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$AlVO_3$, a Metal-Deficient Spinel

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Hydrogen reduction of $AlVO_4$ at 1000°C yields $AlVO_3$ with a metal-deficient spinel structure $(Al_{2/3})[Al_{2/3}V_{1\,1/3}]O_4$. X-ray, neutron, and electron diffraction examination of the compound showed that aluminium atoms randomly occupy two-thirds of the available tetrahedral sites within a spinel unit cell of edge 8.422 ± .003 Å. Magnetic suseptibility measurements showed a Néel point at approximately 270°K, and neutron diffraction data taken at 4.2°K is consistent with an antiferromagnetic alignment of the V^{3+} ions in the B spinel sites such that spin cancellation occurs within the symmetry of the cubic cell. The compound is thermally stable to 1300°C, but at 100 kbar and 900°C was transformed to two corundum-type phases very close to the end-member compositions Al_2O_3 and V_2O_3.

Introduction

The Al_2O_3–V_2O_3 corundum-type solid solution shows a wide miscibility gap (*1*, *2*, *3*) as do the solid solutions of Al_2O_3 with Fe_2O_3 (4) and Ti_2O_3 (*5*, *6*). This behaviour is most likely due to differences in metal-metal interactions in the end members. In V_2O_3 for example there is an anomalously short V^{3+}–V^{3+} separation in the *c*-axis direction (*7*), associated with metal–metal bonds (*8*) and high electrical conductivity (*9*). No such interaction exists in diamagnetic Al_2O_3.

Burdese (*3*) has reported that hydrogen reduction of $AlVO_4$ (*10*, *11*) leads to the separation of two corundum-type phases with widely different compositions (*3*). The presence of free Al_2O_3 or V_2O_5 is hard to avoid in $AlVO_4$ preparations, and could on hydrogen reduction lead to "seeding" of end-member compositions. We have, therefore, repeated this work with very carefully prepared $AlVO_4$ in an attempt to synthesize corundum-type $AlVO_3$, the composition limit obtained by Foex and Martinez (*1*).

The product obtained was a new cubic form of $AlVO_3$, whereas hydrogen reduction of $CrVO_4$ (*12*) gave corundum-type $CrVO_3$. The present paper describes the structural, magnetic and spectral properties of $AlVO_3$ and its behaviour at elevated temperatures and pressures.

Experimental

$AlVO_4$ melts incongruently (*3*, *10*, *13*) and must be made at temperatures below 695 °C. Reaction between preformed Al_2O_3 and V_2O_5 is incomplete, and it was found necessary to react ammonium vanadate with aluminium hydroxide freshly precipitated by the hydrolysis of aluminium ethoxide (*14*). For the present purpose it was found unnecessary to isolate the ethoxide; instead, ethanol containing 10% of water was slowly added to the stirred slurry of alkoxide and ethanol. After filtration the hydroxide product was washed in ethanol and dried at 80 °C. $CrVO_4$ was prepared by the reaction of a finely ground mixture of Cr_2O_3 and either V_2O_5 or ammonium vanadate, first at 650 °C and then at 1000 °C.

Both $AlVO_4$ and $CrVO_4$ were reduced in a stream of dry oxygen-free hydrogen. Initial evolution of water was observed at 500–600 °C, and in both cases the preparations were finally heated to 1000 °C for 4–6 hr. For $AlVO_4$ preparations containing residual Al_2O_3 or V_2O_5 large quantities of corundum phases were present in the product. The weight losses from the $AlVO_4$ and $CrVO_4$ samples were precisely those required for the conversion of V^{5+} to V^{3+}, and a corresponding weight gain was obtained when the products were heated in air at 650–700 °C.

X-ray diffraction data were obtained with CuKα radiation using a diffractometer fitted with a proportional counter. Reflection intensities were measured from the areas of diffraction peaks recorded at slow scan rates, and for the estimation of lattice parameters finely ground KCl was included in a separate sample. Neutron powder patterns were taken on a triple axis spectrometer with the analyser set to pass only elastically scattered neutrons (*15*). The neutron wavelength was 1.08 Å. In subsequent calculations scattering factors for X-rays and neutrons were taken from Tables 3.3.1A and 3.3.4A, respectively, of International Tables for Crystallographers (*16*).

