

Review

Materials belonging to the CrVO_4 structure type: preparation, crystal chemistry and physicochemical properties

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Crystallographic data of vanadates, phosphates, chromates, sulphates and selenates belonging to the CrVO_4 ($\beta\text{-CrPO}_4$) structure type and of some of its most important polymorphs, are reported. Characteristic structural peculiarities and the effect of pressure on the phase transformations are discussed. A definitive stability field for this structure type could be established. Synthetic procedures for the preparation of the different compounds adopting this and closely related structures are presented and its thermal, spectroscopic and magnetic properties are discussed. A brief overview on the most important characteristics of materials adopting the $\alpha\text{-CrPO}_4$ structure is also presented. © 1998 Chapman & Hall

1. Introduction

The structure of CrVO_4 , described about 50 years ago, is one of the typical ABO_4 structure types adopted by different oxide systems. Although the number of compounds with this structure (often also called $\beta\text{-CrPO}_4$ or NiSO_4 structure) is rather small, new materials belonging to this structure type have recently been prepared and characterized. Therefore, it seems timely to give a general, systematic overview of the crystal chemistry and of the most important physical and chemical properties of these materials.

To begin with, some general structural features are presented of the different materials adopting this structure, including comments and remarks on their most common and important polymorphs, followed by a general crystallochemical discussion.

In the second part, some aspects related to the synthesis of these materials are presented and discussed.

The third part is devoted to the discussion of the most relevant physicochemical properties of these compounds, emphasizing thermal, spectroscopic and magnetic properties.

The final section offers a brief overview of the few materials belonging to the $\alpha\text{-CrPO}_4$ structural type.

2. Structural aspects

2.1. Main characteristics of the CrVO_4 structure

CrVO_4 is orthorhombic space group $D_{2h}^{17} - \text{Cmcm}$ -, with $Z = 4$ [1]. The structure consists of infinite

chains of *trans* edge-sharing CrO_6 octahedra which run parallel to the *c*-axis. These chains are linked together by VO_4 tetrahedra, as shown schematically in Fig. 1. The metal atoms are in the following special positions: Cr (4a) and V (4c). As adjacent elements in the periodic table, vanadium and chromium have nearly the same X-ray scattering powers and it was initially difficult to assess which atom is in position 4a and which in 4c. However, by means of X-ray absorption spectroscopy it became evident that vanadium was the tetrahedrally coordinated ion [2].

The CrVO_4 structure has a fairly high tolerance and can accommodate octahedral ions as small as Fe(III) and as large as Tl(III) and Cd(II).

Five classes of ABO_4 materials are found in this structural type: trivalent cation phosphates and vanadates, $\text{M}^{\text{III}}\text{PO}_4$, $\text{M}^{\text{III}}\text{VO}_4$, and divalent cation sulphates, selenates and chromates, $\text{M}^{\text{II}}\text{SO}_4$, $\text{M}^{\text{II}}\text{SeO}_4$, $\text{M}^{\text{II}}\text{CrO}_4$. Only recently, LiMnO_4 has been shown to be the first, and so far unique, permanganate adopting this structure.

An analysis of the structural information available so far for ABO_4 compounds shows that for phases with r_A (C.N. = 6) between 0.07 and 0.10 nm and r_B (C.N. = 4) < 0.060 nm, CrVO_4 is the only possible structure [3,4]. With increasing A cationic radius, zircon, monazite or barite type structures are preferred; with increasing B radius the structural type changes substantially, generating octahedral coordination of this ion. A greatly simplified structural field map, in the region around CrVO_4 , is shown in Fig. 2.

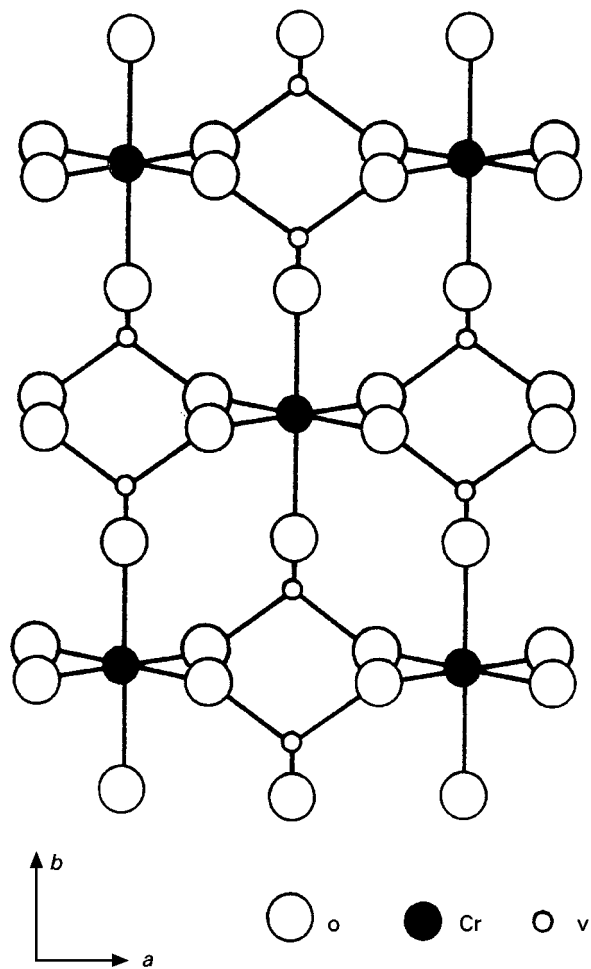


Figure 1 Schematic representation of the CrVO_4 structure.

Interestingly, most of the CrVO_4 -type materials can be obtained in other polymorphic modifications, generally by increasing temperature and/or pressure. These aspects are also covered in this review.

Finally, it should be mentioned that the structure most closely related to CrVO_4 is that of ZnSO_4 . This compound is also orthorhombic, space group $D_{2h}^{16}-Pnma-$ with $Z = 4$ [5]. This structure is built up of chains of shared ZnO_6 octahedra linked by SO_4 tetrahedra. These building units are similar to those found in CrVO_4 , but their orientations are slightly different and the octahedra and tetrahedra have a lower site-symmetry than in the CrVO_4 structure. On the other hand, the CrVO_4 structure is about 2% denser than that of ZnSO_4 [6].

2.2. Structural data and polymorphism of CrVO_4 -type materials

2.2.1. Vanadates

2.2.1.1. Vanadates belonging to the CrVO_4 -type. Only four orthovanadates of trivalent cations are so far known to adopt this structural type.

The Cr(III) orthovanadate, which is the structural prototype of the reviewed materials, was first characterized by Brandt [1] in 1943. Only in 1975 could a second vanadate of this type, namely FeVO_4 (usually

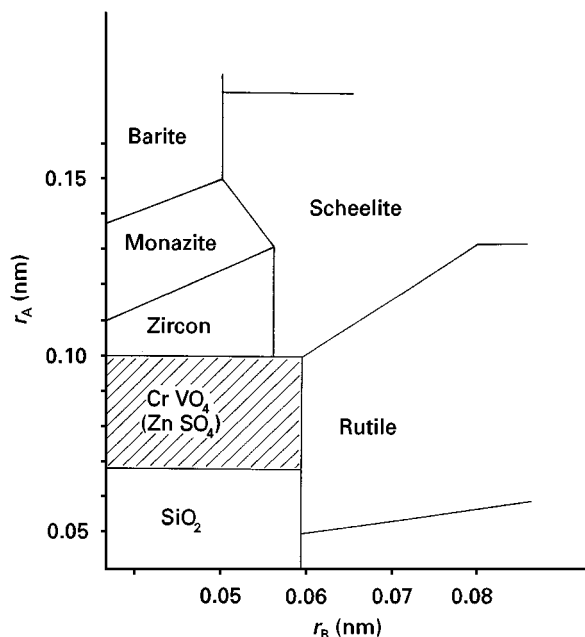


Figure 2 Structure field map in the region of the $\text{CrVO}_4/\text{ZnSO}_4$ and neighbouring structures.

called FeVO_4 -II), be prepared under high temperatures and pressures [7], although more recently it has been synthesized by a hydrothermal method [8]. The stability range of this phase is very narrow, and at about 570°C it transforms to the normal triclinic form [9]. The other two known vanadates of this type are InVO_4 [10] and TlVO_4 [11].

Crystallographic data for these four materials are given in Table I.

2.2.1.2. Other vanadate polymorphs. CrVO_4 can also be obtained with the rutile structure at high temperatures (750°C) and pressure (60 000 atm) [7, 13], and also with the α - MnMoO_4 structure, by mild heating of amorphous precursors (*chimie douce process*) [14, 15].

FeVO_4 exists in other three different structural modifications [7, 8]. The normal form is triclinic, space group $P\bar{1}$ and $Z = 6$, with the Fe(III) in two different coordinations (five and six) [9], and is isotopic with AlVO_4 [16, 17]. A second form adopts the α - PbO_2 structure, with both the Fe(III) and V(V) ions located in octahedral voids, in a totally disordered distribution [7]. A third, ordered modification, with the wolframite structure, can be obtained by treating the normal form at high temperature and pressure in sealed platinum ampoules [7].

In the case of InVO_4 , the existence of one [18] or two [11] other forms, apart from the CrVO_4 modification, has been postulated. Nevertheless, only one different form could be clearly characterized. It can be obtained by gentle heating of precipitated amorphous indium vanadate, and adopts the α - MnMoO_4 structural type [19, 20].

For TlVO_4 , no other polymorphic forms have so far been found.

