Short Communications

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High pressure forms of $CrVO_4$ and $FeVO_4$.

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The three main forms of SiO_2, quartz, tridymite, and cristobalite, and the high pressure modification, coesite, are built up of SiO_4 4:2 coordinated tetrahedra with various linkage arrangements. Stishovite, another high pressure modification and the densest form of SiO_2 known to date, has the 6:3 coordinated rutile structure (Stishov & Popova, 1961). It is apparent that high pressure phases in oxides may arise either by changes in linkage between similar polyhedra or by forming new polyhedra with higher coordination number. Roy & Dachille have attempted to transform quartz type ABO_4 compounds to rutile type under pressure (Dachille & Roy, 1959).

$CrVO_4$ in the normal form is orthorhombic (Brandt, 1943). Six oxygen atoms surround each chromium atom and form a somewhat distorted octahedron. Four oxygen atoms group around each vanadium atom and form a nearly regular tetrahedron. Since $CrTaO_4$ and $CrNbO_4$ are normally rutile type compounds (Brandt, 1943), it seemed likely that pressure might transform $CrVO_4$ to rutile with an increase to six oxygen atoms around the vanadium atoms.

The powder X-ray diffraction pattern of $FeVO_4$ in the normal form is very complicated and the structure has not been determined. However, $FeTaO_4$ and $FeNbO_4$ are normally rutile. It was possible that $FeVO_4$ might also have a high pressure modification.

Pressure samples of $CrVO_4$ and $FeVO_4$ were synthesized from mixtures of $Cr_2O_3 + V_2O_5$ and $Fe_2O_3 + V_2O_5$, respectively, at 750 °C. and 60,000 atm. for 24 hr. The samples were encapsulated in platinum tubes which also served as heaters. The high pressure apparatus was of the Hall 'Belt' type (Hall, 1960).

The high pressure form of $CrVO_4$ has the rutile structure with $a = 4{\cdot}551$ and $c = 2{\cdot}884$ Å. The d-values for this material are shown in Table 1. The cell volume is 60 Å^3 with $Z = 1$ as compared with a cell volume in the orthorhombic $CrVO_4$ of 273 Å^3 with $Z = 4$. The high pressure rutile modification is 13·7% denser than the normal form.

Table 1. *Indexing of high pressure rutile type* $CrVO_4$

hkl	*d*	I/I_1	*hkl*	*d*	I/I_1
110	3·20	100	002	1·442	20
101	2·43	40	310	1·438	20
200	2·27	15	301	1·342	30
111	2·146	30	112	1·316	20
210	2·030	25	202	1·218	< 5
211	1·660	70	212	1·177	20
220	1·607	25	321	1·156	25

The high pressure modification of $FeVO_4$ exhibited a much simpler pattern than the normal compound. The pattern of the high pressure modification was compared with the patterns of normal $CrVO_4$ and other ABO_4 compounds. There was no resemblance.

The pattern of high pressure $FeVO_4$ was indexable on an orthorhombic cell with

$$a = 4{\cdot}491,\ b = 4{\cdot}900, \text{ and } c = 5{\cdot}530 \text{ Å}.$$

The observed and calculated d-values are shown in Table 2. The 5·530 c-axis in the $FeVO_4$ cell can be compared to $2c = 5{\cdot}768$ Å in the $CrVO_4$ cell. Further comparison shows shrinkage from 4·551 to 4·491 Å along the a-axis and elongation from 4·551 to 4·900 Å along the b-axis. The cell volume is 121 Å^3 almost exactly twice the cell volume in $CrVO_4$. From this near equality, it seems reasonable to assume that the Fe and V atoms are also in 6:3 coordination in a cell with $Z = 2$. In high pressure $FeVO_4$, the Fe and V atoms may be in preferred sites with resulting doubling of the normal rutile cell and distortion of the octahedra around the Fe and V atoms. Growth of crystals of this material large enough for single crystal analysis would require higher pressures and temperatures than were used in this investigation.

Table 2. *Indexing of high pressure* $FeVO_4$ *on orthorhombic cell*

hkl	d_c	d_o	I/I_1	*hkl*	d_c	d_o	I/I_1
101	3·49	3·48	50	220	1·648	1·648	15
111	2·83	2·83	100	221	1·642	1·640	40
002	2·77	2·77	30	113	1·609	1·610	< 5
020	2·42	2·42	20	023	1·468	1·466	20
012	2·41	2·40	20	131	1·467		
200	2·247	2·242	< 5	123	1·395	1·396	30
112	2·118	2·119	40	032	1·395		
121	1·991	1·991	10	004	1·383	1·383	15
211	1·913	1·915	< 5	104	1·321	1·323	15
022	1·823	1·823	20	231	1·277	1·276	< 5
202	1·744	1·741	15	040	1·213	1·212	< 5
103	1·703	1·704	30	124	1·160	1·161	< 5

$CrVO_4$ and possibly $FeVO_4$ are examples of high pressure phases of increased density, with an increase in the coordination number around one of the cations.

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