X-ray powder diffraction study
of chromium-vanadium oxide compounds
prepared by "soft chemistry" methods

O. Pozdnyakova[1], J. Megyeri[1], E. Kuzmann[2], L. Szirtes[1*]

[1] *Institute of Isotopes,
Hungarian Academy of Sciences,
P.O. Box 77, H-1525 Budapest, Hungary*

[2] *Department of Nuclear Chemistry,
Research Group of Nuclear Methods in Structural Chemistry HAS,
Eötvös Lóránd University,
P.O. Box 32, H-1518 Budapest, Hungary*

Abstract: A novel aqueous method was used to synthesise mixed chromium-vanadium oxide hydrates with various chromium content, via the reaction of peroxo-polyacids of chromium and vanadium. The resulting materials are gelatinous. The dehydration of the gels result in a brown coloured amorphous powder. Depending on the chromium content, the compounds have a different characteristic crystallisation temperature upon the further heating. The crystalline compounds, except for the low chromium ones, go on a phase transition and decompose with increasing temperature.

By refining the XRPD measurement data of the compounds, the type and parameters of the unit cells were determined. The experimental data were in concordance with the calculated values, using the PWC code. The lattice parameters and the crystalline structure were changed with the variation of chromium content.

© Versita Warsaw and Springer-Verlag Berlin Heidelberg. All rights reserved.

Keywords: Sol-gel synthesis, crystal structure, x-ray diffraction, chromium-vanadium oxide

1 Introduction

During the previous two decades, there has been an interest in various chromium-vanadium oxides because of their use in oxidative catalysis, in the field of adsorption-, sensor-,

---

* E-mail: szirtes@iki.kfki.hu

magnetic-, and ceramic technologies. Additionally, their alkali metal intercalates can be potentially applied as secondary catode material for lithium batteries [1].

Possible ways to synthesize such compounds are the ceramic (calcination at high temperature) and the so-called "soft chemistry" ones. The latter include the sol-gel, hydrothermal and co-precipitation methods [2–4]. We have recently reported on a novel aqueous method used to synthesise the chromium-vanadium oxide-hydrates via the reaction of peroxo-polyacids that of chromium and vanadium [5].

Only a few works (including extensive discussion) on crystal properties have been published [6, 7] regarding the structure of chromium-vanadium- oxide materials. Zavalij and Whittingham [8] reported a detailed work in which they gave numerous comprehensive models of possible structural variation of different vanadium oxide compounds.

The goal of the present work was to investigate the structure of a series of chromium-vanadium oxide samples with different chromium content, prepared by a novel aqueous method. This paper reports our study on three selected samples (with different chromium content) exhibiting a nano-phase character based on the data of preliminary XRPD measurements.

2   Experimental

2.1   Synthesis

A series of samples (15 them) with Cr/V atomic ratio $[z]$ in the range of $0.008 < z < 3$, were prepared due to the reaction of peroxo-polyacids of chromium and vanadium. The typical process was as follows: V_2O_5 (Aldrich, p.a.) was dissolved in H_2O_2 (Fluka, p.a.) at 5 ± 1 °C. The various amounts of 0.001 M aqueous solution of CrO_3 (reanal, p.a.) than were added, at vigorous stirring, to the 0.5 M solution of peroxo-vanadate. The pH of the initial solution was in the range of 1.66-1.77. The reacting solutions were maintained at 5 ± 1 °C for 1 hour; then the temperature was slowly increased to 25 °C. At this temperature a gelatinous process occurred. The dark brown gelatinous substance was then dehydrated at 60 °C, till a constant weight was obtained. This process resulted in a dark brown powder- like material.

2.2   Analysis

The Cr/V ratios of the final compounds were verified by means of a ICP (GBP-Integra XM) analysis. The results were presented earlier [5].

The XRD study was performed with Bragg-Brentano geometry, using powder samples with a Philips PW-1050/25 powder diffractometer (at 45 kV and 35 mA) with the β filtered Cu$_{k\alpha}$ radiation (λ= 1.540598). The powder diffraction patterns were scanned in increments of 0.01 °(2Θ) with fixed accounting times (20 s) in the range of 2Θ = $-120°$. Upon completion of the data collection, the first few lines of the pattern were re-measured to control the stability of the X-ray source. The diffraction patterns were

evaluated using "EXRAY" peak searching computer software [9]. For refinement, the Ritveld method [10] was used. For modeling, the Powder Cell 2.3 software was used [11]. During the evaluation, an effect of the texture on the line intensity was also taken into consideration. In addition to the XRPD study, thermal analytical investigations (using DTATG technique) were also conducted. The results were published earlier [12].

