
16	1 0 4	0.27424	0.27425	9
17	2 0 0	0.26921	0.26913	41
18	0 3 1	0.26657	0.26665	3
19	1 1 4	0.26009	0.26002	4
20	0 3 2	0.25068	0.25062	8
21	2 0 2	0.24786	0.24794	2
22	1 3 0	0.24337	0.24317	3
23	1 3 1	0.23884	0.23886	3
24	2 1 2	0.23731	0.23727	10
25	0 3 3	0.22946	0.22944	11
26	1 3 2	0.22731	0.22720	9
27	2 2 0	0.22457	0.22480	5
28	2 2 1	0.22146	0.22138	18
29	2 1 3	0.21913	0.21906	19
30	0 2 5	0.21626	0.21636	1
31	0 0 6	0.21252	0.21249	4
32	1 3 3	0.21101	0.21106	3
33	0 3 4	0.20716	0.20715	2
34	0 4 1	0.20202	0.20185	3
35	2 2 3	0.19873	0.19871	1
36	1 0 6	0.19771	0.19764	3
37	0 4 2	0.19450	0.19466	1
38	1 3 4	0.19333	0.19333	14
39	1 4 1	0.18893	0.18900	8
40	0 2 6	0.18862	0.18854	14
41	0 3 5	0.18610	0.18621	1
42	0 4 3	0.18428	0.18422	4
43	2 3 2	0.18342	0.18341	30
44	2 1 5	0.18055	0.18053	5
45	1 2 6	0.17789	0.17794	3

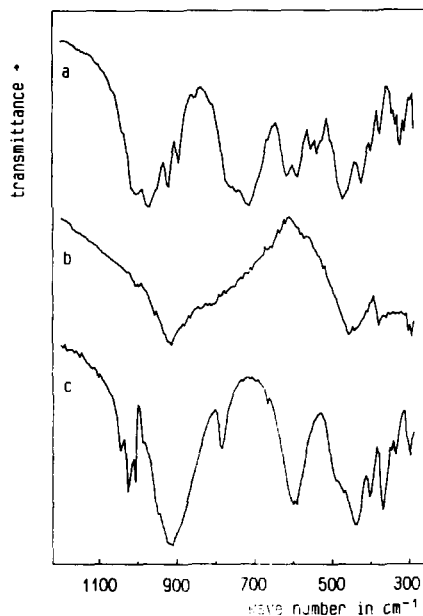


Fig. 1. IR spectra of: a, AlVO_4 ; b, $\text{Al}_2(\text{MoO}_4)_3$; c, AlVMoO_7 .

The IR spectrum of the AlVMoO_7 suggests that the compound is built of VO_4 , MoO_4 and AlO_4 tetrahedra, as well as AlO_6 octahedra. The occurrence of absorption bands due to the stretching vibrations of the bridging bonds, $\text{M-O-M}'$, suggests linkage of suitable coordination polyhedra, but fails to provide information about their arrangement. Hence, these studies have only a qualitative character, allowing, however, the identification of AlVMoO_7 in the mixtures.

3.3. Synthesis of AlVMoO_7 from oxides

X-ray diffraction studies on the synthesis of AlVMoO_7 from oxides made in situ with the use of a high-temperature X-ray attachment have shown that the reaction started very slowly at 773 K. Measurements made during several hours of heating at 823 K showed a considerable progress in the reaction. XRD studies implied that the first stage of the synthesis resulted in negligible amounts of AlVMoO_7 and $\text{Al}_2(\text{MoO}_4)_3$. During the second stage of the reaction, an increase in the intensity of reflections characteristic of $\text{Al}_2(\text{MoO}_4)_3$ can be observed, while the intensity of reflections produced by AlVMoO_7 was still low. However, the intensity of the reflections due to MoO_3 decreased considerably. When the total amount of MoO_3 detectable by XRD was actually processed ($\alpha \approx 1$), reflections characteristic of $\text{Al}_2(\text{MoO}_4)_3$, V_2O_5 and AlVMoO_7 appeared in the X-ray diffraction patterns of reaction mixtures. From that moment on, the amount of the AlVMoO_7 steadily increased, whereas that of V_2O_5 and $\text{Al}_2(\text{MoO}_4)_3$ decreased. Obtaining pure AlVMoO_7 took a considerable time.