TABLE I Crystallographic data of $M^{III}VO_4$ materials belonging to the $CrVO_4$ structure type

Compound	a (nm)	b (nm)	c (nm)	Volume (10^{-3} nm ³)	Reference
$CrVO_4$	0.5589	0.8252	0.5993	276.40	[12]
$FeVO_4$	0.5628	0.8272	0.6112	284.54	[8]
$InVO_4$	0.5765	0.8542	0.6592	324.62	[10]
$TiVO_4$	0.5839	0.8687	0.6800	344.92	[11]

TABLE II Crystallographic data of $M^{III}PO_4$ materials belonging to the $CrVO_4$ structure type

Compound	a (nm)	b (nm)	c (nm)	Volume (10^{-3} nm ³)	Reference
$TiPO_4$	0.5299	0.7910	0.6368	266.92	[27]
VPO_4	0.5230	0.7772	0.6284	255.43	[27]
$CrPO_4$	0.5165	0.7750	0.6131	245.41	[28]
$FePO_4$	0.5227	0.7770	0.6322	256.76	[25]
$InPO_4$	0.5308	0.7851	0.6767	282.00	[23]
$TiPO_4$	0.5395	0.8010	0.7071	305.56	[23]
$AlPO_4$	0.511	0.748	0.609	233.9	[28]

2.2.1.3. *Other related materials.* The fact that the phases of composition $(Cr_{1-x}Fe_x)VO_4$ are isomorphous with α - $MnMoO_4$, rather than adopting the $CrVO_4$ or $FeVO_4$ structures [21] is of special interest. This is very unusual behaviour and may represent a compromise between the distorted cationic environment in triclinic $FeVO_4$ and the more regular $CrVO_4$ structure. Nevertheless, at a pressure of 3000 atm, a reversible transformation to the $CrVO_4$ structure takes place [21].

Another structure closely related to that of $CrVO_4$ is found in $NaCaVO_4$, in which chains of CaO_6 octahedra are linked by VO_4 tetrahedra, whereas Na(I) is present in a very distorted tetrahedral environment [22].

2.2.2. Phosphates

2.2.2.1. *Phosphates belonging to the $CrVO_4$ -type.* These materials show the great flexibility of this structural type with respect to the cationic radii, ranging from trivalent first row transition metal cations to In(III) and Tl(III).

Crystallographic data for the known phosphates belonging to this structure are shown in Table II.

The Cr(III), In(III) and Tl(III) phosphate can be obtained by simple thermal or hydrothermal reactions [23, 24], whereas the Fe(III) and Al(III) compounds can only be obtained at high pressures [25, 26]. The Ti(III) and V(III) phosphates were obtained under reducing conditions [27] although VPO_4 can also be prepared by means of other procedures (see Section 3).

It is interesting to remark that although $AlPO_4$, $InPO_4$ and $TiPO_4$ could be characterized with the $CrVO_4$ structure, the formation of an isostructural Ga(III) phosphate has not been reported so far.

2.2.2.2. *Other phosphate polytypes.* A great number of $M^{III}PO_4$ materials, mainly crystallizing in some of the

SiO_2 structures, have been reported. A detailed discussion of these compounds lies outside the scope of this review. Therefore, only some brief comments and remarks are given.

Generally speaking, one can state that the well-known polymorphic modifications of SiO_2 have their counterparts in several ABO_4 systems, with specially numerous examples found in phases with B = phosphorus or arsenic.

$AlPO_4$ is probably the most studied of these compounds. It undergoes reconstructive transformations of the same type as SiO_2 , i.e., quartz \rightarrow tridymite \rightarrow cristobalite. In addition, all the three polymorphs have at least one high–low displacive transition [3]. Some other high-pressure forms, different from that with the $CrVO_4$ structure, are also known [28]. Another, monoclinic $AlPO_4$ form, in which Al(III) is apparently in octahedral coordination, can also be prepared [29].

Specially interesting in relation to this review is the existence of some materials closely related to those presented in Table II, but which have not been obtained in the $CrVO_4$ lattice. Thus, two $MnPO_4$ modifications, with the quartz and cristobalite structures, respectively, are known [30]. $GaPO_4$ has also been reported with quartz and cristobalite structures [30, 31]. In the case of $FePO_4$, a normal pressure form adopting the quartz structure is known [26, 31, 32].

$RhPO_4$ and the high-temperature form of $CrPO_4$, belong to another structural type, usually known as α - $CrPO_4$. They are discussed in detail in Section 5.

2.2.2.3. *Other related materials.* Al(III) and Ga(III) arsenates are only found in quartz-like structures [31, 33, 34], whereas $FeAsO_4$ compounds are known to exist in three different modifications [35, 36]. $FeAsO_4$ -II belongs to the $ZnSO_4$ structure and $FeAsO_4$ -III to the low-temperature quartz modification

TABLE III Crystallographic data of $M^{II}CrO_4$ materials belonging to the $CrVO_4$ structure type

Compound	a (nm)	b (nm)	c (nm)	Volume (10^{-3} nm ³)	Reference
CoCrO ₄	0.5505	0.8281	0.6207	282.96	[1]
NiCrO ₄	0.5482	0.8237	0.6147	277.56	[37]
CuCrO ₄	0.5433	0.8968	0.5890	286.97	[38]
ZnCrO ₄	0.5505	0.8383	0.6219	287.00	[1]
CdCrO ₄	0.5678	0.8723	0.6926	343.04	[37]
MgCrO ₄	0.5494	0.8363	0.6324	290.56	[39]

TABLE IV Crystallographic data of $M^{II}SO_4$ materials belonging to the $CrVO_4$ and $ZnSO_4$ structure types

Compound	a (nm)	b (nm)	c (nm)	Volume (10^{-3} nm ³)	Reference
CrVO₄ structure					
MnSO ₄	0.5248	0.8048	0.6842	288.98	[45]
FeSO ₄	0.5261	0.8013	0.6454	272.08	[45]
CoSO ₄	0.5192	0.7856	0.6530	266.35	[46]
NiSO ₄	0.5166	0.7846	0.6362	257.87	[46]
CuSO ₄	0.4973	0.7730	0.6702	257.63	[45]
ZnSO ₄	0.5217	0.7848	0.6500	266.13	[45]
CdSO ₄	0.5310	0.8157	0.7180	311.00	[47]
MgSO ₄	0.5182	0.7893	0.6506	266.11	[48]
ZnSO₄ structure					
MnSO ₄	0.4821	0.8774	0.7069	299.01	[49]
FeSO ₄	0.4765	0.8671	0.6777	280.01	[45]
CoSO ₄	0.4738	0.8603	0.6699	273.06	[45]
CuSO ₄	0.4833	0.8409	0.6709	272.66	[50]
ZnSO ₄	0.4774	0.8604	0.6746	277.10	[50]
MgSO ₄	0.4742	0.8575	0.6699	272.40	[51]

[35]. The third form, FeAsO₄-I, is monoclinic, space group $P2_1/n$ with $Z = 4$, and contains octahedral FeO₆ and tetrahedral AsO₄ polyhedra [36].

The high- and low-temperature forms of CrAsO₄, adopting the ZnSO₄ and the α -CrPO₄ structures, respectively, are also discussed in Section 5.

2.2.3. Chromates

2.2.3.1. *Chromates belonging to the CrVO₄-type.* The crystal structures of a number of $M^{II}CrO_4$ materials adopting this structure type, were first reported by Brandt [1]. Most of them have been reinvestigated in recent years by different authors. The pertinent crystallographic data are given in Table III.

2.2.3.2. *Other chromate polytypes.* MgCrO₄ and CdCrO₄, synthesized at high pressures belong to the α -MnMoO₄ structural type [37,40]. If CdCrO₄ is treated at higher pressures (40 kbar at 200–450 °C) it adopts the tetragonal scheelite structure [41].

2.2.3.3. *Other related materials.* The very interesting compound LiCr₃O₈, containing simultaneously Cr(III) and Cr(VI), i.e. LiCr^{III}(CrO₄)₂, also belongs to the CrVO₄ structure with $a = 0.5504$ nm, $b = 0.8289$ nm, $c = 0.6117$ nm and $Z = 2$ [42]. In this phase, the Li(I) and Cr(III) cations are randomly distributed in the octahedral strings. Similar materials, containing

sodium, potassium or rubidium instead of lithium adopt a different, monoclinic, structure, space group $C2/m$ with $Z = 2$ [43,44].

2.2.4. Sulphates

2.2.4.1. *Sulphates belonging to the CrVO₄-type.* The crystal chemistry of $M^{II}SO_4$ materials is particularly interesting due to the existence of different polymorphic forms for most of them. First-row transition metal sulphates (M^{II} = manganese to zinc) with the CrVO₄ structure have been reported and this structure is also found in CdSO₄ and MgSO₄.

Table IV gives the crystallographic data of the CrVO₄-type sulphates. The corresponding Mn(II), Fe(II), Co(II), Ni(II) and Mg(II) salts adopt this structure under ordinary pressure and temperature conditions, whereas CuSO₄, ZnSO₄ and CdSO₄ adopt it only at high temperatures.

2.2.4.2. *Other sulphate polymorphs.* CuSO₄ is known as the rare mineral chalcocyanite [52] found as a product of volcanic exhalations [53]. A natural ZnSO₄, the mineral zincosite, is also known [54]. Both minerals belong to the ZnSO₄ structure type [50]. This structure is also adopted by most of the CrVO₄-type sulphates, on changing the experimental conditions of preparation.

MnSO₄ takes the ZnSO₄ structure at temperatures above 430 °C [49, 55] but this phase is unquenchable.

TABLE V Crystallographic data of $M^{II}SeO_4$ materials belonging to the $CrVO_4$ and $ZnSO_4$ structure types

Compound	a (nm)	b (nm)	c (nm)	Volume (10^{-3} nm ³)	Reference
CrVO₄ structure					
MnSeO ₄	0.548	0.818	0.680	304.8	[69]
CoSeO ₄	0.5439	0.810	0.6522	287.33	[69]
NiSeO ₄	0.5399	0.8089	0.6376	278.45	[70]
CuSeO ₄	0.542	0.855	0.661	306.3	[69]
ZnSeO ₄	0.5511	0.8110	0.6585	294.31	[72]
MgSeO ₄	0.542	0.814	0.652	287.6	[69]
ZnSO₄ structure					
MnSeO ₄	0.4932	0.9131	0.7023	316.27	[69]
CoSeO ₄	0.4892	0.9050	0.6741	298.44	[69]
CuSeO ₄	0.5099	0.9390	0.7005	335.40	[69]
ZnSeO ₄	0.4905	0.9012	0.6293	278.17	[73]
MgSeO ₄	0.4903	0.9001	0.6741	297.49	[69]

Apparently, other high-pressure phases can be formed, but they are not clearly identified [45].