3   Results and discussion

The oxidation state of vanadium and chromium in the initial materials has been deduced by chemical redoxtitration and was found 5 and 3, respectively.

Samples with a chromium-vanadium ratio of 0.067, 0.5 and 1.0 have been selected for the structural investigations. The transformation of hydrated phases upon heat treatment were shown by the DTA-TG results. It was determined that upon heating, they became anhydrous and crystalline at different temperatures with an increasing of the chromium content of the compound [13].

The general profile of the XRPD sample patterns treated at 60 °C is characteristic of amorphous material containing the same sign of micro-crystals, independently from the chromium content of the compound.

The XRPD sample patterns **with a Cr/V ratio of = 0.067** at various temperatures in comparison with that of V_2O_5 are presented in Fig. 1. The XRPD sample patterns showed crystallisation occurring (in agreement with the thermal analytical data) at 280 °C and concluding the process when the temperature had reached 330 °C.
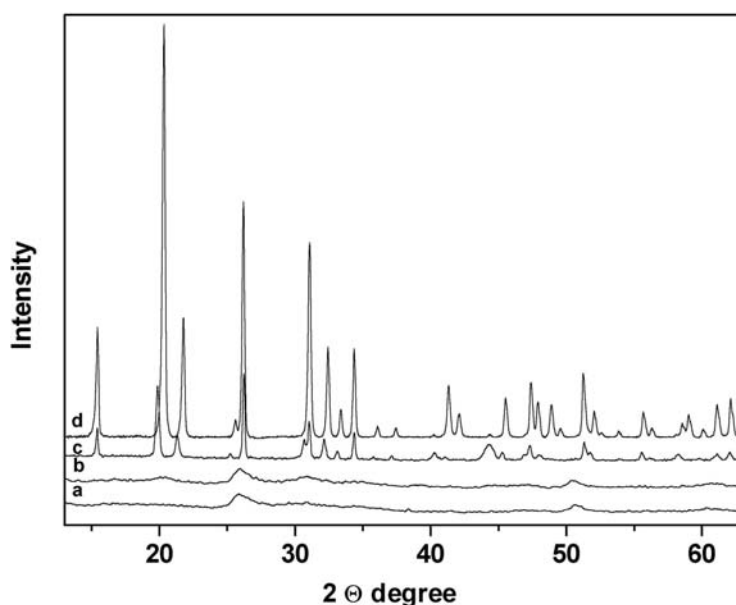

Fig. 1 A fragment of the XRPD sample pattern with composition of $Cr_{0.13}V_2O_5$ a – 200 °C; b – at 280 °C; c – at 330 °C; d – V_2O_5.

Attempts were made to understand the XRPD sample patterns in details. The optimum evaluations were found when an orthorhombic form was considered for the sample.

Comparing the XRPD patterns of V_2O_5 and $Cr_{0.13}V_2O_5$ ($z=0.067$) we found that the majority of the peaks are in concordance to each other.

Based on a refined pattern analysis a structural periodicity of the $Cr_{0.13}V_2O_5$ was indicated. The cell parameters were derived by indexing the 50 corresponding well determined reflections of the XRPD patterns. The existence of hk0 reflections suggests a random layer structure; this structure consists of layers which are arranged in a parallel, equidistant and random fashion, parallel to the layer and rotating about the axis "c". These data and that presented by M. Hibito et al. [14] are in concordance. This indicates that the (00l) reflection is a two-dimensional lattice reflection of the (hk) plane and not a general reflection of (hkl) one. The d spacing obtained from the (001) reflection was 4.3891 Å for sample $Cr_{0.13}V_2O_5$; this value approximates that of V_2O_5. Consequently, it can be proposed, that the crystal structure of the mixed chromium-vanadium oxide compound with low chromium content is very close to that of the structure of V_2O_5.