In order to confirm the XRD results, two samples were examined by IR spectroscopy. One of the samples, prepared from the oxides V_2O_5 , MoO_3 and Al_2O_3 mixed in the proportion 1:2:1, was heated in a high-temperature X-ray attachment at 863 K for 10 min. X-ray diffraction studies showed that the resultant sample, for which $\alpha \approx 0.5$, contained considerable amounts of MoO_3 , V_2O_5 and $Al_2(MoO_4)_3$ and traces of $AlVMoO_7$. The other sample was heated at 863 K for 210 min. The degree of conversion was $\alpha \approx 1$, and the sample contained considerable amounts of V_2O_5 and $Al_2(MoO_4)_3$ with a small amount of $AlVMoO_7$.

Fig. 2 shows the IR spectrum of the mixture of oxides as well as IR spectra of sample Nos. 1 and 2. From the vibrational bands produced by the mixture of V_2O_5 , MoO_3 and Al_2O_3 (Fig. 2, curve a), a narrow band at 1020 cm^{-1} can be discerned, which may account for the vanadium pentoxide [6]; it appears to be the only selective band to characterize V_2O_5 . The bands at 994 and 868 cm^{-1} are characteristic of MoO_3 only. The frequency regions characteristic of Al_2O_3 could not be separated from those of the two other oxides. The IR spectrum of the sample with $\alpha \approx 0.5$ (Fig. 2, curve b) includes, apart from absorption bands of the initial mixture, an intensive absorption band with a maximum at 908 cm^{-1} . In addition, the molybdenum(VI) oxide bands at 994 and 868 cm^{-1} have markedly lower intensities. The intensities of the other bands decrease to a negligible extent. The IR spectrum does not give an indication of the presence of $AlVO_4$ or $AlVMoO_7$.

Thus the sample contained much less MoO_3 , whereas the amount of V_2O_5 decreased only to a slight extent. From the spectrum, the quantitative change in Al_2O_3 could not

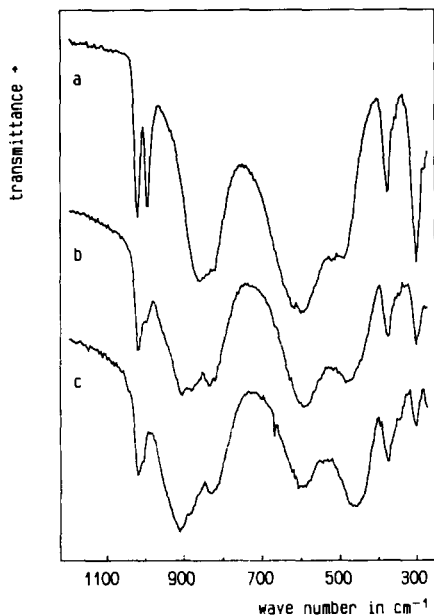


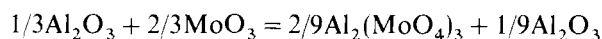
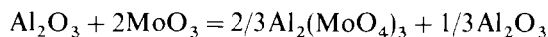
Fig. 2. IR spectra of: a, initial mixture of Al_2O_3 , V_2O_5 and MoO_3 ; b, sample for which $\alpha \approx 0.5$; c, sample for which $\alpha \approx 1$.

be established. The IR spectrum also showed a 908 cm^{-1} band, characteristic of $\text{Al}_2(\text{MoO}_4)_3$ and AlVMoO_7 . As there were no other bands distinctive of AlVMoO_7 , the 908 cm^{-1} band was assumed to characterize mainly $\text{Al}_2(\text{MoO}_4)_3$. Accordingly, one can conclude that molybdenum(VI) oxide reacted with Al_2O_3 to give aluminium molybdate(VI); the slight decrease in the amount of V_2O_5 suggested that the oxide was involved to some extent in the reaction taking place in the mixture.

