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The Crystal Structure of Beta Strontium Pyrovanadate

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β-$Sr_2V_2O_7$ is tetragonal, space group $P4_1$ with eight formula units per unit cell and $a = 7.055(2)$ Å, $c = 25.64(2)$ Å. The compound is isomorphous with β-$Ca_2P_2O_7$. The structure was determined from three-dimensional data collected on an automatic diffractometer with both Cu$K\alpha$ and Mo$K\alpha$ radiation. It was solved by comparing a Patterson section at $z = \frac{1}{2}$ with a difference Fourier map. The phases for the latter were calculated from the Ca and P coordinates of β-$Ca_2P_2O_7$. The oxygen atoms were subsequently located from successive difference Fourier maps, and the structure was refined by full-matrix least squares with isotropic temperature factors. The two different sets of data were refined separately, and the final R is 0.058 and 0.046 for data using Cu and Mo radiations, respectively. The compound has the dichromate-type structure with nearly eclipsed V_2O_7 groups. The bond distances for the two independent pyrovanadate anions are separable into two sets: the bridging bonds whose lengths are ~1.81 Å and the nonbridging bonds whose lengths range between 1.63–1.77 Å. The $\mathrm{V}{\diagup}\mathrm{O}{\diagdown}\mathrm{V}$ bond angles are 123°. The coordination number of strontium ranges from 7 to 9.

Introduction

The class of compounds with composition $R_2M_2O_7$ offers a good illustration of the major role of cation size in determining the structure of a crystal. As shown in Fig. 1, they can be divided into three classes according to the radii of both M and R. Those compounds in which the ionic radius (*1*) of M is greater than approximately 0.5 Å crystallize with structures related to that of atopite (*2*) where the coordination number of M is 6. Those compounds in which the ionic radius of M is less than 0.5 Å crystallize with either the thortveitite $(Sc,Y)_2Si_2O_7$ (*2*) or the dichromate-type structures (*3*) where the coordination number of M is 4. The latter structures, which consist of isolated edge-sharing $(M_2O_7)^{-2n}$ double tetrahedra and R^+ cations, differ with respect to the relative conformation of the $(M_2O_7)^{-2n}$ groups. In the thortveitite structures the oxygen atoms lie in a nearly staggered configuration while in the dichromate structures they are nearly eclipsed. For a given $(M_2O_7)^{-2n}$ group the size of R^{+n} determines whether staggered or eclipsed configurations will occur.

Members of the thortveitite group include cadmium pyrovanadate (*4*), zinc and magnesium pyroarsenates (*5*), a number of pyrophosphates (*6, 7*) rare-earth pyrosilicates (*8–10*) and pyrogermanates (*10, 11*). They display dimorphism: the high-temperature forms are isomorphous with the mineral thortveitite and contain linear M–O–M groups while the low-temperature forms show greater diversity in structure and $\mathrm{M}{\diagup}\mathrm{O}{\diagdown}\mathrm{M}$ bond angles are between 139° to 156°.

The dichromate group includes pyrophosphates (*12–14*), alkali dichromates (*3*), rare-earth pyrosilicates (*8, 9*) and lead pyrovanadate (*15*). Most of these structures are composed of stacked sheets with each sheet consisting of units of two centrosymmetrically or pseudocentrosymmetrically related $(M_2O_7)^{-2n}$ groups with the $\mathrm{M}{\diagup}\mathrm{O}{\diagdown}\mathrm{M}$ bond angles ranging from 123 to 138°. A dozen or more different structures can be derived from the various stacking arrangements of these sheets (*3*).