It is well known that V_2O_5 has an orthorhombic layered structure built up from square pyramids which share edges and corners and which lead to V_2O_5 sheets linked together via weak V-O interactions parallel to the "c"-axis [15]. Based on these similarities, we propose the same P mmn space group position. Taking into consideration this symmetry condition, the XRD patterns were calculated and compared to those which were obtained experimentally. As it is shown in Fig. 2 a good conformity exists between them.
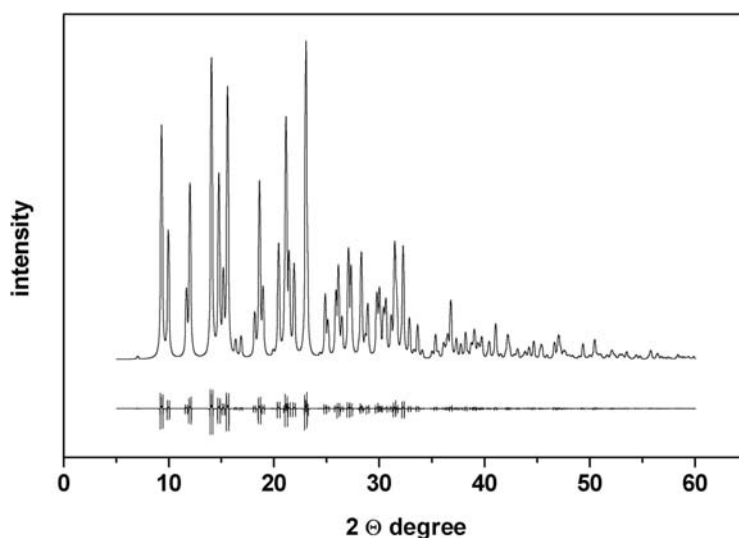

Fig. 2 A fragment of the XRPD patterns of $Cr_{0.13}V_2O_5$ in comparison with that of the calculated one.

The cell parameters were derived from 50 reflections. They are: a=11.605 Å, b=3.557 Å, and c=4.388 Å. Additional parameters were calculated: atoms in a-symmetric unit 6, atoms in unit cell 18 generated positions, volume of cell 181.19 Å^3, relative mass of cell 409.28, X-ray density 3.7508 g.cm^{-3}, and mass absorption coefficient 0.00 cm^2.g^{-1}. Comparing the cell parameters with those for sol-gel V_2O_5 (a=11.525 Å, b=3.564 Å, and c=4.371 Å), a slight increase in "c" parameter could be observed which corresponds to an

increase of the unit cell volume. On the other hand, the "b" parameter characteristic of distances V – O – V is unchanged. The above data indicated that the chromium atoms were located in the 2b sites, near the centre of average plane formed by four oxygen atoms of the V_2O_5 sheet. Similar results were presented by Cato et al. [6] for low chromium containing vanadium oxide.

The two oxygen atoms O4 and O4[1], had to be added along with the "c"-direction, to ensure an octahedral oxygen environment the for chromium atom. The distance of O4-Cr-O4[1] was found close to the "c" value.

The calculations were made on the basis of the following ground data:
- Herman-Mauguin: P mmn
- Laue group: m m m
- Point group: m m m
- Positions: 4 f x, 1/4, z -x+1/2, 1/4, z -x, 3/4, -z x+1/2, 3/4, -z

The positional parameters of the atoms (Table 1), the calculated bond length and bond angles (Table 2) are presented, respectively.

Table 1 Positional and thermal parameters of ions in $Cr_{0.13}V_2O_5$.

Ion	x	Y	z	B_{iso}
V	0.1019	0.25	0.1155	3.1
Cr	0.25	0.75	0.0114	2.0
O1	0.1139	0.25	0.4723	2.8
O2	0.9268	0.25	0.9952	2.4
O3	0.25	0.25	0.0056	1.9
O4	0.25	0.75	0.5121	0.9

Table 2 Selected bond length in Å and bond angles of $Cr_{0.13}V_2O_5$.

No	distance		angle	
1	V-O1	1.552	O1-V-O3	100.592
2	V-O3	1.785	O1-V-Cr	96.914
3	V-Cr	2.515	O1-V-O2	105.903
4	V-O2	1.873	O2-Cr-O2	178.382
5	O2-Cr	2.052	O2-Cr-O4	90.809
6	O3-Cr	1.778	O3-Cr-O4	90.820
7	CrO4	2.197	O3-Cr-V	45.213
8			O3-V-Cr	45.009
9			O3-V-O2	95.803
10			Cr-V-O1	96.915

A (001) projection of the crystal structure of $Cr_{0.13}V_2O_5$ is given in Fig. 3.