At high temperatures (800–850 °C) and at a pressure of 5 kbar, a quenchable FeSO₄ modification, belonging to the ZnSO₄-type can be obtained [45, 56]. More recently, a third form of FeSO₄ was identified. It is probably monoclinic [57] and structurally related to the third CoSO₄ polymorph (see below).

CoSO₄ also adopts the ZnSO₄ structure at higher temperatures [45, 58–60] whereas a third, monoclinic, modification with the probable space group $P2_1/n$ could also be identified [61]. Other polymorphic forms can apparently exist at very high pressures [45].

As stated above, both CuSO₄ and ZnSO₄ adopt the ZnSO₄ structure under normal temperature and pressure conditions [50, 62]. In the case of the Zn(II) compound, another high-temperature modification has been reported. It represents the first example of a sulphate adopting the cristobalite structure ($a = 0.717$ nm) [63].

MgSO₄ also presents a high-temperature form, adopting the ZnSO₄ structural type [51]. In the case of CdSO₄ a second polymorphic form was reported by different authors [47, 64–66]. Different space groups were proposed for this low-temperature form. The correct one may be $Pn2_1m$, with $Z = 2$ [66].

The crystallographic data for the sulphates belonging to the ZnSO₄ structure type are also included in Table IV.

It is especially interesting to mention that NiSO₄ has only been obtained in the CrVO₄ modification so far. Its structure was initially investigated by Dimaras [67] and confirmed by Poljak [68]; a structure refinement has recently been reported by Wildner [46].

2.2.4.3. Other related materials. HgSO₄ also has the same structure as the low-temperature form of CdSO₄ [64–66].

2.2.5. Selenates

2.2.5.1. Selenates belonging to the CrVO₄-type. In a similar way to the case of the sulphates, most of the $M^{II}SeO_4$ materials are polymorphic. Nevertheless, in

these cases the CrVO₄ modification is usually only generated at high pressures and can be prepared by quenching after treatment at 40 kbar and at temperatures near 400 °C [69].

Interestingly, in comparison to the sulphates, only NiSeO₄ has been obtained in the CrVO₄ modification [70, 71] with neither FeSeO₄ nor CdSeO₄ reported so far.

Table V shows the crystallographic data of the divalent metal selenates belonging to the CrVO₄ type.

2.2.5.2. Other selenate polytypes. The selenates of Mg(II), Mn(II), Co(II), Cu(II) and Zn(II), obtained under normal temperature and pressure conditions, crystallize in the ZnSO₄ type. Crystallographic data for these materials are also included in Table V.

2.2.6. Lithium permanganate

Anhydrous lithium permanganate, LiMnO₄, obtained by dehydration of the trihydrate at 60 °C in a vacuum over P₄O₁₀, constitutes the first example of a permanganate adopting the CrVO₄ structure type [74]. The following unit-cell data were determined for this compound, by neutron diffraction measurements: $a = 0.5514$ nm, $b = 0.8397$ nm and $c = 0.6359$ nm ($Z = 4$) [74].

2.3. Crystal chemistry of the CrVO₄ structure type

As stated in Section 1, the CrVO₄ structure is the only possible ABO₄ structure type with r_A between 0.07 and 0.10 nm and $r_B < 0.06$ nm.

Close correlations between ionic size and the structure and properties of crystals have been pointed out by many authors [3, 75–77]. Such correlations also allow an analysis of the quality of available structural data and a verification of the stability fields of a given structure type.

Using the crystallographic data tabulated in the preceding section and the ionic radii of Shannon and Prewitt [78], the cube roots of the orthorhombic unit cell have been plotted as a function of the ionic radii of

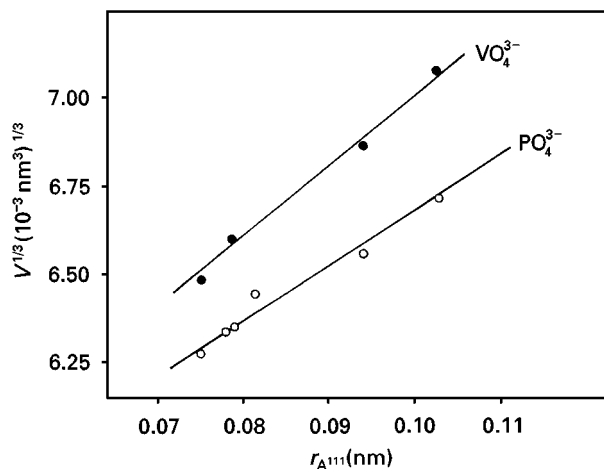


Figure 3 Plot of the cubic roots of the unit-cell volumes as a function of the ionic radii of the trivalent cations, for vanadates and phosphates belonging to the CrVO_4 structure type.

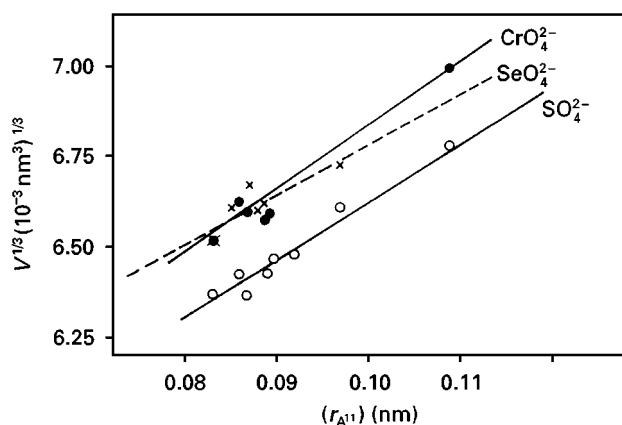


Figure 4 Plot of the cubic roots of the unit-cell volumes as a function of the ionic radii of the divalent cations, for chromates, sulphates and selenates belonging to the CrVO_4 structure type.

the octahedrally coordinated cations (A). Fig. 3 shows this plot for the trivalent metal vanadates and phosphates, whereas a similar plot for the divalent metal sulphates, selenates and chromates is shown in Fig. 4. The data were fitted with a standard least-squares procedure, with plotted lines corresponding to the best fit. From this analysis one can define correlation coefficients in order to verify the quality of the fits and of the plotted correlations.

The correlation coefficient used, R , is defined as

$$R = (J/M)^{1/2} \quad (1a)$$

with

$$J = B[\sum XY - \sum X \sum Y/n] \quad (1b)$$

and

$$M = \sum Y^2 - (\sum Y)^2/n \quad (1c)$$

where B is the calculated slope of the plot and n the number of experimental points.

On the other hand, the estimated standard errors (ESE) are defined as

$$\text{ESE} = [(M - J)/(n - 2)]^{1/2} \quad (2)$$

TABLE VI Numerical analysis of the plots of Figs 4 and 5

System	R	ESE
Vanadates	0.996	2.6%
Sulphates	0.978	3.2%
Chromates	0.978	4.0%
Phosphates	0.970	5.1%
Selenates	0.697	6.5%

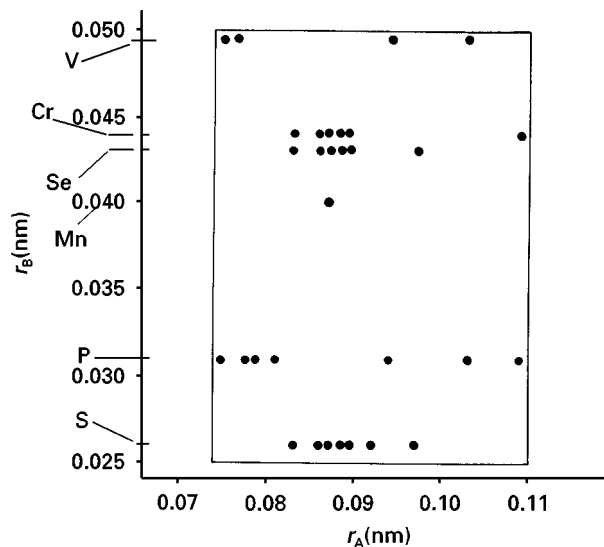


Figure 5 Stability field of the CrVO_4 structure type.

The results of the analysis of the five fitted lines in Figs 3 and 4 are given in Table VI. As can be seen, the correlations are fairly good, except in the case of the selenates, in which greater dispersions are observed, suggesting the need for a re-examination of crystal data of most of these materials.

Finally, in Fig. 5 a plot of r_B as a function of r_A is presented, to define exactly the stability field of the CrVO_4 structure on the basis of all the known compounds which adopt this structure. From this plot, we can now establish more precisely the exact limits of existence of this type: it is stable for r_A values ranging between 0.075 and 0.110 nm and for r_B values between 0.025 and 0.050 nm (referred to Shannon and Prewitt's ionic radii).

Most of the available crystal data and structural information have been obtained by powder diffraction. The scarcity of single crystal data limits, to some extent, the knowledge of finer structural characteristics which, at this time, would be highly desirable. Nevertheless, in recent years, several structural refinements have brought new insights into a number of peculiarities of this structure type. A recent refinement of the structures of NiSO_4 and CoSO_4 , has shown that the M(II) cations are octahedrally coordinated to two nearer O(1) atoms whereas the other four, coplanar, M–O(2) bonds are longer (7% in CoSO_4 and 4.9% in NiSO_4) [46]. This means a (2 + 4) oxygen coordination of the M(II) cations.

The very short interpolyhedral O(1) ... O(1) distances (0.2687 nm in NiSO_4 and 0.2722 nm in CoSO_4)

[46] constitute another peculiar feature of these structures. This is a very remarkable situation taking into account that only few structures are known, in which such non-bonded interpolyhedral distances are shorter than 0.290 nm [46, 79].