Associated with the interest in the crystal chemistry of these compounds is their use as host materials for ions with unique magnetic, electrical, and optical properties. For example, alkaline earth pyrophosphates doped with Eu^{+2}, Mn^{+2} and Sn^{+2} have been found to show efficient fluorescence under electron-beam and uv excitation (*16, 17*). This fact, together with the knowledge that the orthovanadates doped with rare-earth ions exhibit high quantum efficiencies for emission of visible light, has led us to

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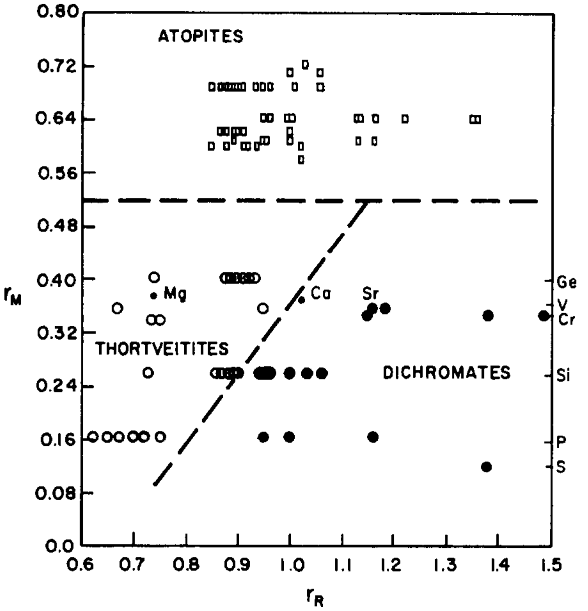

FIG. 1. Approximate stability regions for compounds with composition $R_2M_2O_7$ [see also Ref. (*10*)]. The ionic radii are taken from Shannon and Prewitt (*1*). Each circle represents either an individual structure or a collection of polymorphs which crystallize in the same structure type. The two dots correspond to $Mg_2V_2O_7$ and $Ca_2V_2O_7$, whose structures have not yet been determined.

study the luminescence and crystallographic properties of alkaline earth pyrovanadates. Structural information, moreover, should enable us to test the hypothesis that Sr and Ca pyrovanadates crystallize with the dichromate structure while Mg pyrovanadate should crystallize with the thortveitite-type structure (see Fig. 1). If the above hypothesis is verified, then it would also be of interest to correlate the luminescence properties with changes in configuration of the pyrovanadate anion. In this paper we will discuss the structure of β-$Sr_2V_2O_7$.

Experimental

A single crystal of β-$Sr_2V_2O_7$ was prepared by first reacting stoichiometric amounts of $SrCO_3$ and V_2O_5 at 800°C. This polycrystalline product was subsequently blended with $NaVO_3$ (7 g $Sr_2V_2O_7$ to 50 g $NaVO_3$), the mixture was heated to 1050°C and then cooled to room temperature at a rate of 7° per hour. A clear parallelepiped (dimensions $2 \times 2 \times 0.1$ mm^3) was washed free of $NaVO_3$ with boiling water and a portion (dimensions $0.1 \times 0.08 \times 0.1$ mm^3, for *a*, *b* and *c* directions, respectively) of the original crystal was used for optical and X-ray studies. Microscopic examinations of this crystal indicated that it was uniaxial.

The crystal was aligned along the *b* axis and the unit cell parameters and space group were obtained from Weissenberg films calibrated with reflections from silicon powder. The crystal system is tetragonal with space group $P4_1$ and lattice parameters $a = b = 7.055(2)$ Å, $c = 25.64(2)$ Å. There are 8 formula weight units per unit cell and ρ (calc) = 4.05 g/cm^3. Comparison of the lattice-parameter, space-group and intensity data with those reported for β-$Ca_2P_2O_7$ (*14*) shows that these compounds are isomorphous.

Recently, Fortiev and Makarov (*18*) have examined single crystals of $Sr_2V_2O_7$ with a polarizing microscope and reported them to be monoclinic with β of 96°. We were, however, unable to index all their reported powder diffraction lines with the lattice parameters obtained from our crystal. The apparent discrepancy between their results and those reported above can be resolved by assuming that, as with most "pyro" compounds, $Sr_2V_2O_7$ is dimorphic. Their crystals are apparently the higher-temperature α phase, while ours are the low-temperature β phase. This conclusion is consistent with the fact that the high-temperature α phase of $Ca_2P_2O_7$ is also monoclinic with β of 90.3° (*12*), while the low-temperature phase is tetragonal. Attempts to index the X-ray powder diffraction pattern reported by Fortiev and Makarov with lattice parameters similar to those reported for α-$Ca_2P_2O_7$ were, however, unsuccessful.