The environment for the chromium ion, mentioned above, corresponds to the V^{5+} - Cr^{3+} -V^{5+} distances equal to 5.030 Å, i.e. distance of V^{5+}- Cr^{3+} equal to 2.515 Å.

According to the charge balance of the chemical formulae of this compound, only 13 % of the possible Cr^{3+} sites are occupied, i.e. that there are numerous octahedral of V_2O_5 without Cr^{3+} ions.
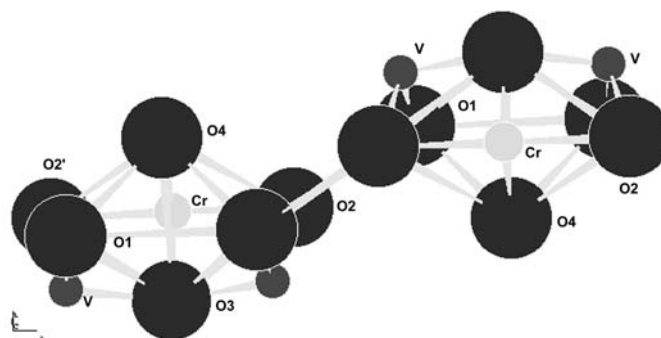

Fig. 3 A 001 projection of structure of $Cr_{0.13}V_2O_5$.

The sample with the ratio of Cr/V ≅ 0.5 contains 39.8 % and 20.34 % vanadium and chromium ions, respectively, as determined by chemical analysis. Based on analytical data, the $Cr_2V_4O_{13}$ composition is proposed for this compound. This compound (in agreement with thermal analytical data) became crystalline at temperature 650 °C.

Regarding this sample, the best evaluation for the monoclinic structure was found within the P_{12} space group. Taking these symmetry conditions into consideration, the XRPD pattern was calculated and compared to those which were experimentally obtained (50 Bragg peaks). Negligible discrepancies were found between the measured and calculated patterns, as it is shown on the Fig.4.
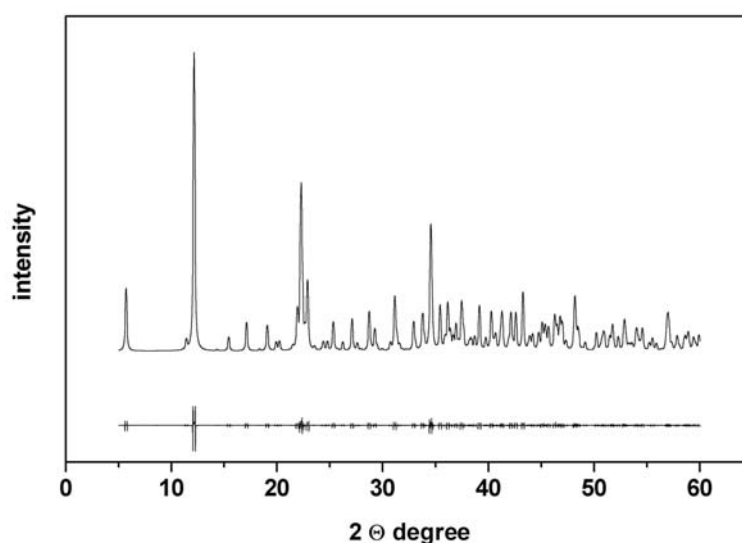

Fig. 4 A fragment of XRPD pattern of $Cr_2V_4O_{13}$sample in comparison with that of the calculated one.

Refining the XRPD patterns, the following parameters were derived: a=8.267 Å, b=9.303 Å, c=7.552 Å and β=101.8 °. The d spacing obtained from the (-101) reflection was 6.116 Å, at 2Θ=14.47 °. The volume of unit cell=568.62 Å^3. The relative mass was 2063.01. The X-ray density was 6.024 g.cm^{-3} and the mass absorption coefficient was 148.95 cm^2.g^{-1}. In the unit cell are 76 atoms in generated positions, from them 19 are in asymmetric units 145th row [17].

Comparing these data with those presented by Filipek et al. [16] a slight difference in unit cell parameters were found. This discrepancy is probably due to the differences in syntheses.