The general geometry of the MO_6 polyhedra described above, i.e. two short axial bonds and four longer equatorial bonds, seems to be the usual coordination of the octahedral cation in the CrVO_4 structure. This peculiarity of coordination was also found in a recent structural refinement of the structures of TiPO_4 and VPO_4 [80]. In addition, in the case of Cu(II) compounds, the usual tetragonally distorted coordination with four shorter and two longer axial bonds, due to the Jahn–Teller effect, may be expected. This type of CuO_6 polyhedron has actually been established by a single crystal study of CuCrO_4 [38].

Interesting to mention is also the fact that another recent refinement of the TiPO_4 structure, suggests the existence of a superstructure of CrVO_4 with monoclinic symmetry [81]. It would be interesting to confirm this finding and to search for a similar behaviour in other CrVO_4 -related materials.

In relation to the XO_4 tetrahedra, all the available information shows that they present two longer and two shorter X–O bonds, generating a moiety with C_{2v} symmetry.

In the case of the ZnSO_4 structure, the MO_6 polyhedra appear significantly more distorted than in the VCrO_4 structure. This is considered to be a characteristic attribute of the Pnma structure type, mainly caused by interatomic connecting principles [50]. In the case of ZnSO_4 itself, three different Zn–O distances are found in the ZnO_6 polyhedron, generating a $(2 + 2 + 2)$ arrangement [50].

As we have previously shown, numerous phase transitions in CrVO_4 and related structures occur under high-pressure conditions. Therefore, it is relevant to conclude this section with some general comments on the effect of pressure on the phase transformations in ABO_4 systems.

Different authors have attempted to explain and to predict crystal structures of ABO_4 high-pressure phases (cf. for example [28, 82–85]). In the context of the present review, the ideas advanced by Fukunaga and Yamaoka [84] are particularly enlightening. They analyse these transformations on the basis of two parameters, $k = r_A/r_B$ and $t = (r_A + r_B)/2r_O$, where r_A , r_B and r_O are the ionic radii of the A and B cations and of the oxygen anion, respectively. When ABO_4 -type compounds are plotted in a diagram of k versus t , it is found empirically, that a compound transforms to the structure type associated with a compound lying in a classified area of the diagram with the same k and larger t .

For simple MO_2 dioxides under increasing pressure, phase transformations generally occur with an increase of the cation coordination number. In these cases, the crystal structures are primarily governed by the radius ratio r_M/r_O . When a high-pressure phase transformation occurs, a new structure is found to be one with the increased coordination number, which is characterized by a larger r_M/r_O value. This is explained

qualitatively from the tendency of the larger O^{2-} anion to be more compressible than the smaller M^{2+} cation under high pressure. In ternary oxides, however, the increase of coordination number is usually not sufficient to explain all the possible high-pressure transformations.

In ternary oxides of the type $\text{A}_x\text{B}_y\text{O}_z$, the radius ratio of A or B to oxygen, r_A/r_O or r_B/r_O , also increases with increasing pressure but in a different magnitude for both cations. Nevertheless, the ratio of the average radius of A and B to that of oxygen, $t = r_C/r_O$, increases with increasing pressure, where r_C is the average cation radius $r_C = (xr_A + yr_B)/(x + y)$. In other words, the parameter t is assumed to correspond to the cation/anion radius ratio r_M/r_O in binary MO_2 oxides. On the other hand, the radius ratio r_A/r_B , is considered to remain nearly constant due to the small compressibility of cations compared to that of the oxide anion [84]. Therefore, a displacement at constant k parallel to the t -axis, in the direction of larger t -values, in a k versus t diagram, represents an increased pressure.

For our purposes, a diagram like that shown in Fig. 6 can be constructed, showing CrVO_4 and its immediate neighbourhood. The solid arrows indicate transformations actually observed; the dotted arrow represents a predicted, but not observed phase change.

Table VII shows again, in an ordered way, all the high-pressure changes so far reported for materials structurally related to CrVO_4 . Worthy of note is that all the pressure-induced changes summarized in this table are predicted by the k/t rule, and can be visualized in Fig. 6. Only the α - MnMoO_4 structure is not included in this figure, but they certainly lie near to the CrVO_4 region [3], slightly displaced to higher t -values.

Interesting is also the fact that divalent metal selenates, $\text{M}^{\text{II}}\text{SeO}_4$, which present the ZnSO_4 structure under normal conditions, adopt the CrVO_4 structure at higher pressures, whereas some of the related sulphates belonging to the CrVO_4 -type under normal conditions, transform to the ZnSO_4 -type at higher temperatures. This behaviour indicates, again, the close relationship between both structure types.

In the case of InVO_4 , the low-temperature form (α - MnMoO_4 -type) is probably a metastable phase,

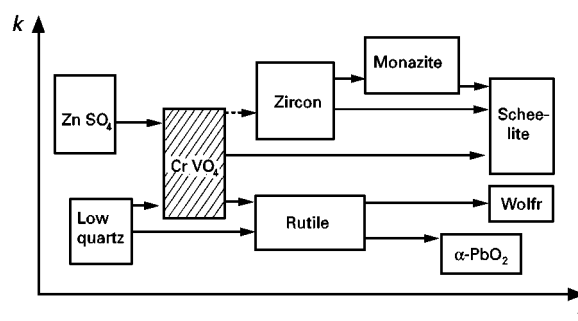


Figure 6 Schematic representation of pressure-induced phase transformations in materials with the CrVO_4 and related structures, based on k versus t (for definitions, see text). Adapted from [84].

TABLE VII High-pressure (P) transitions in compounds structurally related to CrVO_4

Compound	Normal form	High P form
CrVO_4	CrVO_4	Rutile
FeVO_4	Triclinic	CrVO_4 α - PbO_2 Wolframite
AlPO_4	Quartz	CrVO_4 Other quartz forms
FePO_4	Quartz	CrVO_4
MgCrO_4	CrVO_4	α - MnMoO_4
CdCrO_4	CrVO_4	α - MnMoO_4 Scheelite
NiSO_4	CrVO_4	–
$\text{Mg/Mn/Co/Cu/ZnSeO}_4$	ZnSO_4	CrVO_4
NiSeO_4	CrVO_4	–

stabilized intermediately between an amorphous form and the most stable CrVO_4 modification [11, 19]. This supposition is supported by the behaviour of MgCrO_4 and CdCrO_4 , which transform from CrVO_4 to α - MnMoO_4 at higher pressures [37, 40].

3. Synthesis of materials belonging to the CrVO_4 structure type

3.1. General aspects

Most of the phosphates and vanadates can be obtained by solid-state reactions at temperatures around 800–1000 °C. Chromates, sulphates and selenates are usually prepared in solution; but, as stated in the preceding section, some of them as well as some other CrVO_4 -type materials can only be obtained under special conditions of pressure and/or temperature.

In the following sections, a brief account on the synthesis of all these materials is given. *Gmelin's-Handbook of Inorganic Chemistry* [86] should also be consulted in this context and to obtain information on the general chemical properties of these compounds.

3.2. Vanadates

The prototype material of the series, CrVO_4 , can be easily prepared by a solid-state reaction between Cr_2O_3 and V_2O_5 at 750–800 °C [1, 12]. More recently, it has also synthesized by heating of amorphous precursors (*chimie douce* process) [14].

A similar procedure (reaction between $\text{In}_2\text{O}_3/\text{V}_2\text{O}_5$ mixtures at 850 °C) can be used to prepare InVO_4 [10].

The synthesis of TlVO_4 presents some difficulties, due to its low thermal stability. It can only be obtained by reaction between Tl_2O_3 and V_2O_5 at 250 °C, under hydrothermal conditions [87].

Phase diagrams of the systems $\text{In}_2\text{O}_3/\text{V}_2\text{O}_5$ and $\text{Tl}_2\text{O}_8/\text{V}_2\text{O}_5$ and of some ternary systems, including one or both of the vanadates, have also been investigated in detail [88].

Pure crystalline samples of FeVO_4 can be obtained using a hydrothermal method (aqueous $\text{VOCl}_2/\text{FeCl}_3$ solutions, treated at 280 °C for 40 h) [8].

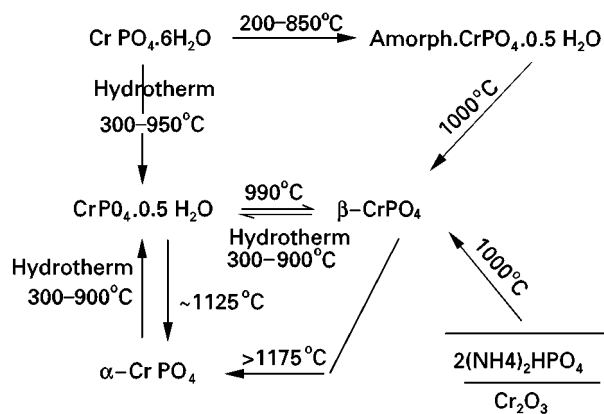


Figure 7 Relation between the different anhydrous and hydrated forms of CrPO_4 .

3.3. Phosphates

Most of the phosphate materials can be prepared by solid-state reactions under different experimental conditions.

TiPO_4 and VPO_4 can be obtained by solid-state reactions at 950 °C between $(\text{NH}_4)_2\text{HPO}_4$ and TiO_2 (anatase) or NH_4VO_3 , respectively, working at very low oxygen partial pressure. Furthermore, gaseous NH_3 , generated by the decomposition of the starting reagents, acts as a reducing agent in the initial stage of reaction [27]. Recently, well-developed single crystals of TiPO_4 have been grown by a chemical transport reaction (1000 → 900 °C) using I_2 as the transport agent [89].

In addition, VPO_4 can be obtained by reduction of VOPO_4 in a H_2/N_2 stream; the reduction is completed at around 800 °C [90]. Another procedure which generates very pure VPO_4 is the thermal degradation of the complex compound $(\text{NH}_4)_2 [(\text{VO})_2 (\text{HPO}_4)_2 \text{C}_2\text{O}_4] \cdot 5\text{H}_2\text{O}$ [91].