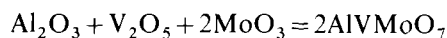
The IR spectrum of the other sample (Fig. 2, curve c) (in which $\alpha \approx 1$) was essentially different from the IR spectra of both the initial mixture and that of the sample with $\alpha \approx 0.5$. The vibrational spectrum of the sample lacked the 994 cm^{-1} absorption band, characteristic of molybdenum(VI) oxide. The most intensive band in the IR spectrum of the sample was the band at 908 cm^{-1} , characteristic of both $\text{Al}_2(\text{MoO}_4)_3$ and AlVMoO_7 . The occurrence of AlVMoO_7 in the sample can also be confirmed by the shoulders at frequencies 1040 and 784 cm^{-1} .

The high intensity of the band lying at 908 cm^{-1} , according to XRD results, indicated the occurrence of $\text{Al}_2(\text{MoO}_4)_3$. The other bands of the IR spectrum indicated the presence of V_2O_5 and AlVMoO_7 in the sample. This proved that the molybdenum(VI) oxide reacted completely with Al_2O_3 to yield $\text{Al}_2(\text{MoO}_4)_3$. The bands characteristic of AlVMoO_7 found in the IR spectrum of the sample were indicative of a reaction giving rise to AlVMoO_7 .

Thus the experimental results suggested that the reaction between the oxides leading to AlVMoO_7 took the following route



Nonetheless, direct inter-reaction of the oxides should not be precluded from the initial stage of the synthesis



In contrast to the speed of the reaction yielding AlVMoO_7 either from oxides or with the participation of $\text{Al}_2(\text{MoO}_4)_3$, the reaction speed of the synthesis of $\text{Al}_2(\text{MoO}_4)_3$ seemed high. No AlVO_4 was detectable in the reaction mixtures.

3.4. Synthesis of AlVMoO_7 from AlVO_4 and MoO_3

X-ray diffraction study has shown that the inter-reaction of AlVO_4 and MoO_3 starts at 773 K . Analysis of the degree of conversion indicates that, at similar temperatures after similar times, the degree of conversion of the reaction involving AlVO_4 and MoO_3 was much higher than that of the reaction between the oxides. The reaction mixtures contained $\text{Al}_2(\text{MoO}_4)_3$ in addition to AlVO_4 , MoO_3 and AlVMoO_7 . The course of the synthesis of AlVMoO_7 from AlVO_4 and MoO_3 suggests that the reaction proceeds through a stage in which $\text{Al}_2(\text{MoO}_4)_3$ is formed as an intermediate product. The

intensity of the reflections characteristic of $\text{Al}_2(\text{MoO}_4)_3$ first increased and then decreased with the progress of the synthesis process. However, traces of AlVMoO_7 in the reaction products were detectable at the very beginning of the reaction. When $\alpha \approx 1$, the reaction mixture contained AlVMoO_7 , $\text{Al}_2(\text{MoO}_4)_3$ and AlVO_4 , the amounts of the latter two compounds decreasing gradually with the progress of the reaction.

IR spectroscopy was applied to monitor the actual process of the inter-reaction of AlVO_4 and MoO_3 in two samples. The first sample, with $\alpha \approx 0.5$, was prepared by heating a mixture of AlVO_4 and MoO_3 in the mole proportion 1:1, in a high-temperature X-ray attachment at 833 K for 13 min. XRD phase analysis showed considerable amounts of MoO_3 , AlVO_4 , $\text{Al}_2(\text{MoO}_4)_3$ and a small amount of AlVMoO_7 in this sample. The second sample, with $\alpha \approx 1$, was heated at 833 K for 180 min and after such treatment contained a considerable amount of AlVMoO_7 and relatively small amounts of AlVO_4 and $\text{Al}_2(\text{MoO}_4)_3$.