The calculations were carried out on the basis of the following ground data:
- Hermann-Mauguin: P 1 2_1/a1
- Laue group: 2/m unique axis b
- Point group: 2/m
- Position: 4 e x, y, z -x+1/2, y+1/2, -z -x, -y, -z x+1/2, -y+1/2, z

The positional parameters of the atoms (Table 3), the selected bond length (Table 4) and bond angles (Table 5) are presented, respectively.

On the basis of our calculated data, we assume an octahedral arrangement of oxygen atoms around vanadium ion in the layers, similarl to that of the V_4O_{13} structure [17] example.

Table 3 Positional and thermal parameters of the ions in $Cr_2V_4O_{13}$.

Ion	x	y	z	B_{iso}
V1	0.5480	0.5474	0.5869	0.28
V2	0.2597	0.0453	0.6837	0.25
V3	0.4360	0.2322	0.3025	0.28
V4	0.1057	0.7988	0.3576	0.31
O1	0.1915	-0.1580	-0.1275	0.52
O2	-0.0866	0.3284	-0.0480	0.58
O3	0.2144	-0.0209	0.1790	0.41
O4	-0.2714	-0.1465	0.0190	0.55
O5	0.8779	0.2423	0.6378	0.52
O6	0.5205	0.5640	0.4190	0.44
O7	0.0225	0.7275	0.5630	0.44
O8	0.5865	0.7301	0.7198	0.37
O9	0.4634	0.4310	0.0969	0.58
O10	0.3982	0.2820	-0.2140	0.61
O11	0.3075	0.0755	0.4700	0.44
O12	0.7490	0.0510	0.3160	0.51
O13	0.0590	0.5095	0.2745	0.57
Cr1	0.9200	0.4290	0.7580	0.37
Cr2	0.7561	0.6400	0.6010	0.31

Table 4 Selected bond length in Å for $Cr_2V_4O_{13}$ compound.

No		distance	No		distance
1	V1 - O6	1.2540	27	O2 - Cr2	2.2375
2	V1 - O8	1.9610	28	O3 - O5	2.6786
3	V1 - O3	1.4260	29	O3 - Cr2	1.3267
4	V1 - O6	1.1797	30	O3 - O9	2.4955
5	V2 - O11	1.7533	31	O3 - O11	2.3528
6	V3 - O11	2.3280	32	O3 - Cr1	1.8874
7	V3 - O4	1.3423	33	O4 - O7	1.9511
8	V3 - O2	1.3108	34	O4 – O10	2.3427
9	V3 - O5	1.2655	35	O4 - O12	3.0670
10	V3 - O8	0.4130	36	O4 - O6	2.8225
11	V3 - O13	2.1615	37	O5 - O12	3.0253
12	V4 - O7	1.9388	38	O5 - Cr1	1.9691
13	V4 - O4	2.0041	39	O5 - O4	1.6787
14	V4 - O5	0.4054	40	O5 - O7	1.8886
15	V4 - O8	1.0578	41	O5 - O8	1.0633
16	V4 - O9	1.4266	42	O5 - O9	1.8121
17	O1 - O7	2.6849	43	O5 - O11	3.1794
18	O1 - O6	1.7615	44	O5 - O10	2.7095
19	O1 - O10	1.3901	45	O5 - O13	2.4309
20	O1 - O12	1.8818	46	O6 - O8	2.7095
21	O1 - O4	2.9871	47	O6 - O9	2.6804
22	O2 - O5	2.4665	48	O6 - Cr2	2.2543
23	O2 - Cr1	1.7484	49	O6 - O2	2.6642
24	O2 - O3	3.1416	50	O6 - O3	2.3022
25	O2 - O11	1.2754	51	O6 - O4	2.7797
26	O2 - O13	2.3256	52	O6 - O10	2.3098

In such a structure the chromium atoms are co-ordinated by three oxygen atoms, while the vanadium atoms are co-ordinated by a distorted tetrahedral of oxygen atoms. The V – O distance varied from 2.328 Å (V3 – O11) to 0.413 Å (V3 – O8). This variation of the V – O distances imply that the vanadium atoms were slightly displaced from the conventional position in a similar V_2O_5 structure.

These data show few similarities with those presented by Enjalbert et al. [17] for the $As_2V_4O_{13}$ compound.