CrPO_4 can be obtained by solid-state reaction between $(\text{NH}_4)_2\text{HPO}_4$ and Cr_2O_3 at 900–1000 °C [92]. Different hydrates of CrPO_4 are also known [24, 93, 94]; its dehydration, under certain conditions, allows the anhydrous material to be obtained in its two polymorphic forms: the CrVO_4 modification ($\beta\text{-CrPO}_4$) is formed at temperatures of about 1000 °C, the $\alpha\text{-CrPO}_4$ form at temperatures above 1175 °C (see also [95]). Fig. 7 shows, in a schematic way, the most important and interesting relations between these systems (see also [24]).

FePO_4 can only be obtained by treating the normal, pre-formed, quartz-like material at pressures of about 50 kbar and at temperatures between 800 and 900 °C [25, 26]. AlPO_4 can also be prepared in a similar way, by transforming the quartz-type phase (ca. 100 kbar and 1000 °C) [28].

In(III) and Tl(III) orthophosphates can be prepared under hydrothermal conditions at temperatures between 350 and 400 °C, by suspending the appropriate oxide (In_2O_3 or Tl_2O_3) in diluted H_3PO_4 in a reaction bomb for a week or more [23].

3.4. Chromates

A general method for the synthesis of $\text{M}^{\text{II}}\text{CrO}_4$ materials (M^{II} = nickel, cobalt, zinc, copper, cadmium) is the

hydrothermal reaction between the respective metal carbonates (or basic carbonates) and concentrated CrO₃ solutions. Working temperatures range between 185 and 220 °C, with reaction times of around 5 h [1,96].

MgCrO₄ can be obtained by careful dehydration of MgCrO₄·5H₂O (this last salt is prepared by crystallization from a neutral magnesium chromate solution [97,98]); this process is complete at around 340 °C [39], but the product is poorly crystalline. Better quality crystals can be obtained by the reduction of the MgCrO₄ formed in hydrogen (2MgCrO₄ + 3H₂ → MgCr₂O₄ + MgO + 3H₂O) and subsequent oxygenation of the reaction mixture at 360–500 °C (MgCr₂O₄ + MgO + 3/2O₂ → 2MgCrO₄) [39].

3.5. Sulphates

All the M^{II}SO₄ compounds belonging to the CrVO₄ structure type may be prepared by evaporation of a solution of one of its stable hydrates in sulphuric acid, at temperatures of around 250–300 °C. MgSO₄ can also be obtained from the respective oxide in H₂SO₄, evaporating the solution and tempering the resulting crystals at 400 °C for several days [48]. In the case of CdSO₄, one must heat the low-temperature form to temperatures above 800 °C and then quench the material rapidly [47]. Recent experiments carried out in our laboratory with this compound show that it is very difficult to obtain totally pure samples of the CrVO₄ modification of this sulphate.

Certain of the sulphates can also be obtained from its hydrates, in a dynamic vacuum system, by stepwise temperature increments [99].

The reaction of anhydrous Co(II) and Ni(II) sulphites with SO₂ in dimethylsulphoxide (DMSO) generates the corresponding pyrosulphates, which can be obtained as the crystalline DMSO complexes, M^{II}(DMSO)₆ S₂O₇. The thermal decomposition of these complexes allows anhydrous CoSO₄ and NiSO₄ to be obtained [100]. Although no details of crystal quality and structural characteristics have been reported, it is certain that the CrVO₄ modifications were generated.

Another interesting and general procedure for the synthesis of these M^{II}SO₄ materials seems to be the reaction of dimethylsulphate, with fine powdered metals, or their oxides/halides, according to [101]:



3.6. Selenates

Anhydrous M^{II}SeO₄ (M^{II} = manganese, cobalt, nickel, copper, zinc, magnesium) selenates can be obtained by careful dehydration of their hydrates. However, only NiSeO₄ belongs to the CrVO₄ structure type [70,71]. All the other materials obtained in this way adopt the ZnSO₄ structure [69,73]. Only by heating at 400 °C at a pressure of 40 kbar for 30 min, followed

by rapid quenching under pressure, can these selenates be obtained with the CrVO₄ structure [69,72].

The starting, hydrated selenates may be obtained by oxidation of the respective metal selenites with H₂O₂ [102] or by treatment of the metal carbonates or oxides with selenic acid [103–105].

4. Physicochemical properties

In this section, the most important physicochemical properties of the CrVO₄-type materials are presented and discussed. The main aspects to be covered are the thermal behaviour, the vibrational spectra and the magnetic properties. Some other, miscellaneous, physicochemical data will also be included and discussed.

4.1. Thermal behaviour

A significant amount of information on the thermal properties of the compounds discussed in this review is available so far. But not all of this is directly relevant, because much of the accumulated information refers to hydrated forms of these materials. Therefore, we have attempted to concentrate the discussion, as much as possible, on those aspects which directly involve CrVO₄-type compounds.

4.1.1. Vanadates and phosphates

The greatest part of these materials are thermally quite stable.

CrVO₄ itself is known to melt incongruently at 860 °C (see [106] and references therein), whereas the corresponding phosphate is more stable. It changes to the high-temperature form (α-CrPO₄) at temperatures above 1175 °C, as previously discussed (see also Fig. 7).

As commented in previous sections, FeVO₄ is only stable in a small temperature range (540–570 °C) [7].

No concrete data are so far available concerning the behaviour of FePO₄, AlPO₄, TiPO₄ and VPO₄ at higher temperatures.

TiPO₄ seems to be stable up to 600 °C, but in the temperature range between 615 and 680 °C, it loses oxygen, generating a Ti(I) polyphosphate, probably a chain polyphosphate, as shown by chromatographic analysis. The enthalpy associated with this decomposition was determined to be 51.2 kcal mol⁻¹ [107].

The corresponding vanadate, TiVO₄, is much more unstable. It decomposes above 300 °C, generating a Ti(I) metavanadate [11,87].

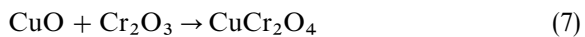
InVO₄, on the other hand, melts incongruently at 1134 °C [11], whereas the corresponding phosphate does not decompose up to 1600 °C. At this temperature, it melts and loses P₄O₁₀, above 1800 °C [108].

4.1.2. Chromates

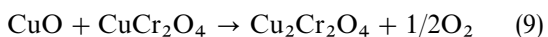
Different authors have reported information concerning the thermal behaviour of the chromates under study. This information is particularly abundant in the case of CuCrO₄, due to its relation to the

so-called Adkins' catalyst (the CuO/CuCr₂O₄ system) [109, 110].

Investigations by Charcosset *et al.* [111] and Walter-Levy and Goreaud [112] showed that the decomposition of CuCrO₄ occurs in the following steps, between 420 and 510 °C



However, above 800 °C, the following reaction takes place

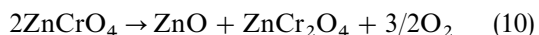


Working isothermally at 430 °C, the final product is the CuO/CuCr₂O₄ mixture [112].

An initial kinetic study of this thermal decomposition, under isothermal conditions, between 575 and 650 °C has shown that the isotherms follow a kinetic law of the type $\log(1/1-x) = kt$, giving an activation energy $E_a = 401.7 \text{ kJ mol}^{-1}$ [113]. Recently, this process was analysed more thoroughly. The rate of oxygen release, measured by isothermal TG methods obeys an Avrami–Erofeev equation, $[-\ln(1-\alpha)]^{1/n} = kt$, with $n = 2$ and activation energy values of 248.1 and 229.3 kJ mol^{-1} in air and flowing nitrogen atmospheres, respectively [114, 115].

The thermal decomposition of MgCrO₄ was reported to start at about 600 °C [116]. On the other hand, Darrie *et al.* [117], using DTA measurements showed that dehydration of MgCrO₄·5H₂O was complete at about 500 °C and that the decomposition of the anhydrous phase begins at 610 °C. The kinetic study of the isothermal decomposition of MgCrO₄ between 600 and 672 °C showed no acceleratory period and the obtained results were well represented by the contracting sphere model $1-(1-\alpha)^{1/2} = kt$ (for α -values between 0.0 and 0.98) and gave an activation energy of 330.5 kJ mol^{-1} . This value is of the same order as those found for the thermal degradation of the chromates of calcium, neodymium and samarium [117]. The decomposition products were identified as MgO and MgCr₂O₄ [39, 118].

The thermal decomposition of ZnCrO₄ in vacuum proceeds in a single step between 400 and 600 °C, according to [119]



However, in air the decomposition begins around 255 °C [120]. In the same conditions, decomposition of NiCrO₄ starts at 470 °C [120, 121].

The thermal stability of the zinc, nickel and copper chromates increases in the order ZnCrO₄ < CuCrO₄ < NiCrO₄ both in air and in vacuum as well as in inert atmospheres [120].

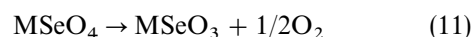
4.1.3. Sulphates and selenates

The thermal behaviour of a great number of hydrated sulphates and selenates has been investigated by TG and DTA methods. As described in Section 3, only in

the case of the sulphates are materials belonging to the CrVO₄-type obtained by this procedure.

From TGA/DTA measurements, Ostroff and Sanderson were able to give a complete set of decomposition temperatures for anhydrous sulphates [122]. These authors also summarize older literature data on the dehydration and decomposition of sulphates. Their data are reproduced in Table VIII. The formation of intermediate basic sulphates of the type 2CuO·SO₃ or 3ZnO·2SO₃ was also determined [122] and confirmed by other authors [123]. Some other studies on sulphates can be found elsewhere [124–128].

Anhydrous selenates are usually more unstable thermally than the corresponding sulphates [129, 130]. In the case of anhydrous selenates, thermal decomposition usually occurs in the following steps [129–133]



Also in these materials, in certain cases other intermediate or final products, such as 2ZnO·ZnSeO₃ [131] have been postulated.

