Structural Chemistry of $Sr_3Cr_2WO_9$, $Ca_3Cr_2WO_9$, and $Ba_3Cr_2WO_9$

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We have studied the preparation and crystallographic structure of three perovskite-type compounds: $Sr_3Cr_2WO_9$, cubic, the lattice parameter of which is $a = 7.812$ Å; $Ca_3Cr_2WO_9$, tetragonal, the lattice parameters of which are $a = 5.408$ Å and $c = 7.635$ Å; and $Ba_3Cr_2WO_9$, hexagonal, the lattice parameters of which are $a = 5.691$ Å and $c = 13.957$ Å. We have compared these three structures and shown the relationship between the dimensions of the alkaline-earth metal and the existence of the different structures.

Introduction

In the continuation of our work about perovskite type compounds, the formula of which is $A_3BB'_2O_9$, we report here the preparation and structure of three new phases, $Sr_3Cr_2WO_9$ (*1*), $Ca_3Cr_2WO_9$, and $Ba_3Cr_2WO_9$. The last phase has been mentioned by Ward (*2*).

We have reported before (*1*) the method used in preparing $Sr_3Cr_2WO_9$ and its probable structure. In a continuation of this work, we report the preparation and structural study of $Ca_3Cr_2WO_9$ and $Ba_3Cr_2WO_9$. Then we will compare the different structures of $Sr_3Cr_2WO_9$, $Ca_3Cr_2WO_9$, and $Ba_3Cr_2WO_9$.

Preparation Process of $Ca_3Cr_2WO_9$ and $Ba_3Cr_2WO_9$

The method used for preparing $Ca_3Cr_2WO_9$ and $Ba_3Cr_2WO_9$ is the same as that employed for $Sr_3Cr_2WO_9$ (*1*). Mixtures of Ca_3WO_6 and Cr_2O_3 or Ba_3WO_6 and Cr_2O_3 are ground and heated in evacuated quartz ampoules, between 1150 and 1200°C. The vacuum must reach 10^{-6} mmHg. Thus, the single phases $Ca_3Cr_2WO_9$ and $Ba_3Cr_2WO_9$ are obtained.

$$Ca_3WO_6 + Cr_2O_3 \rightarrow Ca_3Cr_2WO_9$$

$$Ba_3WO_6 + Cr_2O_3 \rightarrow Ba_3Cr_2WO_9$$
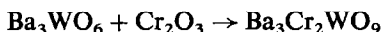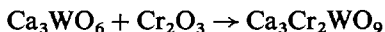
We check, by X ray diffraction powder diagrams, that the phases are well crystallized, and that they do not contain any additional compound.

It is also possible to heat the mixtures in a helium atmosphere furnace, the helium being purified by passing on zirconium rolls heated at 700°C, so that the gas loses even the smallest trace of oxygen (*3*).

Structures Determination

Lattice parameters and X ray diffraction intensities were obtained from a Philips diffractometer, using Co K_α radiation. For the parameters determination, we used a least-squares fit of the data on an UNIVAC 1110 computer, by Taupin's method (*4*). The scattering factors are obtained by Cromer's method (*5*).

(a) $Sr_3Cr_2WO_9$

By the least-square refinement we found the lattice parameter in cubic system to be $a = 7.812 \pm 0.001$ Å. X ray intensity data fit with the space-group Fm3m (*6*), the positions of which are reported in Table I. Chromium and tungsten may be completely or partially ordered on the 4a and 4b positions,

TABLE I

WYCKOFF POSITIONS OF THE SPACE GROUP
Fm3m

Ions	Wyckoff notations	Wyckoff positions (translation 0, $\frac{1}{2}$, $\frac{1}{2}$)$\gtrless$
Sr	8 c	$\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
Cr, W	4 b	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
Cr, W	4 a	0, 0, 0
O	24 e	$\pm(0, 0, x)\gtrless$

and we may represent Sr$_3$Cr$_2$WO$_9$ by a general formula:

$$Sr_3[Cr_{(3/2-\lambda)}W_\lambda]_{4b}[Cr_{(1/2+\lambda)}W_{(1-\lambda)}]_{4a}O_9 \quad (1).$$

Refinement on the computer yielded the order parameter $\lambda = 0.28$ and the atomic parameter $x = 0.242$. These values give a good agreement between experimental intensities and calculated ones ($R = 0.05$).

(b) Ca$_3$Cr$_2$WO$_9$

Using Taupin's program (4), we calculated the lattice parameters of Ca$_3$Cr$_2$WO$_9$ on the basis of a tetragonal cell: $a = 5.408 \pm 0.001$ Å and $c = 7.635 \pm 0.001$ Å. Comparing the X ray powder patterns of Ca$_3$Cr$_2$WO$_9$ and Sr$_3$Cr$_2$WO$_9$, we have considered the Ca$_3$Cr$_2$WO$_9$ cell to be pseudocubic and its structure is issued from the distortion of the Fm3m cell that we studied in last paragraph. The space-group theory allows us to know which space group the tetragonal structure of Ca$_3$Cr$_2$WO$_9$ will belong (7).