It was observed that the crystalline $Cr_2V_4O_{13}$ sample decomposed above 760 °C, immediately depositing to orthorhombic $CrVO_4$, + V_2O_5. The thermal analytical data revealed this process to be irreversible [12].

The XRPD sample pattern **with a ratio of Cr/V $\cong$ 1.0** annealed at 550 °C showed the presence of monoclinic $CrVO_4$. It was found that the originally amorphous material became crystalline at a temperature ∼450 °C. By increasing the temperature up to 800

Table 5 Selected bond angles of atoms in $Cr_2V_4O_{13}$.

No	atoms	angle
1	V1 - O6 - O2	75.9887
2	V1 - O8 - O6	25.2242
3	V1 - O6 - O10	136.2458
4	V1 - O8 - Cr1	154.5167
5	V3 - O5 - O9	104.1876
6	V3 - O2 - Cr1	58.5246
7	V3 - O8 - O6	122.3499
8	V4 - O5 - O12	64.4939
9	V4 - Cr1 - O5	140.7713
10	V4 - O9 - O12	90.5928
11	Cr1 - O3 - O2	106.7779
12	Cr1 - O2 - O11	81.7012
13	Cr2 - O6 - O2	53.3297
14	Cr2 - O6 - O12	77.7247
15	O2 - O13 - O5	62.4245
16	O2 - O8 - O3	107.8835
17	V2 - O12 - O1	124.7361
18	V2 - O12 - O4	51.5752
19	V2 - O12 - O7	141.1809
20	O3 - O4 - O12	95.0300

°C, the compound progressively converted from monoclinic to orthorhombic. This process was found to irreversible as well.

The XRPD sample pattern heated at 450 °C with a monoclinic structure, can be seen in Fig. 5; the following unit cell parameters were derived as follows: a=10.098 Å, b=9.381 Å, c=6.979 Å and $\beta = 106.1$ °. The d spacing obtained at a (001) reflection was 6.979 Å.

The XRPD pattern of the sample above 800 °C was compared by the **JCPDS 83-0761** card.

The best evaluation fir this latter sample was found in case of orthorhombic structure with the C_2 space group.

Taking symmetry into consideration, the XRPD pattern was calculated and compared to those which were experimentally obtained (40 Bragg peaks). Between the data negligible discrepancies were observed as shown in the Fig. 6.

Refining the XRPD pattern, the following unit cell parameters were derived: a=5.864 Å, b=8.682 Å and c=6.675 Å; the cell volume 332.94 Å^3, the relative mass 1335.48, the X-ray density 6.660 g.cm^{-3} and the mass absorption coefficient 0.00 cm^2.g^{-1}.

The atoms in the unit cell were 48 (48 generated positions) 6 of which were in the asymmetric unit. The d spacing obtained from 001 reflection was 6.775 Å.
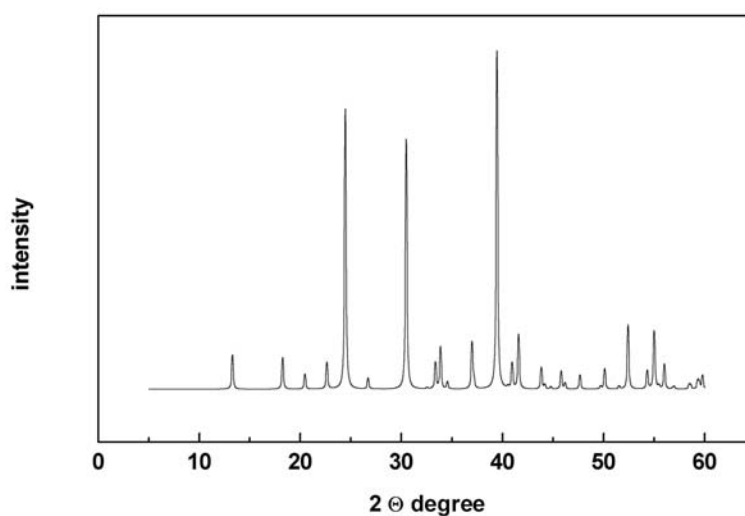
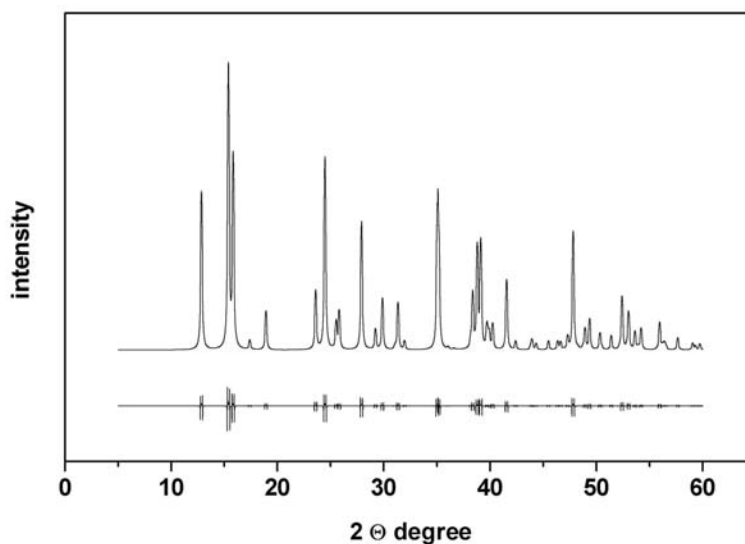**Fig. 5** A fragment of XRPD pattern of monoclinic $CrVO_4$.