Kinetic studies of the thermal degradation of some of these sulphates and selenates were also undertaken [134–136]. The degree of decomposition of CoSO₄ (between 840 and 880 °C) and of MgSO₄ (between 1020 and 1060 °C) was practically a linear function of time, whereas that of CuSO₄ increases parabolically [134]; the data were interpreted by means of the Roginsky–Todes equation [134]

$$1 - (1 - \alpha)^{1/3} = kt \quad (13)$$

On the other hand, it has been shown that the kinetics of the reduction of CoSO₄ and CoSeO₄, in a hydrogen atmosphere, agreed with the branched chain model of Prout and Tompkins [136].

A more recent study indicates that the thermal decomposition of the nickel, cobalt, copper and zinc sulphates occurred at the phase boundary between the undecomposed sulphate and the oxide product and that the boundary proceeds uniformly from the surface to the interior of the material. The activation energies lie very close to the enthalpies of decomposition of these sulphates [135].

TABLE VIII Decomposition temperatures of M^{II}SO₄ materials and final pyrolysis residues (from [122])

Compound	Decomp. temp (°C)	Final residue
MgSO ₄	895	MgO
CdSO ₄	816	CdO
MnSO ₄	755	Mn ₃ O ₄
CoSO ₄	708	Co ₃ O ₄
NiSO ₄	675	NiO
ZnSO ₄	646	ZnO
CuSO ₄	598	CuO
FeSO ₄	537	Fe ₂ O ₃

4.2. Vibrational spectra

4.2.1. Theoretical vibrational analysis of the CrVO₄ lattice

In recent years, infrared and Raman spectra of most of the reviewed materials have been recorded and analysed. In order to discuss systematically the available spectroscopic information, we begin with a brief theoretical vibrational analysis of the CrVO₄ structure.

On the basis of its structural data it is possible to perform a factor group analysis of this lattice. This analysis has been undertaken using the tables of Adams and Newton [137] (see also [138, 139]). The results are presented in Table IX. On the other hand, and in order to facilitate the discussions of the next sections, we present in Table X a conventional correlation between the point group of the “free” VO₄³⁻ units (T_d), its site group (C_{2v}) and its factor group (D_{2h}). In Table X, the 18 species corresponding to the internal modes, as determined by the analysis summarized in Table IX, were also assigned to specific vibrational modes of the VO₄³⁻ moieties: the symmetric (ν₁) and antisymmetric (ν₃) stretching vibrations and the symmetric (ν₂) and antisymmetric (ν₄) bending modes, respectively.

In the following sections, we discuss the spectroscopic results obtained for the different materials adopting the CrVO₄ structure type.

4.2.2. Vanadates

The infrared spectrum of CrVO₄ was first investigated by Olivier [140, 141], although in these studies some assignments and suppositions were not totally convincing. Further studies on this [92] and on the related indium and thallium vanadates [142] and on some of the isostructural chromates [143] allowed a definitive insight into the vibrational properties of this type of material to be obtained.

In the first studies [140, 141], the assignment of the higher frequency doublet was not totally clear and also mixing between VO₄ and CrO₆ vibrations, in the high-frequency region, was supposed. A more convincing assignment was given later [92], which definitively showed the existence of important coupling effects between the two mentioned building blocks, only in the bending region of the tetrahedral units.

The symmetric stretching vibration, ν₁, is often not observed in the infrared spectra, even though its activity is theoretically predicted. This is probably due to its overlapping by one of the strong and broad ν₃ components.

The IR spectrum of CrVO₄ is shown in Fig. 8. In this case, the ν₁ mode is visualized at 910 cm⁻¹, and this assignment is confirmed by comparison with the vibrational spectrum of InVO₄ in which the strongest Raman line, assignable unambiguously to this mode, lies at 915 cm⁻¹ [142].

The most interesting aspect of the stretching region is the large separation between two of the ν₃ components (870, 715, 660(shoulder) cm⁻¹) which is in agreement with the structural characteristics of the VO₄³⁻ units, which, as formerly discussed, present two very different V–O bond distances. On the other hand, all the bands predicted by the site-symmetry analysis are observed in this region. The complexity observed in the bending region supports the existence of strong coupling effects in this spectral region. Probably only the ν₄ mode of the tetrahedral units (components at 490, 457, 420 and 391 cm⁻¹) remains as a somewhat “pure” mode, whereas all the other bands are surely of mixed nature.

No vibrational spectroscopic data are so far available for the Fe(III) orthovanadate adopting the CrVO₄ structure, but the infrared spectrum of the normal (triclinic) modification has been reported [17].

TABLE IX Factor group analysis of the CrVO₄ lattice (Cmcm-D_{2h}¹⁷, Z/2 = 2)

Atom no.	Position	A _g	B _{1g}	B _{2g}	B _{3g}	A _u	B _{1u}	B _{2u}	B _{3u}
Cr	2a	0	0	0	0	1	2	2	1
V	2c	1	1	0	1	0	1	1	1
O(1)	4f	2	1	1	2	1	2	2	1
O(2)	4g	2	2	1	1	1	1	2	2
N _{TOT.} (= 3N = 36)		5	4	2	4	3	6	7	5
T _{ACUST.} (= 3)							1	1	1
T _{TOT.} (= 12)		1	1	0	1	1	3	3	2
Rotat. (= 6)		0	1	1	1	1	1	0	1
N (internal) (= 18)		4	2	1	2	1	2	4	2

TABLE X Correlation between the point group (T_d), the site symmetry (C_{2v}) and the factor group (D_{2h}) for CrVO₄

Vibration modes	T _d	C _{2v}	D _{2h}
ν ₁	A ₁	A ₁	A _g + B _{2u}
ν ₂	E	A ₁ + A ₂	A _g + B _{2g} + A _u + B _{2u}
ν ₃	F ₂	A ₁ + B ₁ + B ₂	A _g + B _{2u} + B _{3g} + B _{1u} + B _{1g} + B _{3u}
ν ₄	F ₂	A ₁ + B ₁ + B ₂	A _g + B _{2u} + B _{3g} + B _{1u} + B _{1g} + B _{3u}

T_d: A₁, E, F₂: Raman; F₂: IR.

C_{2v}: A₁, A₂, B₁, B₂: Raman; A₁, B₁, B₂: IR.

D_{2h}: A_g, B_{1g}, B_{2g}, B_{3g}: Raman; B_{1u}, B_{2u}, B_{3u}: IR; A_u: inert.

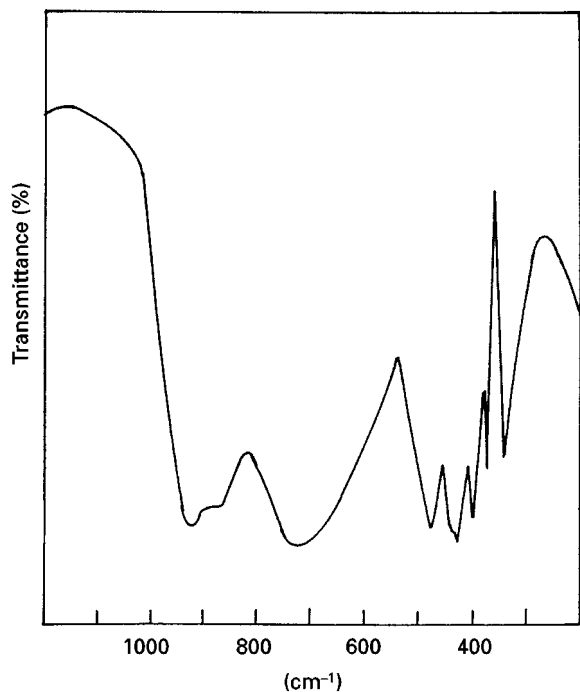


Figure 8 Infrared spectrum of CrVO_4 .

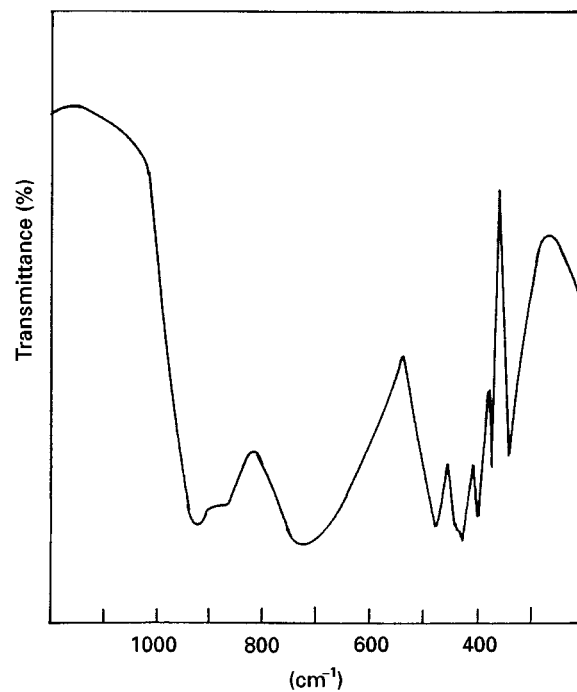


Figure 9 Infrared spectrum of $\beta\text{-CrPO}_4$.

Infrared spectra of the low-temperature form of InVO_4 [19] and for a series of phases of the type $(\text{Cr}_{1-x}\text{Fe}_x)\text{VO}_4$ [144] have been analysed in detail. These materials belong, as discussed above, to the $\alpha\text{-MnMoO}_4$ structural type. Recently, a detailed Raman study of this structure, including a normal coordinate analysis, has been published [145].

Finally, it is interesting to comment that the infrared spectrum of NaCaVO_4 , with a structure closely related to that of CrVO_4 [22], also presents a spectral pattern which in the stretching region is very similar to those of all the related vanadates [146].

4.2.3. Phosphates

The $\text{M}^{\text{III}}\text{PO}_4$ phosphates adopting this structure type also present very characteristic spectra. As an example, Fig. 9 shows the infrared spectrum of the corresponding chromium(III) compound, $\beta\text{-CrPO}_4$. As can be seen, also in this material, the splitting in the PO_4 stretching region is very important and the broad ν_3 -components usually overlap the weaker symmetric stretching mode.

The infrared spectra of TiPO_4 and VPO_4 have been recently investigated [147] and vibrational data for InPO_4 and TIPO_4 were also known [148–50]. In these last cases, the noted splitting in the stretching region is still more important than in the other phosphates.