Two sets of intensities were collected on a "Pailred" diffractometer equipped with a pulse-height analyzer and scintillation detector. One set of data was obtained with Cu$K\alpha$ radiation and a silicon monochromator and the other with Mo$K\alpha$ radiation and a graphite monochromator. In both cases the data were taken from *hkl* layers $k = 0$ to 6. Reflections were scanned at 0.5°/min through an angle of 5.0° (ω scan). Background was measured for 0.2°/min at the extremes of each scan. Only those reflections for which $\Delta I/I \leqslant 0.3$, as estimated from counting statistics, were processed for refinement. A total of 805 independent reflections were collected with Cu$K\alpha$ and 685 with Mo$K\alpha$, each one representing the average of two or more symmetry related reflections. The measurement of the weak reflections in the high-angle region as well as some of the very low-angle reflections were not repeated with Mo$K\alpha$ radiation.

The intensities were corrected for Lorentz factors, polarization and absorption. The method used for the latter was that of Busing and Levy (*19*). The direction cosines needed to make the corrections for upper layer lines were calculated from equations derived by Wells (*20*). Because no extinction corrections were applied, the very intense 008 reflection was given zero weight in the refinements and was not included in the calculation of the *R* values.

TABLE I

FINAL CRYSTALLOGRAPHIC PARAMETERS[a, b]

Atom	x	y	z	β (Å)^2
Sr_1	−0.2831(5)	0.3133(5)	0.0(0)	1.1(1)
Sr_2	0.4940(5)	0.1652(5)	0.1524(2)	0.91(8)
Sr_3	0.3155(4)	−0.0643(4)	0.0034(2)	0.86(8)
Sr_4	0.0854(5)	−0.2172(4)	0.1423(2)	0.94(8)
V_1	−0.1723(8)	0.7768(8)	0.0168(2)	0.6(3)
V_2	−0.4350(8)	0.7046(8)	0.1161(3)	0.6(3)
V_3	0.2303(8)	0.3948(8)	0.0300(3)	0.6(3)
V_4	−0.0350(8)	0.3082(8)	0.1278(3)	0.7(3)
O_1	−0.100(4)	0.643(4)	−0.036(1)	1.7(6)
O_2	−0.310(4)	0.948(4)	−0.010(1)	0.9(7)
O_3	0.012(3)	0.865(3)	0.047(1)	0.5(4)
O_4	−0.308(4)	0.622(3)	0.058(1)	0.9(5)
O_5	0.445(4)	0.537(4)	0.148(1)	1.7(7)
O_6	0.393(3)	0.871(3)	0.098(1)	0.7(5)
O_7	−0.286(3)	0.823(4)	0.154(1)	1.4(7)
O_8	0.317(4)	0.581(4)	−0.004(1)	1.0(5)
O_9	0.410(4)	0.247(4)	0.048(1)	0.9(5)
O_{10}	0.089(4)	0.261(3)	−0.010(1)	1.1(5)
O_{11}	0.094(3)	0.470(3)	0.086(1)	0.3(5)
O_{12}	−0.128(3)	0.439(3)	0.176(1)	0.8(5)
O_{13}	0.119(4)	0.144(4)	0.158(1)	0.2(5)
O_{14}	−0.214(3)	0.201(3)	0.096(1)	0.9(5)

[a] Estimates of the standard deviations are in parentheses.

[b] The numbering system is the same as that of Webb (14).