Magnetic susceptibilities were measured on a Gouy balance; visible and near infrared spectra were obtained with a Beckman DK-2A spectrophotometer fitted with a reflectance sphere, and far-infrared spectra were recorded with a Beckman IR-12 instrument.

Results

$AlVO_3$ was obtained as a black micro-crystalline powder. It was cubic, with $a_0 = 8.422 \pm 0.003$ Å, and the diffraction pattern corresponded to that of a spinel. $CrVO_3$ was also black. Its diffraction pattern was that of a corundum phase with $a_0 = 4.982 \pm 0.002$, $c_0 = 13.752 \pm 0.004$ Å, and intensities very similar to those of a sample of Cr_2O_3. No superlattice lines were observable in the diffraction pattern, nor in an electron diffraction pattern of a single crystal of micron dimensions. In particular, 100 and 111 reflections, which would result from an ilmenite-like ordering, were absent. Since the scattering power of atoms is very much stronger for electrons than for X-rays, electron diffraction is a particularly sensitive means of detecting superlattices. Their absence in the present case shows that Cr and V atoms are randomized in corundum-type $CrVO_3$ not only with respect to successive metal–atom layers, but also within such layers.

For $AlVO_3$, electron diffraction projections on (*hh*0) and (*hhh*), the two most likely planes of ordering, again showed no traces of superlattice reflections. As expected from this result, X-ray diffractometer scans at high gain failed to show any superlattice peaks of the kind found for example in γ-Fe_2O_3 (*17*, *18*). Structure factor calculations were therefore carried out for the various possibilities of randomizing $Al_{1\,1/3}V_{1\,1/3}O_4$ into the spinel structure. The results given in Table I show that a model with Al atoms randomized into 2/3 of the available tetrahedral sites and the remaining Al atoms, together with all the V atoms, randomized into the octahedral sites, i.e. $(Al_{2/3})[Al_{2/3}V_{1\,1/3}]O_4$, gave close agreement between observed and calculated structure factors, with $R_{F_0} = 9.5\%$. Placing V atoms in tetrahedral sites gave increasingly poor agreement between observed and calculated structure factors, and allowing octahedral instead of tetrahedral vacancies gave even worse agreement. The oxygen positional parameter $u = 0.385 \pm 0.004$, was obtained by least-squares refinement of the structure factors for the preferred model. Calculated intensities, corrected for multiplicity and Lorentz polarization, are compared in Table II with those observed.

TABLE I

DISTRIBUTION OF METAL IONS IN $AlVO_3$[a]

	Metal Ion Distribution		
Vacancies	Tetrahedral	Octahedral	$R_{F_0} = 100\Sigma(F_0 - F_c)/\Sigma F_0$
Tetrahedral	$Al_{2/3}$	$Al_{2/3}V_{1\,1/3}$	9.5
Tetrahedral	$Al_{1/3}V_{1/3}$	Al, V	15.0
Tetrahedral	$V_{2/3}$	$Al_{1\,1/3}V_{2/3}$	28.7
Octahedral	Al	$Al_{1/3}V_{1\,1/3}$	18.3
Octahedral	$Al_{1/2}V_{1/2}$	$Al_{5/6}V_{5/6}$	37.3
Octahedral	V	$Al_{1\,1/3}V_{1/3}$	51.7

[a] Based on structure factor calculations for noncoincident reflections, Table II, with $u = 0.385$.

TABLE II

X-RAY POWDER DIFFRACTION PATTERN OF CUBIC $AlVO_3$[a]
$CuK\alpha_1$, KCl Internal Standard

hkl	$\sin^2\theta_{obsd}$	$\sin^2\theta_{calcd}$	I_{obsd}	I_{calcd}[b]
111	0.02506	0.02510	631	816
220	0.06697	0.06692	96	87
331	0.09207	0.09202	727	862
222	0.10036	0.10038	101	27
400	0.13389	0.13384	867	712
331	0.15918	0.15894	44	52
422	0.20102	0.20076	28	27
511, 333	0.22598	0.22586	170	343
440	0.26788	0.26768	710	567
531	0.29271	0.29278	72	89
533	0.36017	0.35970	77	79
622	0.36815	0.36806	70	39
444	0.40126	0.40152	121	83
711, 551	0.42693	0.42662	14	44
731, 553	0.49363	0.49354	65	116
800	0.53531	0.53536	88	66
751, 555	0.62755	0.62738	39	80
662	0.63572	0.63574	41	21
840	0.66912	0.66920	149	109
911, 753	0.69432	0.69430	14	29
931	0.76155	0.76122	93	84
844	0.80300	0.80304	297	205