Especially worthy of comment is the fact that, as in the case of the phosphate materials, the P–O stretching bands appear in a higher frequency range than for the corresponding vanadates, the possibilities of coupling of these vibrations with MO_6 motions are further reduced. The fact that also in these cases two largely split groups of bands can be observed in this region, demonstrates conclusively that the splitting is independent of coupling effects [92].

In addition, some spectroscopic studies have been made with mixed systems containing InPO_4 . As expected, this compound forms solid solutions with the isostructural InVO_4 in the full concentration range and their vibrational behaviour changes stepwise with varying substitutional degree [149]. On the other hand, in the $\text{InPO}_4/\text{ScPO}_4$ system only partial substitutions are possible: InPO_4 accepts 25 mol % ScPO_4 , whereas ScPO_4 only accepts InPO_4 in amounts not exceeding 5 mol %. These solid solutions, therefore, present a more complex spectroscopic behaviour [150].

4.2.4. Chromates

Infrared data for all the chromates belonging to the CrVO_4 structure type have been reported [143, 151, 152]. Raman data were only available for CdCrO_4 [151] and CuCrO_4 [152], but its assignment in the first case was not totally correct. Also in these cases, important splittings of the ν_3 components are observed and ν_1 can usually not be identified.

Approximate force constants for the Cr–O bonds in these materials were also estimated [151].

Infrared spectra for the phases MgCrO_4 and CdCrO_4 , belonging to the $\alpha\text{-MnMoO}_4$ structure, were also reported [143].

4.2.5. Sulphates and selenates

Spectroscopic studies on sulphates and selenates of the CrVO_4 -type are very scarce and practically no Raman data have so far been published.

The infrared spectra of MgSO_4 , MnSO_4 , FeSO_4 , CoSO_4 and NiSO_4 have been published and assigned [99, 153], although the factor group analysis given in [153] is incorrect. Curiously, in most of these sulphates, more components than those predicted by the

factor group analysis could be observed in the ν_3 -region and its splitting is also very large [153]. On the other hand, the symmetric stretching mode ν_1 usually appears as a very well-defined band, clearly differentiated from the ν_3 components.

The bending region also appears better defined than in the other previously analysed materials, suggesting less important coupling effects.

Infrared spectra for some sulphates adopting the ZnSO_4 structure have also been investigated [99, 153, 154]. The spectra of these materials show a good resolution in all the spectral ranges, too.

Vibrational spectroscopic data for selenates adopting the CrVO_4 structure are totally lacking.

4.3. Electronic spectra

A very limited number of studies devoted to the analysis of electronic spectra of these materials have so far been undertaken. They are mainly restricted to some of the chromates and the information is essentially centred on the analysis of the charge transfer transitions within the CrO_4^{2-} anion. The materials investigated include MgCrO_4 [117], ZnCrO_4 [155] and CuCrO_4 [152].

No data on the characteristic “d–d” transitions of the many first-row transition metal cations present in the materials of the reviewed type are available.

4.4. Magnetic properties

Because of the short cation–cation distances along the CrO_6 chains in the CrVO_4 structure, strong exchange interactions can be expected. They generate an interesting, but complex magnetic behaviour and at present no unified model exists which allows the behaviour of all these materials to be explained. Much experimental and theoretical work is evidently necessary to obtain a complete understanding.

Magnetic susceptibility studies have been performed for most of the materials belonging to this structure. In numerous cases, the magnetic structure has also been investigated by means of neutron diffraction studies. These investigations have sometimes been complemented by calorimetric and ESR measurements.

Table XI summarizes the available magnetic data for all materials belonging to the CrVO_4 structure type. A brief analysis of this information is given in the following sections.

4.4.1. Vanadates

A thorough magnetic susceptibility study of CrVO_4 [12] showed that above 100 K the susceptibility obeys the Curie–Weiss law with a magnetic moment of 2.1 BM and a Weiss temperature, θ , of -214 K, indicative of antiferromagnetic coupling. Below 100 K, a broad minimum is observed in the χ^{-1} versus temperature plot which implies the existence of a low-dimensional magnetic ordering. Intrachain and interchain interactions have been analysed and discussed from these experimental results [12].

TABLE XI Magnetic data for materials belonging to the CrVO_4 structure type

Compound	μ_{eff} (BM)	θ (K)	T_N (K)	Reference
CrVO_4	2.1	-214	49.5	[12,160]
FeVO_4	6.29	-201		[8]
CrPO_4	3.9	-80	37	[27,161]
VPO_4	3.62	$-529(?)$	25.5	[27,162]
TiPO_4	2.0 ^a			[27]
FePO_4	6.02	-128	60	[25,26]
CoCrO_4	5.02	-24	14	[165]
NiCrO_4	3.08	-105	23	[165]
FeSO_4	5.20	-30.5	21	[156]
NiSO_4	3.82	-82	37	[156]
CoSO_4	5.65	-47	15.5	[156]
MnSO_4	5.8	-26	11.5	[170]
NiSeO_4	2.14 ^b		27	[176]
MnSeO_4	4.76 ^c		20.5	[177]

^a Below 100 K.

^b At 4.2 K.

^c at 5 K.

Earlier work on CrVO_4 , showed that it has antiferromagnetically ordered chains which are coupled together ferromagnetically [156]. For the Néel temperature, contradictory values of 50 K [156] and 62 K [157] have been reported. ESR data show a single peaked absorption with a g -value of 1.972 ± 0.005 at all temperatures [158] (see also [159, 160]). From these data the best value for the Néel temperature seems to be 49.5 K [160]. The ESR results also suggest considerable short-range order above the Néel temperature [158].

A similar magnetic behaviour has been observed for FeVO_4 . The magnetic susceptibility curve exhibits a broad maximum at around 52 K. Above 100 K the material obeys the Curie–Weiss law with a Weiss constant of -201 K and an effective magnetic moment of 6.29 BM [8].

Some results are available for the normal (triclinic) form of FeVO_4 [157].

4.4.2. Phosphates

The magnetic susceptibility of β - CrPO_4 follows the Curie–Weiss law above 78 K, with an effective magnetic moment of 3.9 BM [27]. Measurements at lower temperatures have shown that the compound orders antiferromagnetically at around 37 K and their magnetic structure has been determined by powder neutron diffraction at 5 K [161]. This structure consists of cycloidal spiral of moments which propagates along [001].

The temperature dependence of the magnetic susceptibility of VPO_4 shows a broad minimum for χ^{-1} at about 140 K [27] and an effective magnetic moment of 3.62 BM was determined in the high-temperature region. A more detailed study of this material, including the determination of its magnetic structure by means of neutron diffraction, has been recently published and allowed a wider insight into finer details of the magnetic behaviour of this compound [162].

In the case of TiPO_4 , the magnetic susceptibility is nearly independent of temperatures above about

140 K. Below this temperature, the susceptibility decreased to about half that at high temperature, and then increased again on going to liquid helium temperature [27]. This peculiar behaviour has been discussed admitting a defect structure [27], but this view has been recently refuted [81]. The analysis of the magnetic structure, from neutron diffraction data, has also not allowed a clear explanation of the different behaviour of TiPO_4 and VPO_4 [162].

For polycrystalline TiPO_4 , an ESR spectrum has been recorded at 292 K [27] and also a detailed study of the magnetic properties of the $(\text{Ti}_{1-x}\text{V}_x)\text{PO}_4$ system has been published [163].

For FePO_4 , a value of 6.02 BM was determined for the magnetic susceptibility, in good agreement with the value calculated for a high-spin Fe(III) ion [25]. Other measurements indicate that this material becomes antiferromagnetically ordered at 4.2 K. Its magnetic structure apparently consists of weakly ferromagnetic [001] chains, coupled together antiferromagnetically [26].

In addition, magnetic data for the quartz-like modification of FePO_4 have been reported [164].

4.4.3. Chromates

The magnetic susceptibilities of CoCrO_4 and NiCrO_4 were determined between liquid helium and room temperature and their magnetic structures investigated by neutron diffraction [165]. In the temperature range between 150 and 300 K both materials obey the Curie–Weiss law. Néel temperatures for both compounds are similar (23 K for NiCrO_4 and 14 K for CoCrO_4).

In the case of CuCrO_4 , only ESR measurements were performed. The spectra only show a very broad signal with a mean g -value of 2.16 and a band width of around 650 G [166] (see also [119]).

4.4.4. Sulphates

Using low-resolution powder neutron diffraction data, Frazer and Brown found that both FeSO_4 and NiSO_4 exhibit antiferromagnetic chain coupling with spin directions parallel to the b -axis [156]. On the other hand, CoSO_4 was found to present a non-collinear variant of the former magnetic structure [156].

The results obtained for CoSO_4 were also explained on the basis of different arguments [167]. Further studies have also shown that for FeSO_4 and NiSO_4 , the dominant interactions occur between the first and second neighbours [168].

The remaining member of the series, MnSO_4 , has an even more complicated behaviour. It presents a cycloidal cone spiral of moments in the (001) plane with the propagation vector directed along a and spiral components in the ab plane; the moments are antiferromagnetically coupled along the chains [169]. In this case there are indications that the value of the Néel temperature lies below 20 K [169]. This prediction was confirmed some years later [170].

On the other hand, Sólyom has suggested that this particular magnetic structure should arise after

cooling, through three separate phase transitions and should be elliptical with an oscillating z -component [171]. These predictions have been confirmed by specific heat measurements [170] and neutron diffraction studies at different temperatures [172]. The specific heat measurements show that the three phase transitions occur at 11.5 K (Néel temperature), 10.5 and 7.2 K, respectively [170].

Investigations of the magnetic properties of CoSO_4 [173, 174], FeSO_4 [168] and CuSO_4 [175], belonging to the ZnSO_4 structure type, have also been performed.

4.4.5. Selenates

Only a few magnetic data are available for $\text{M}^{\text{II}}\text{SeO}_4$ materials. The magnetic structure of NiSeO_4 was determined from powder neutron diffraction data; it is similar to that of other CrVO_4 phases, consisting of ferromagnetic (001) sheets which are antiferromagnetically coupled with other sheets [176].