Fig. 3 illustrates the infra-red spectra of samples 1 and 2, in addition to the IR spectrum of the initial mixture of AlVO_4 and MoO_3 . The IR spectrum of the initial mixture (Fig. 3, curve a) contains the vibrational bands of AlVO_4 , but no bands selective of MoO_3 . Thus it does not allow the spectroscopic monitoring of changes in the oxide content at different degrees of conversion. The IR spectrum of the sample with $\alpha \approx 0.5$ (Fig. 3, curve b) differs from the spectrum of the AlVO_4 – MoO_3 initial mixture in the number and intensity of the bands. Their positions do not confirm or exclude the occurrence of $\text{Al}_2(\text{MoO}_4)_3$ or AlVMoO_7 . According to XRD measurements, the

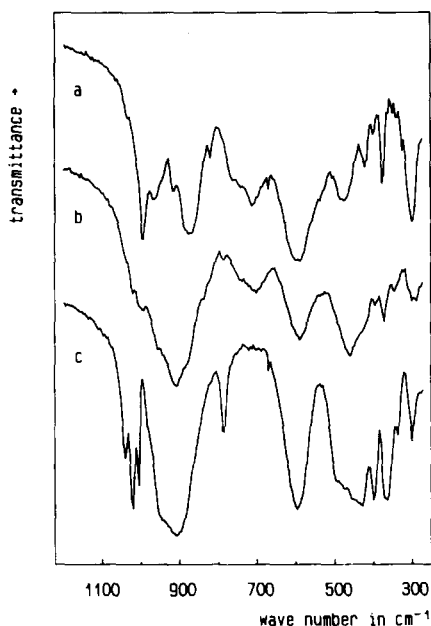
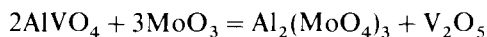


Fig. 3. IR spectra of: a, initial mixture of AlVO_4 and MoO_3 ; b, sample for which $\alpha \approx 0.5$; c, sample for which $\alpha \approx 1$.

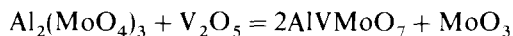
intensive absorption band at 908 cm^{-1} gives clear indication of the presence of $\text{Al}_2(\text{MoO}_4)_3$.

The infra-red spectrum of the sample for which $\alpha \approx 1$ (Fig. 3, curve c) is essentially different from the IR spectrum of the $\text{AlVO}_4\text{--MoO}_3$ initial mixture and the sample with $\alpha \approx 0.5$. Only the bands at 962 and 420 cm^{-1} are not due to AlVMoO_7 . The positions and intensities of the other bands reveal the presence of AlVMoO_7 . However, they do not exclude the possibility of the presence of $\text{Al}_2(\text{MoO}_4)_3$, because the frequency regions characteristic of the phase coincide with some of those characteristic of AlVMoO_7 . However, the 962 and 420 cm^{-1} absorptions may be indicative of AlVO_4 , which could imply that the reaction leading to AlVMoO_7 has not reached completion.

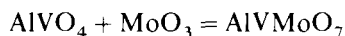
These results suggest the following reaction



The diffraction lines characteristic of V_2O_5 were not found, which implies that the liberated V_2O_5 reacted immediately, according to the equation



A direct reaction may also take place



The studies on the mechanism of the inter-reaction between the oxides or between AlVO_4 and MoO_3 , carried out using a high-temperature X-ray attachment, indicate that the synthesis of AlVMoO_7 comprises a stage at which $\text{Al}_2(\text{MoO}_4)_3$ arises as an intermediate product. Infra-red spectroscopy confirms that such a reaction mechanism takes place with the oxides. Conversely, the absorption bands due to the reaction products of the synthesis carried out using AlVO_4 and MoO_3 do not show any evidence of the mechanism proposed for the reaction.

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