Fig. 6 A segment of the XRPD pattern of orthorhombic $CrVO_4$ compared to the calculated one.

The calculations were made on the ground data:
- Herman-Mauguin: C m 2 m
- Laue group: m m m
- Point group: m m 2
- Positions: 8f x, y, z -x, y, -z -x, y, z x, y, -z

The positional atomic parameters, the selected bond length and bond angles are collected and presented respectively in Table 6 and Table 7.

Table 6 Positional and thermal parameters of the ions of $CrVO_4$ compound.

Ion	x	y	z	B_{iso}
V	0.25	0.75	0.1900	1.35
Cr	0.25	0.75	0.0110	1.96
O1	0.25	0.75	0.2940	1.07
O2	0.558	0.25	0.9550	1.49
O3	0.25	0.25	0.0061	1.66

Table 7 Selected bond length in Å and bond angles of the atoms in $CrVO_4$ compound.

No	distance		angle	
1	V - O4	2.2100	O4 - V - O2	117.416
2	V - O1	0.7046	O1 - V - O2	117.416
3	V - Cr	1.2127	V - O1 - O4	180.000
4	V - O2	2.1335	V - Cr - O2	83.066
5	O4 - O1	1.5054	V - O2 - O3	60.217
6	O1 - O3	3.1638	O4 - O1 - O2	131.693
7	O1 - Cr	1.9173	O3 - O1 - O2	65.791
8	O1 - O2	2.5363	O2 - O1 - O2	96.614
9	O2 - O3	3.1403	O4 - O2 - Cr	52.496
10	O2 - Cr	1.9078	O2 - Cr - O2	166.131

The monoclinic model shows a strongly distorted octahedral similar to that found in V_2O_5. This can be due to the phase transition which was also observed during the thermal treatment of this compound.

Regarding the orthorhombic form, the Cr^{3+} atom is co-ordinated by four oxygen atoms. The V^{5+}-Cr^{3+} distance is = 1.212 Å.

The data demonstrates that the monoclinic form is not stable from a crystallographic point of view

Taking the above data into consideration, the synthesised compounds with different chromium content have a different structure. The samples with low chromium content have a structure similar to that of V_2O_5. The structure of these compounds proved to be stable under the heat treatment.

The structure of the compound having Cr/V ratio of $\approx$ 0.5 is different from the previous one. This crystalline structure seemed non-stable while the temperature was being increased. It decomposed and went under phase transition, as was clearly observed for $Cr_2V_4O_{13}$.

The samples having a Cr/V ratio of $\approx$ 1.0 in stable form also had an orthorhombic structure.

It became clear that the chromium-vanadium oxide compounds in crystalline form

mainly have orthorhombic structure. The other monoclinic structure seemed to be unstable.

4   Conclusion

The mixed chromium-vanadium oxide hydrates, prepared by a novel aqueous method, were gelatinous, independent of their chromium content.

The dehydration of these compounds resulted in amorphous coloured materials.

These materials became crystalline as they underwent heating. The crystallisation temperature increased with the increase of the chromium content of the compound.