Structure Determination

Attempts to refine the structure using the positional coordinates of β-$Ca_2P_2O_7$ as starting parameters were unsuccessful. The structure could not be refined below $R = 35\%$ $(R = \sum |F_0 - |F_c||/\sum F_0)$. The heavy atoms were then located by comparing a Patterson section at $z = \frac{1}{2}$ with a difference Fourier map. The phases for the latter were calculated from the Ca and P coordinates reported for β-$Ca_2P_2O_7$. The oxygen atoms were subsequently located from successive difference Fourier maps, and the structure was refined by full-matrix least squares with isotropic thermal parameters. Cromer and Waber's (*21*) values of the scattering factors, together with Cromer's (*22*) values of $\Delta f'$ and $\Delta f''$, were used for Sr^{+2} and V^{+5}. The atomic scattering factors for O^{-2} were those evaluated by Tokonami (*23*). The function minimized was $\sum w(F_0 - F_c)^2$. Two different weighting schemes were used. The first was $w = 1/\Delta I$, where ΔI was estimated from counting statistics; in the other scheme $\sqrt{w} = 100/|F_0|$ for $|F_0| \geqslant 75$, and $w = 1$ for $|F_0| < 75$. The data were placed on a common scale during the course of the refinement by calculating separate layer line constants after each cycle. The final discrepancy index *R* was 5.8% with Cu radiation and 4.6% with Mo radiation.

The parameters obtained from the two sets of intensity data differed in all cases by less than three and in most cases by less than two times the estimates of the standard deviations (e.s.d.). We found, moreover, that these differences were of the same magnitude as those found by using the same wavelength but different weighting schemes. The final coordinates, listed in Table I, are averages of the four determinations (2 weighting schemes and 2 wavelengths), with the standard deviations reported for each coordinate being largest of these four. The calculated structure factors which were obtained from these averaged final coordinates and the observed data are available.[1] Although it would probably be more proper to combine the Cu and Mo data in the refinement calculations, it is not convenient to do this with the present version of our refinement program. Furthermore, the results to be expected from a calculation of this type would not be more reliable than those reported here because of the above-mentioned effect of weighting schemes.

It was our experience in refining this structure that the inclusion of the real and imaginary part of the dispersion corrections is necessary in obtaining reasonable V–O bond distances. For instance the 4 V–O bridging bond lengths which range from 1.80 to 1.82 Å showed a much larger spread in values (1.75–1.88 Å) when the dispersion corrections were omitted. The large spread in these values, moreover, were associated with the rather large differences that were found in the *z* coordinates of the vanadium atoms upon substituting Mo for Cu radiation (approximately 6 times the e.s.d.'s).

Description of the Structure

The structure is essentially the same as that reported for β-$Ca_2P_2O_7$. There are eight layers per unit cell consisting of four metal ions per layer (see

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[1] A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-01509 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 866 Third Avenue, New York, NY 10022. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $2.00 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.

Figs. 2 and 3). If these layers are considered in pairs, then the four pairs are related by the fourfold screw axis along *c*. Within each pair the layer containing (V_3, Sr_3, Sr_1 and V_1) is separated by $(1/8)c$ from the layer containing (V_4, Sr_4, Sr_2 and V_2). Moreover, the top of one layer (V_4, Sr_4, Sr_2 and V_2) is also separated by $(1/8)c$ from the bottom of the adjacent level (Sr_3', V_1', V_3' and Sr_1'), which explains the characteristically strong (008) reflections observed in compounds with this structure. The pairs V_1–V_2 and V_3–V_4 form isolated $[V_2O_7]^{-4}$ ions which are related to each other by a pseudocenter of symmetry located at $x = 0.40$, $y = 0.55$, and $z = 0.073$. Oxygen atoms of the pyrovanadate group extend above and below the layers and provide bonding between adjacent pairs through Sr^{+2} ions, thus forming infinite chains throughout the structure. The pairs Sr_1–Sr_4 and Sr_2–Sr_3 are likewise related by the pseudocenter.