From the point group m3m, we get, after substracting certain symmetry elements the seven tetragonal point group. The matrix

$$\begin{vmatrix} 1/2 & \bar{1}/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

gives the h, k, l indexes of the lattice in the tetragonal unit cell, from the h, k, l in the cubic unit cell. In the tetragonal system, we obtain a body centered cell.

The matrix M', reciprocal and reverse-ordered of M:

$$\begin{vmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

gives the Wyckoff positions in the tetragonal system. Hence, we find the Wyckoff positions of two tetragonal space groups I422 and I4/mmm. We have reported in Table II the Wyckoff positions of the Fm3m space group, and correspondingly, the Wyckoff positions of the tetragonal space group.

The cell being centrosymmetric, we based our calculation on the I4/mmm space group. Refinement on the computer gave the atomic parameters $x = z = 0.260$ (with $R = 0.06$), chromium and tungsten being completely ordered on the Wyckoff positions a and b.

(c) Ba$_3$Cr$_2$WO$_9$

The lattice parameters were obtained on the basis of the hexagonal system: $a = 5.691 \pm 0.002$ Å and $c = 13.957 \pm 0.01$ Å. Comparing

TABLE II

	Space group Fm3m			Space group I422 or I4/mmm	
	Wyckoff notations	Wyckoff positions (translation 0, $\frac{1}{2}$, $\frac{1}{2}$)		Wyckoff notations	Wyckoff positions (translation $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)
O	24 e	$\pm(x, 0, 0)\gtrless$		8g or 8h 4e	$\pm(x, x, 0; x, \bar{x}, 0)$ $\pm(0, 0, z)$
Sr or La	8 c	$\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$		4 d	0, $\frac{1}{2}$, $\frac{1}{4}$; $\frac{1}{2}$, 0, $\frac{1}{4}$
Cr, W	4 b	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$		2 b	0, 0, $\frac{1}{2}$
Cr, W	4 a	0, 0, 0		2 a	0, 0, 0.

TABLE III

WYCKOFF POSITIONS IN THE SPACE GROUP P6₃/mmc

Ions	Wyckoff notations	Positions
Ba_I	$2\,b$	$0, 0, \frac{1}{4}; 0, 0, \frac{3}{4}$
Ba_{II}	$4\,f$	$\frac{1}{3}, \frac{2}{3}, z; \ldots$
(Fe, Te)	$2\,a$	$0, 0, 0; 0, 0, \frac{1}{2}$
(Fe, Te)	$4\,f$	$\frac{1}{3}, \frac{2}{3}, z; \ldots$
O_I	$6\,h$	$x, 2x, \frac{1}{4}; \ldots$
O_{II}	$12\,k$	$x, 2x, z; \ldots$

TABLE IV

ATOMIC PARAMETERS OF $Ba_3Cr_2WO_9$

Ions	Wyckoff notation	Parameters
Ba	$4\,f$	$z = 0.122$
(W, Cr)	$4\,f$	$z = 0.833$
O	$6\,h$	$x = 0.530$
O	$12\,k$	$z = -0.018; x = 0.878$

this to $Ba_3Fe_2TeO_9$ (8), we observed that $Ba_3Fe_2TeO_9$ and $Ba_3Cr_2WO_9$ were isostructural, with a $BaTiO_3$ isotypic cell. Then we used the space group P6₃/mmc to solve the structure. The Wyckoff positions of this space group are reported in Table III. The general formula of $Ba_3Cr_2WO_9$ is $Ba_6[Cr_{(2-y)}W_y]_{2a}$ $[Cr_{(2+y)}W_{(2-y)}]_{4f}O_{18}$, where $0 \leqslant y \leqslant 2$. The best solution, obtained by square refinement, led to the atomic parameters reported in Table IV, with $R = 0.05$.

Discussion of the Structures

By replacing strontium by calcium and barium, we notice: (1) the tetragonal deformation of the cubic cell, when strontium is replaced by calcium; and (2) the hexagonal perovskite structure, when strontium is replaced by barium.

Note that the different structures of these three compounds could be imagined by considering the perovskite structure existence diagram (Fig. 1), established by Poix (9). In this diagram, the existence areas of the different perovskite structures are represented:

the cubic, the orthorhombic, and the hexagonal. Coordinates are the distance $\beta = [Me-O]_6$, the metal-oxygen distance in the sixfold coordination, and $\theta = [Me-O]_{12}$, the metal-oxygen distance in the twelve coordination. β and θ are characteristics of atoms (10, 11). The different areas are determined by the Goldschmidt factor $t = \theta/(\beta\sqrt{2})$, and the curve $\theta = 0.406\,\beta^2 + 2.165\beta$ (9).