In case of sample with $Cr/V = 0.067$ from the possible Cr^{3+} sites only 13% are occupied. No seeing on the Cr^{3+} content, the structure (at 330 °C) of the chromium-vanadium oxide composition ($Cr_{0.13}V_2O_5$) closely to the orthorhombic structure of V_2O_5.

The $Cr_2V_4O_{13}$ sample has a monoclinic structure at a temperature of 660 °C. It can only exist in relative narrow temperature intervals (up to 760 °C); then it decompose to orthorhombic $CrVO_4 + V_2O_5$.

The sample composed of $CrVO_4$ has a monoclinic structure at around 450 °C. By increasing the temperature up to 800 °C, it undergoes a phase transition resulting in an orthorhombic structure.

The latter processes were shown to be irreversible.

Acknowledgment

References

[1]   M.S. Whittingham, R. Chen, T. Chirayil and P.Y. Zavalij: "Cathode materials for advanced batteries in "Exploratory Research and development of batteries for electric and hybrid vehicles"", *Electrochem. Soc. Proc.*, Vol. 96(5), (1996), p. 76.

[2]   E. Baundin, S. Denis, F. Orsini, L. Seguin, M. Touboul and J.M. Tarascon: "On the synthesis of mono-, di-, and trivalent element vanadates", *J. Mater. Chem.*, Vol. 9, (1999), p. 101.

[3]   D. Oliver: "C.R. Préparation et contribution á l'étude des métavanadates de chrome", *Acad. Sci. Paris*, Vol. 264C, (1967), p. 1176.

[4]   D. Oliver: "C.R. Vanadates de chrome: contribution á l'étude de la structure des vanadates de chrome non stoechiometriques á deficit d'oxygéne", *Acad. Sci. Paris*, Vol. 272, (1971), p. 1225.

[5]   O. Pozdnyakova, E. Kuzmann and L. Szirtes: "Preparation of a new vanadium-chromium oxide with a two-dimensional structure", *Sol. State Ionics*, Vol. 161, (2003), p. 301.

[6]   V.K. Kato, E.T. Muromatchi and Y. Kanke: "Die structur der kupfer-vanadium bronze $Cu_{0.261}V_2O_5$; Eine verfeinerung", *Acta Cryst.*, Vol. C45, (1989), p. 1845.

[7]   G. Gregorie, N. Baffier, A. Khan-Harari and J.C. Badot: "X-ray powder diffraction study of a new vanadium oxide $Cr_{0.11}V_2O_{5.16}$ synthesised by a sol-gel process", *Mater. Chem.*, Vol. 8, (1998), p. 2103.

[8]   P.Y. Zavalij and M.S. Whittingham: "Structural chemistry of vanadium oxides with open frameworks", *Acta Cryst.*, Vol. B55, (1999), p. 627 and references herein

[9]   Z. Klencsár: *"EXRAY" peak searching computer software*, Personal communication, 1998.

[10] H.M. Ritveld: "Profile refinement method for nuclear and magnetic structures", *J. Appl. Crystallogr.*, Vol. 2, (1969), p. 65.

[11] W. Kraus and G. Nolze: *Software Powder Cell*, version 2.3, 1999.

[12] O. Pozdnyakova, J. Megyeri, E. Kuzmann and L. Szirtes: "Thermoanalytical characterisation of vanadium-chromium oxide compounds prepared by 'soft chemistry' method", *J. Thermal Anal. Cal.*, Vol. 82, (2005), p. 409.

[13] O. Pozdnyakova, non-published data.

[14] M. Hibino, M. Ugaji, A. Kisgimoto and T. Kudo: "Preparation and Li-interaction of a new vanadium oxide with a two dimensional structure", *Sol. State Ionics*, Vol. 79, (1995), p. 239.

[15] H.G. Bachman, F.R. Ahmed and W.H. Barnes: "The crystal structure of vanadium pentoxide", *Z. Kristallogr.*, Vol. 115, (1961), p. 110.

[16] E. Filipek, J. Walczak and P. Tabero: "Synthesis and some properties of the phase $Cr_2V_4O_{13}$", *J. Alloys Comp.*, Vol. 265, (1998), p. 121.

[17] R. Enjalbert, P. Lecante and J. Galy: "Crystal structure of $As_2V_4O_{13}$", *Acta Cryst.*, Vol. C42(17), (1986), p. 1465.