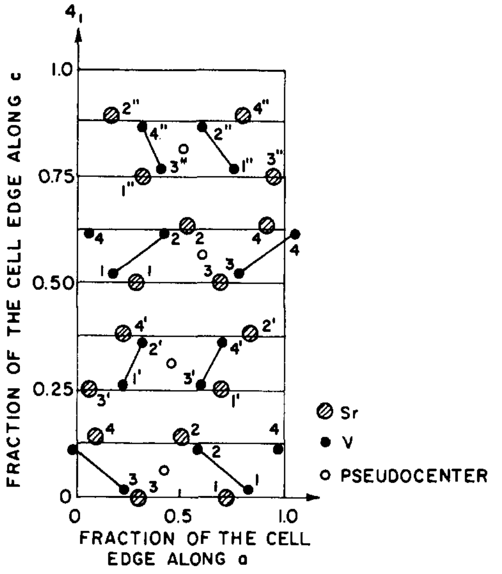

FIG. 2. Projection of the structure along *b*. Only the heavy atoms are shown.

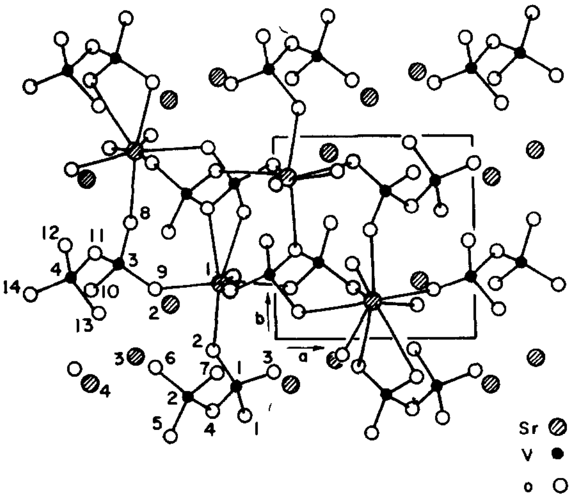

FIG. 3. Section of the structure of β-$Sr_2V_2O_7$ viewed along *c* between $z \approx 0$ and $z \approx 0.2$ only. Oxygen ions above and below the sheets were included in order to complete the coordination shells of the four independent strontium ions.

Pyrovanadate Group

Each of the two independent pyrovanadate anions is tilted approximately 52° from the horizontal (*a*, *b* plane). They are twisted somewhat from the ideal eclipsed configuration with the average twist about the V_1–V_2 axis being 6 ± 3 degrees and about the V_3–V_4 axis being 5 ± 3 degrees. These distortions are similar to those normally found for other members of the dichromate-type structures [see Ref. (*3*)].

The bond distances and angles for the two independent pyrovanadate anions are shown in Fig. 4

TABLE II

BOND LENGTHS AND ANGLES OF $V_2O_7^{-4}$ GROUP IN β-$Sr_2V_2O_7$[a]

Distances (Å)		Angles (in degrees)	
V–O (bridging)		O–V–O (bridging)	
V_1–O_4	1.80(3)	O_1–V_1–O_4	107(1)
V_2–O_4	1.82(3)	O_2–V_1–O_4	112(1)
V_3–O_{11}	1.80(3)	O_3–V_1–O_4	112(1)
V_4–O_{11}	1.81(3)	O_5–V_2–O_4	115(1)
V–O outer		O_6–V_2–O_4	110(1)
V_1–O_1	1.72(3)	O_7–V_2–O_4	109(1)
V_1–O_2	1.70(3)	O_8–V_3–O_{11}	112(1)
V_1–O_3	1.63(3)	O_9–V_3–O_{11}	112(1)
V_2–O_5	1.67(3)	O_{10}–V_3–O_{11}	109(1)
V_2–O_6	1.76(3)	O_{12}–V_4–O_{11}	107(1)
V_2–O_7	1.65(3)	O_{13}–V_4–O_{11}	111(1)
V_3–O_8	1.69(3)	O_{14}–V_4–O_{11}	112(1)
V_3–O_9	1.70(3)	O–V–O (outer)	
V_3–O_{10}	1.71(3)	O_1–V_1–O_2	104(1)
V_4–O_{12}	1.67(3)	O_1–V_1–O_3	110(1)
V_4–O_{13}	1.77(3)	O_2–V_1–O_3	112(1)
V_4–O_{14}	1.68(3)	O_5–V_2–O_6	105(1)
		O_5–V_2–O_7	113(2)
V_2–V_1	3.19(1)	O_6–V_2–O_7	105(1)
V_3–V_4	3.19(1)	O_8–V_3–O_9	110(1)
		O_8–V_3–O_{10}	109(1)
		O_9–V_3–O_{10}	105(1)
		O_{12}–V_4–O_{13}	106(1)
		O_{12}–V_4–O_{14}	108(1)
		O_{13}–V_4–O_{14}	112(1)