MnSeO_4 has been investigated by powder neutron diffraction; it has an antiferromagnetic structure below the Néel temperature (20.5 K) [177], and long-range interactions are evident [168].

On the other hand, information is also available for some selenates adopting the ZnSO_4 structure: CoSeO_4 [176], CuSeO_4 [178], MnSeO_4 [178–180].

4.5. Mössbauer spectra

Mössbauer investigations have been undertaken for some of the iron compounds belonging to this structure type.

For FePO_4 , at 63 K, the spectrum comprises a simple, symmetrical quadrupole doublet with an isomer shift of $+0.539 \pm 0.010 \text{ mm s}^{-1}$ (relative to metallic iron), which is typical for a six-coordinated high-spin Fe(III) ion. The value of the quadrupolar splitting of $1.811 \pm 0.010 \text{ mm s}^{-1}$ [26] indicates a considerable distortion around the Fe(III) site. Below 60 K, the spectrum changes to a six-line pattern due to the onset of long-range magnetic order.

FeVO_4 shows a similar behaviour. At 77 K, an isomer shift of 0.51 mm s^{-1} was found, whereas the quadrupolar splitting (0.39 mm s^{-1}) is appreciably smaller than that of FePO_4 [8].

In the case of FeSO_4 , Mössbauer spectra were obtained for the three known polymorphic modifications in the temperature range between 4.2 and 30 K [57]. The quadrupolar splitting of the CrVO_4 -like material is larger than that of the ZnSO_4 -type phase.

Mössbauer data are available for the quartz-like FePO_4 [164] as well as for the normal (triclinic) form of FeVO_4 [9] and for the $(\text{Cr}_x\text{Fe}_{1-x})\text{VO}_4$ phases, adopting the α - MnMoO_4 structure [181]. Studies were also performed with CoSO_4 (ZnSO_4 structure), labelled with ^{57}Co [182].

4.6. Miscellaneous physicochemical properties and applications

During recent years, a great amount of thermodynamic and thermal data for materials belonging to

the reviewed structure type has been published. As already indicated, many of the compounds present different polymorphic modifications, with structures different from that of the CrVO₄-type.

Thus, only brief comments on data referring to CrVO₄ itself and to some MSO₄ materials, are given as examples.

Heat capacities for CrVO₄ were first determined between 60 and 1080 K [183]. Later, heat capacities were also determined at low (3–80 K) [184] and high (273–873 K) [185] temperatures as well as in the full range between 5 and 300 K [186]. There is an anomaly in the C_p/T relationship, with a maximum at 50.5 K, which is in good agreement with the Néel temperature (50 K) obtained from magnetic susceptibility and ESR measurements (cf. Section 4.4.1). Thermodynamic functions of CrVO₄ were calculated between 5 and 300 K and tabulated in 5 K intervals [186]. The heat of formation of CrVO₄ was also determined [187].

Heat capacity and thermodynamic functions were also determined for the mixed vanadate of composition Fe_{0.5}Cr_{0.5}VO₄ [188].

In the case of MSO₄ materials, lattice energies, calculated with Kapustinskii's equation, have been given for MnSO₄ and ZnSO₄ [189] and heats of formation of the cobalt, nickel, copper and zinc sulphates determined [190]. For the four last-mentioned phases, heat capacities between 50 and 116 K [191] and heats for the polymorphic transitions [192] have also been determined. Thermodynamic data for a number of MSO₄ compounds were also published [193].

Older literature references on thermal properties for most of the reviewed materials can also be found in *Gmelin's Handbuch* [86].

Electro-optical properties of InVO₄ and TiVO₄ have also been investigated, both materials being dielectrics at room temperature [194].

For InPO₄, the band gap between the valence and the conduction band was estimated to be 4.5 ± 0.3 eV, using ultraviolet-photoelectron spectroscopy and electron loss spectroscopy [195].

Electrical transport properties of polycrystalline CrVO₄ have been studied by measuring a.c. and d.c. electrical conductivities, thermoelectric power and relative permittivities in the temperature range between 300 and 1000 K. CrVO₄ is a p-type semiconductor, with an energy gap of 3.6 eV [196].

XANES spectra of CrVO₄, together with those of other vanadium compounds, have been reported [197]. For the quartz modification of FePO₄, XANES and EXAFS studies have also been performed [198, 199].

Interestingly, solid solutions are obtained in the system Li₃VO₄/InVO₄, whereas solid solutions do not occur if InVO₄ is replaced by CrVO₄. On the

other hand, mutual solid solutions between InVO₄ and CrVO₄ are extremely limited [200].

Much work has been done in recent years on the system CrVO₄/MoO₃, and a new phase of composition CrVMoO₇ has been characterized [201–205]. Such a compound, and other related materials, attained some interest in the field of catalysis [205, 206]. A great number of patents can be found in the literature concerning the use of various other of the discussed materials as catalysts. In particular, the chromates of nickel, copper and cadmium are often mentioned.

On the other hand, MgCrO₄ is mentioned as an anticorrosive pigment [207] and ZnCrO₄ as an anti-rust pigment [208].

5. Materials belonging to the α -CrPO₄ structure type

As stated in Section 3.3, heating of β -CrPO₄ at temperature above 1175 °C produces the high-temperature form of this material, usually called α -CrPO₄.

The structure of this polytype has been independently solved by Attfield *et al.* from synchrotron X-ray powder data and neutron diffraction analysis [209, 210] and by Glaum *et al.*, from single crystals, obtained by a chemical transport method [211].

Only two other materials adopt this structure type, namely α -CrAsO₄ [212] and RhPO₄ [213].

The arsenate can be obtained by firing the so-called "grey-violet chromium(III) orthoarsenate" [214] up to 900 °C [212]. A second form of the arsenate, β -CrAsO₄, is known. It can be obtained hydrothermally at 700 °C and belongs to the ZnSO₄ structure ($a = 0.8995$ nm, $b = 0.6237$ nm, $c = 0.4755$ nm and $Z = 4$) [215].

RhPO₄ was first obtained by treating a nitric acid solution of Rh₂O₃ with the stoichiometric quantity of phosphoric acid; the carefully dried mixture was subsequently fired at 970 °C [213]. Another easier preparative method consists of the heating of a well-homogenized equimolecular mixture of [Rh(NH₃)₅Cl]Cl₂ and (NH₄)₂HPO₄ up to 970 °C [216]. Recently, single crystals of this phosphate could be prepared by a chemical transport method [217].

The structural data for the three materials adopting this structure are shown in Table XII. The structure (orthorhombic, space group D_{2h}^{28} -*Imma* and $Z = 12$) is very complex, consisting of an infinite network of linked CrO₆ octahedra and PO₄ tetrahedra. Pairs of edge-sharing Cr(2)O₆ octahedra, interconnected by P(2)O₄ tetrahedra, form sheets in the bc plane. These sheets are linked to each other by chains of alternating Cr(1)O₆ octahedra and P(1)O₄ tetrahedra, running parallel to b , generating large channels in this direction.

TABLE XII Crystallographic data of materials belonging to the α -CrPO₄ structure type

Compound	a (nm)	b (nm)	c (nm)	Volume (10^{-3} nm ³)	Reference
α -CrPO ₄	1.04059	1.28995	0.62994	845.574	[210]
α -CrAsO ₄	1.0577	1.3324	0.6484	913.777	[212]
RhPO ₄	1.03967	1.31124	0.63929	871.516	[217]

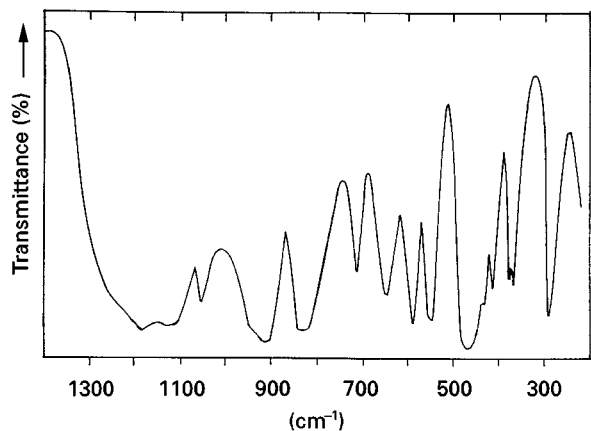


Figure 10 Infrared spectrum of α -CrPO₄.

Another compound directly related to α -CrPO₄ is the material of composition NaV₃P₃O₁₂ (chemical formula NaV^{II}V^{III}₂P₃O₁₂), characterized by Kinomura *et al.* [218]. In this structure (orthorhombic, space group *Imma*, $Z = 4$, $a = 1.0488$ nm, $b = 1.3213$ nm, $c = 0.6455$ nm), the Na⁺ ions are located in the tunnels of the α -CrPO₄ framework.

Infrared spectra for the three materials adopting the α -CrPO₄ structure [216], as well as for NaV₃P₃O₁₂ [219], have been recorded and analysed with a factor group treatment. These spectra are very complex, as can be seen in Fig. 10 for α -CrPO₄ itself. A comparison of this spectrum with that corresponding to β -CrPO₄ (Fig. 9) shows that it is easy to differentiate both CrPO₄ polymorphs by this spectroscopic technique.

The magnetic properties of α -CrPO₄ and α -CrAsO₄ have also been investigated by magnetic susceptibility measurements and powder neutron diffraction [220]. α -CrPO₄ follows the Curie–Weiss law at high temperatures with $\mu_{\text{eff}} = 3.98$ BM and $\theta = -67.7$ K. Its Néel temperature was determined to lie at 9.1 K. In the case of α -CrAsO₄, the antiferromagnetic transition occurs at even lower temperature (7.7 K) and also at higher temperatures the material shows a Curie–Weiss behaviour with $\mu_{\text{eff}} = 3.80$ BM and $\theta = -33.7$ K.

Both materials reveal ferromagnetic and antiferromagnetic interactions, arising from different linkages of CrO₆ octahedra [220].

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