[a] $a_0 = 8.422 \pm 0.003$.
[b] Absolute units × 10^{-2}.

TABLE III

NEUTRON POWDER DIFFRACTION DATA FOR CUBIC $AlVO_3$
$T = 300°K$, $\lambda = 1.0815$ Å

hkl	I_{obsd}	I_{calcd}[a]
220	16	7
222	142	244
400	150	137
331	25	8
422	9	4
440	206	186
622	99	159
444	62	52
642	12	4
800	52	41
733	19	9
662	65	80
840	101	82
844	124	96
666, 10.2.2	78	67
880	48	33

[a] $cm^2 \times 10^{-24}$.

Neutron diffraction data was sought both to confirm the oxygen atom positions and to determine whether magnetic ordering occurred at low temperatures. The room temperature neutron diffraction intensities, Table III, agreed well with the occupancy model derived from the X-ray data of Table II with a value for R_{F_0} (neutrons) of 11.5% corresponding to an oxygen parameter $u = 0.382 \pm 0.005$.

The magnetic susceptibility of $AlVO_3$ was considerably lower than that calculated for a spin-free d^2 system, and was found to show a rather large dependence on applied field. The plots of χ_M versus $1/H$ were however linear at each temperature of observation. The infinite field values contain corrections of up to 30%, with estimated uncertainties of ±2%. Corrections for diamagnetism were also made (*19*). Above 270°K $AlVO_3$ showed an approximation to Curie–Wiess paramagnetism, with $\chi_M = 0.84/(T + 230)$, and an effective moment for V^{3+} of 2.6 μB. At still higher temperatures the limited data may well be asymptotic to a spin-free value of 2.83 μB as observed for $ScVO_3$ (*20*). Below 270 °K the susceptibility remained constant, indicating the onset of spin cancellation caused by antiferromagnetic alignment of V^{3+} spins in the lattice. However, the neutron diffraction pattern of $AlVO_3$ at liquid helium temperature was identical with the pattern obtained at room temperature, thus excluding the possibility of an ordering based on superlattices of the cubic spinel cell.

In the electronic absorption spectrum of $AlVO_3$, Table IV, the band at 9500 cm^{-1} indicates that the local site symmetry for at least some fraction of V^{3+} ions is less than cubic (*21*). Apparently the randomization of V^{3+} ions with Al^{3+} ions in octahedral

TABLE IV

V^{3+} ELECTRONIC ABSORPTION SPECTRA

V^{3+} in Al_2O_3 (*22*)	$V(H_2O)_6^{3+}$ (*23*)	VF_3 complexes (*24*)	$ScVO_3$ (*20*)	$AlVO_3$
34,500	(*)[a]	(*)	(*)	(*)
25,200	25,200	23,000	20,200	21,000
17,400	17,200	14,800	13,900	16,600
		10,200	9,750	9,500
(1200)			4,130	absent

[a] (*) not observed.

sites, or the presence of vacancies in tetrahedral sites adjacent to octahedral V^{3+} sites, is sufficient to lower the cubic symmetry which the spinel lattice would otherwise confer. The electronic spectrum did not indicate the presence of any considerable number of conduction electrons, and the room-temperature resistivity of a pressed and sintered pellet of $AlVO_3$ was found to be of the order of 10^5 Ω cm^{-1}, a value similar to that found by Foex and Martinez (*1*) for the semiconductance of a solid solution of somewhat less than 10% of V_2O_3 in Al_2O_3.