[a] Estimates of standard deviation are in parentheses.

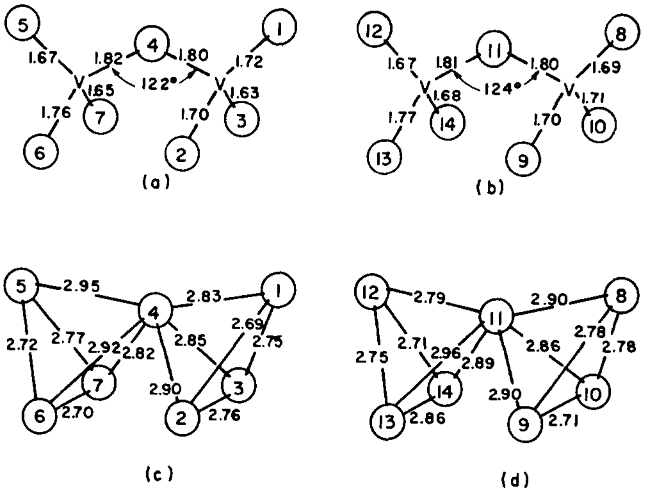

FIG. 4. (a) and (b) Vanadium-oxygen bond distances and V–O–V angles in pyrovanadate groups. (c) and (d) Oxygen-oxygen distances in the pyrovanadate groups.

TABLE III

COMPARISON OF AVERAGE DISTANCES AND ANGLES OF β-$Sr_2V_2O_7$ WITH THOSE FOUND IN OTHER PYROVANADATES

Compound	Average V–O (bridging) [bond length (Å)]	Average V–O (outer) [bond length (Å)]	Structure type
$\beta Sr_2V_2O_7$	1.81	1.70	Dichromate
$Pb_2V_2O_7$	1.82	1.74	Dichromate
$Cd_2V_2O_7$	1.76	1.70	Thortveitite
$Mn_2V_2O_7$	1.76	1.70	Thortveitite
Compound	Average O–V–O (bridging) (in degrees)	Average O–V–O (outer) (in degrees)	Average V–O–V (in degrees)
$\beta Sr_2V_2O_7$	110	108	123
$Pb_2V_2O_7$	110	110	122
$Cd_2V_2O_7$	106	113	180
$Mn_2V_2O_7$	104	115	180

and listed in Table II. These groups are appreciably distorted from the ideal C_{2v} symmetry in which the pyrovanadate anion would consist of two structurally independent V–O bonds: those which are bridging and those which are nonbridging. The 4 bridging V–O bond lengths for the two pyrovanadate groups in β-$Sr_2V_2O_7$ vary from 1.80 to 1.82 Å, while the 12 nonbridging V–O distances vary from 1.63 to 1.77 Å. The spread in these values is similar to that for the 2 bridging V–O bonds in the one independent V_2O_7 anion of $Pb_2V_2O_7$ (1.81–1.82 Å), and is somewhat less than that found for the 6 nonbridging V–O bonds in $Pb_2V_2O_7$ (1.65–1.88 Å). The $V\overset{O}{\diagup\diagdown}V$ bond angles for the two independent groups are 123° and 124°, respectively. These are approximately the same as those reported for $Pb_2V_2O_7$ (122°) and the other "dichromates" (123°–138°; see Table III).