In our case, we obtain:

$$\theta_1 = [Sr-O]_{12} = 2.775 \text{ Å}$$

$$\theta_2 = [Ca-O]_{12} = 2.669 \text{ Å}$$

$$\theta_3 = [Ba-O]_{12} = 2.886 \text{ Å}$$

$$\beta = (2[Cr-O]_6 + [W-O]_6)/3 = 1.958 \text{ Å}.$$

In the case of $Sr_3Cr_2WO_9$, we obtain the point A, the coordinates of which are $\beta = 1.958$ and $\theta_1 = 2.775$, which is placed in the cubic area. In the case of $Ca_3Cr_2WO_9$, we obtain a point B, the coordinates of which are $\beta = 1.958$ and $\theta_2 = 2.669$, placed in the orthorhombic area, at the border line of the cubic one. This is why we found a tetragonal structure, and not an orthorhombic one, since the deformation of the cubic structures is light.
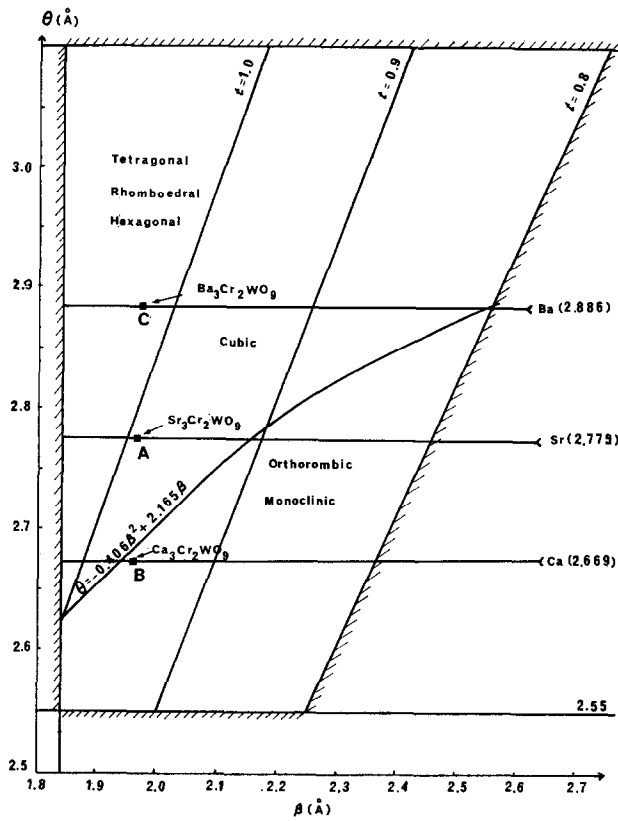
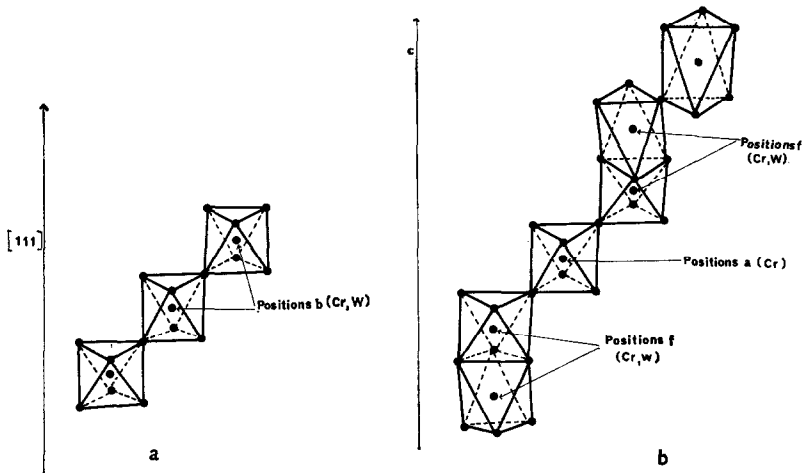FIG. 1. Existence areas of the different perovskite structures.

FIG. 2. (a) Arrangement of oxygen octahedrons in $Sr_3Cr_2WO_9$ cell. (b) Arrangement of oxygen octahedrons in $Ba_3Cr_2WO_9$ cell.

In fact, the deformation of the Fm3m structure is not sufficient to bring an orthorhombic structure. (For example, Pbnm, issued from Fm3m by subtracting more symmetry elements). In the case of $Ba_3Cr_2WO_9$, we obtain a point C, the coordinates of which are $\theta_3 = 2.886$ and $\beta = 1.958$, placed in the hexagonal area.

We may also observe, that the arrangement of the oxygen octahedrons are not the same in the case of $Sr_3Cr_2WO_9$ and $Ca_3Cr_2WO_9$ (Fig. 2a), and in the case of $Ba_3Cr_2WO_9$ (Fig. 2b) (8).

Conclusion

The three perovskite type phases $Sr_3Cr_2WO_9$, $Ca_3Cr_2WO_9$, and $Ba_3Cr_2WO_9$ are examples of three different perovskite type structures, cubic, tetragonal, and hexagonal. The dimension of the alkaline-earth metal is directly related with every different structure. The space group $I4/mmm$, to which $Ca_3Cr_2WO_9$ belongs, is issued from the space group Fm3m by subtracting certain symmetry elements. Differently, $Ba_3Cr_2WO_9$ belongs to the space group $P6/_3mmc$, which is not a subgroup of Fm3m, and the arrangement of oxygen octahedrons is different.

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