Tarte (*25*) has discussed the use of infrared spectral assignments as a means of confirming the site occupancies deduced from X-ray studies. For $AlVO_3$ rather broad bands at 405, 435, 510, 530, 615, and 655 cm^{-1} were observed, the region of octahedral and tetrahedral metal-oxygen stretching frequencies. The broadness of these bands, while indicative of a disordered structure (*25*), makes specific assignments difficult. The two highest frequencies presumably correspond to the vibration of tetrahedral Al–O bonds, the middle two to octahedral Al–O, and the lowest two to octahedral V–O bond stretchings. In the present case Al–O–V couplings appear to have reduced the usual Al–O tetrahedral stretching frequency considerably.

There was no sign of the band at 820 cm^{-1} which is attributed in $MgAl_2O_4$–Al_2O_3 solid solutions to tetrahedral AlO_4 groups (*25*).

Metal deficient spinels can on occasion contain water or hydroxyl groups (*26*, *27*). However, no trace of absorption bands attributable to O–H vibrations or their combinations could be detected either in the infrared or in the near infrared regions of the spectrum of $AlVO_3$. Furthermore a sample of $AlVO_3$ sealed in a platinum capsule and heated at 1300 °C for 20 hr was completely unchanged.

High Pressure Transformation of $AlVO_3$

At 900 °C and a pressure of 100 kbar cubic $AlVO_3$ was transformed to a mixture of two corundum-type phases with a net volume decrease (*27*) of 17%. The vanadium-rich phase had $a_0 = 4.982 \pm 0.008$ Å, $c_0 = 13.86 \pm 0.01$ Å, while the aluminium rich phase had $a_0 = 4.757 \pm 0.008$, $c_0 = 12.999 \pm 0.010$ Å. These latter values are experimentally indistinguishable from those for Al_2O_3 (4), $a_0 = 4.7585 \pm 0.0005$ Å, $c_0 = 12.993 \pm 0.001$ Å, and the intensities of the powder diffraction lines were considerably lower than those for the V_2O_3-rich phase, as required by the relative X-ray scattering powers of Al and V. Thus at very high pressures almost no V_2O_3 enters the Al_2O_3 lattice. The V_2O_3-rich phase did not appear to be pure V_2O_3, which has parameters $a_0 = 4.952$ Å, $c_0 = 14.002$ Å (*28*). However, the formula volumes, 298.0 ± 0.5 Å^3 and 297.9 ± 0.2 Å^3 are experimentally identical, and only a very small amount of alumina must be contained in the V_2O_3 lattice. Although the starting material was single phase $AlVO_3$ the parameters of the phases produced show that the corundum miscibility gap is actually considerably increased by the application of pressure.

In a study of the corundum-type V_2O_3–Cr_2O_3 system we have subsequently found that 2 mole % of Cr_2O_3 in V_2O_3 drastically alters the *c*/*a* ratio of pure V_2O_3 to give lattice parameters very close to those observed for the present V_2O_3-rich phase.

Discussion

The metal-deficient spinel structure of $AlVO_3$ differs from those of γ-Fe_2O_3 (*18*, *29*, *30*) and γ-Al_2O_3 (*31*) in that it contains vacancies at sites normally occupied in spinels by tetrahedrally coordinated ions. In both γ-Fe_2O_3 and γ-Al_2O_3 the vacancies are at octahedral sites and can be regarded as ordered in the (111) planes or, equivalently, along a four-fold screw axis in a tetragonal cell consisting of three spinel blocks one above the other (*18*).

Except that its tetrahedral vacancies are randomized, the $AlVO_3$ structure more closely resembles that of β-In_2S_3 (*31*, *32*). The latter contains tetrahedral vacancies which at room temperature are ordered in rows in the $[10\bar{1}]$ direction in the (111) plane (*34*), again equivalent to ordering along a four-fold screw axis in a unit cell consisting of three spinel subcells one above the other (*31*). This ordering is lost at 450 °C (*33*, *34*) at which temperature the tetrahedral vacancies become randomized as in $AlVO_3$. A further randomization involving octahedral sites occurs in 750° C (*33*). It has also been observed (*35*) that when Fe_3O_4 is treated at elevated temperatures with sulphur, abstraction of Fe atoms leads to a distribution of vacancies over both tetrahedral and octahedral metal atom sites. Randomization of tetrahedral and octahedral sites in $AlVO_3$ was not observed even in samples quenched from 1300 °C. This is consistent with the strong preference for octahedral sites which is exhibited by V^{3+} in oxide lattices. Cr^{3+} has a similar site preference, and $CrVO_3$ made from $CrVO_4$ presumably exhibits the corundum structure because neither metal can occupy the tetrahedral sites in a defect spinel. The occurrence of γ-Cr_2O_3 with such a structure (*36*) would appear to be doubtful.