Strontium Coordination

Since the strontium ions are related in pairs by a pseudocenter of symmetry, one would expect, to the first approximation, that the ions related by this center have the same coordination. This is indeed the case for the pair of ions Sr(1) and Sr(4) which have a coordination number of 7 with 6 nearest neighbors and one at a slightly greater distance (see

TABLE IV

STRONTIUM–OXYGEN BOND LENGTHS IN β-$Sr_2V_2O_7$[a,b]

Sr_1		Sr_2		Sr_3		Sr_4	
O_9	2.53(2)	O_{14}	2.53(2)	O_3	2.47(2)	O_6	2.53(2)
O_7''	2.59(2)	O_6	2.61(2)	O_8	2.51(2)	O_3	2.57(2)
O_2	2.60(2)	O_1'	2.64(2)	O_6	2.52(2)	O_2'	2.59(2)
O_{14}	2.63(2)	O_{13}	2.65(3)	O_9	2.56(2)	O_{13}	2.59(3)
O_4	2.65(2)	O_5	2.65(2)	O_{12}''	2.57(2)	O_{11}	2.64(2)
O_{10}	2.67(2)	O_8'	2.68(2)	O_2	2.67(2)	O_7	2.65(2)
O_1	2.82(2)	O_9'	2.81(2)	O_{13}''	2.76(3)	O_1'	2.79(2)
		O_7	2.87(2)	O_{10}	2.82(2)		
		O_{10}'	2.88(2)				
O_{12}	3.04(2)					O_{12}	2.98(2)
						O_5	3.08(3)

[a] Estimates of standard deviation are in parentheses.

[b] The fourfold screw operation carries O″ to O to O′. The numbering system is the same as that of Webb (*14*).

Table IV). While Sr(2) and Sr(3) also have 6 neighbors in the first zone of coordination, the contribution from the second zone gives Sr(2) a coordination number of 8. The coordination numbers of the four calcium ions in β-$Ca_2P_2O_7$ are Ca(1) = 7, Ca(2) = 9, Ca(3) = 7 and Ca(4) = 8. The differences between these results and those found for β-$Sr_2V_2O_7$ are subtle and depend on a somewhat arbitrary decision as to what oxygen ions are to be included in the primary coordination sphere. In the coordination sphere of Ca(3), for instance, the 7 oxygen ions have bond distances ranging from 2.3 to 2.7 Å while oxygen 13″ lies outside this sphere at 3.25 Å. In β-$Sr_2V_2O_7$ this oxygen ion is considered to be within the coordination sphere of Sr(3) at 2.76 Å. A less subtle difference is found with oxygen 12 which is well within the primary coordination sphere of Ca(4) at 2.37 Å but is considered to be outside the sphere of Sr(4) at 2.98 Å.

The 7-coordinated groups can be described in terms of an octahedron distorted by the presence of an additional oxygen ion on one face. The group with coordination number of 8 may be regarded as an octahedron with two additional oxygens located on the edges while the 9-coordinated group can be pictured as a pentagonal bipyramid with one apical atom replaced by three atoms.

Conclusion

The development and use of simple models to help systematize a large amount of structural information has been pursued by crystal chemists for a considerable number of years (*24*). Even though the models developed so far are not universally applicable, and are specific to certain classes of compounds, they are still quite useful in the systematic search for new materials whose properties can be related to crystal structure. The structural analysis on strontium pyrovanadate has confirmed the prediction that this compound crystallizes with the dichromate-type structure. The controlling factors for the formation of structure type, for compounds with stoichiometry $R_2M_2O_7$, are the ionic radii of the two cations, R and M. It would be of further interest to verify experimentally the prediction for the structure of the magnesium and calcium analogs.

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