$AlVO_3$ was thermally stable with respect to corundum phases to at least 1300 °C. It was indeed transformed to two discrete corundum phases at very high pressure, but such transformations to denser forms occur for large numbers of compounds which are thermodynamically stable at atmospheric pressure. At atmospheric pressure, $AlVO_3$ does not appear to be metastable with respect to corundum formation, unlike γ-Al_2O_3 and γ-Fe_2O_3.

The relatively high resistivity of the compound, $10^5\ \Omega\ cm^{-1}$, is much greater than that of a solution of Al_2O_3 in V_2O_3, $10^2\ \Omega\ cm^{-1}$ (*1*), and approximately equal to that of 10% of V_2O_3 in Al_2O_3 (*1*). The extended metal–metal interactions present in V_2O_3 (8) are obviously not present in $AlVO_3$.

The magnetic susceptibility behaviour of $AlVO_3$, Table V, shows the presence of antiferromagnetism below 270 °K. The neutron powder pattern at 4.2 °K was identical to that at 300 °K, with no discernible superlattice lines nor any changes in intensity such as are observed when Cr_2O_3 becomes antiferromagnetic (*37*, *38*). The behaviour of $AlVO_3$ thus indicates a spin cancellation occurring within the symmetry of the cubic spinel cell, and because of the distribution of vanadium in the structure, one which must be based on octahedral sites alone. This behaviour is similar to that which Plumier and Tardieu (*39*) have found for the spinel MgV_2O_4. In it, the octahedral sites are all occupied by vanadium, and the neutron powder pattern is the same at 4.2 °K as at 300 °K, with the exception of two very weak reflections at (110) and (201). This result is explained by a model in which the four interpenetrating subcells into which the sixteen octahedral sites can be divided have the spins for V^{3+} ions at $z = 0$ and $z = 1/4$ opposed to those at $z = 1/2$ and $z = 3/4$, the spin system being aligned parallel to the z axis. Any magnetic reflections allowed by the cubic face centred spinel structure thus have zero intensity. Only magnetic reflections with h and k even and l odd, or h and k odd and l even, can have nonzero intensity; for MgV_2O_4 the reflections (110) and (201) were extremely weak (*39*), while for $AlVO_3$, with only two-thirds of the octahedral sites containing V^{3+} ions, and with the relatively effective neutron scatterer Al^{3+} as the other metal ion, we were unable to observe them.

TABLE V

MAGNETIC SUSCEPTIBILITY OF $AlVO_3$

T, °K	$\chi_M{}^a$, cgs units × 10^6
127.4	1620
204.6	1620
234.8	1620
264.1	1620
292.6	1560
304.2	1550
333.7	1490
347.5	1430

[a] Susceptibility per gram atom of V^{3+}. Corrected for diamagnetism and field dependence. Estimated error $\pm 30 \times 10^{-6}$ cgs units.

The work of Hastings et al. (*40*) on CaV_2O_4, for which strong magnetic superlattice peaks were observed at 4.2 °K, shows that for V^{3+} the effective magnetic moment for neutron scattering is 1.06 μB rather than the spin-free value of 2.83 μB. Assuming the same effective moment for V^{3+} in $AlVO_3$, and the same form factor as for Mn^{2+} (*41*), the calculated magnetic scattering intensities for the (110), (201) and (112) reflections are each approximately $3\ cm^2 \times 10^{-24}$, i.e., one-third of the weakest observed atomic scattering reflection. The absence of these magnetic reflections from the powder pattern obtained at 4.2 °K is, therefore, consistent with the proposed antiferromagnetic model for $AlVO_3$.

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