A contribution to the crystal chemistry of ellestadite and the silicate sulfate apatites

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Abstract

A series of calcium silicate sulfate apatites from Crestmore, California, which contain the coupled substitution Si IVSVI for 2P V, has been investigated using electron microprobe, powder diffraction, and single-crystal diffraction methods. Chemical analysis of eighteen specimens of different phosphorus contents proves that the Si:S ratio is essentially 1:1 and yields the idealized general formula Ca₁₀(SiO₄)₁₋ₓ(SO₄)ₓ₋₁-P₂O₆₋₁(OH, F, Cl), where x = 0 to 3. The members of this series for which x = 0 and 3/2 have been labelled "ellestadite" and "wilkeite", respectively, by previous workers. "Ellestadite" is actually a solid solution involving the end-members Ca₁₀(SiO₄)₃(SO₄)₂(OH, F, Cl), where Z = OH (hydroxylellestadite), F (fluorellestadite), or Cl (chlorellaadlestadite). The term ellestadite is redefined to make it a group name for all compositions having Σ(Si, S) > P. Wilkeite is not a valid mineral species, since it is only one of many solid solutions involving the six end-members fluorapatite, hydroxyapatite, chlorapatite, fluorellestadite, hydroxylellestadite, and chlorellaadlestadite.

Although natural hydroxylellestadite is monoclinic, precession photographs of type "ellestadite" and "wilkeite" show hexagonal symmetry and no evidence of Si-S ordering as suggested by the Si:S ratio of 1:1. The silicate sulfate apatites from Crestmore show a strong linear relationship between their P and F contents, such that these two variables simultaneously go to zero. Linear relationships also exist between their unit cell parameters and their P, F, and (Si+S) contents. These correlations imply a convergence of the Crestmore apatite series towards a hypothetical member of composition Ca₁₀(SiO₄)₃(SO₄)₂(OH, Cl) and cell constants a = 9.543 and c = 6.917 Å.

Introduction

Crystal structures of the apatite type, general formula A₁₀(XO₄)₆Z₂, are notable for their ability to accommodate a great variety of atoms in their A, X, and Z sites by means of simple or coupled ionic substitutions (Dihn and Klement, 1942; Schwarz, 1967a, b, c; Cockbain, 1968; Ito, 1968; Kreidler and Hummel, 1970; McConnell, 1973). An example of the latter mechanism is the substitution Si IVSVI = 2P V, which occurs in the minerals wilkeite and ellestadite, conventionally formulated as Ca₅(SiO₄, SO₄, PO₄)₃(OH, F, Cl) and Ca₅(SiO₄, SO₄)₃(OH, F, Cl), respectively. Since these phases are of some industrial (Pliego-Cuervo and Glasser, 1978; Trivino Vazquez, 1979) as well as crystal chemical and mineralogical interest and since very little modern analytical data exists for either the natural minerals or their synthetic analogues, we have undertaken a re-examination of ellestadite and wilkeite using type and cotype materials from Crestmore, California. In this report we present new analytical chemical, powder diffraction, and single-crystal diffraction data, which bear upon the crystal chemistry of the silicate sulfate apatites and the interpretations made of it by previous
investigators. Nomenclatural changes were approved prior to publication by the Commission on New Minerals and Mineral Names, I.M.A.

Historical review

The replacement of a substantial portion (~50%) of the PO₄ by (SiO₄,SO₄) in a new mineral of the apatite group was reported by Eakle and Rogers (1914) in their description of wilkeite from Crestmore. This was the first example of a coupled atomic substitution in an apatite structure to be recognized as such. Additional data on wilkeite were given by Rogers (1929), McConnell (1938), and Taylor (1953), who showed the supposed mineral crestmoreite to be a submicroscopic intergrowth of wilkeite and the calcium silicate hydrate, tobermorite. More recently, wilkeite has been reported from Timna', Israel (Wurzberger, 1970), Takiue, Japan (Harada et al., 1971), and the Adirondack Mountains of New York (J. W. Valley, personal communication). Apatites containing a few percent SiO₂ and SO₃ occur at other localities, e.g., the Rhineland (Brauns, 1916) and the Ural and Aldan regions of the Soviet Union (Vasileva, 1958), but these are better termed silicatian sulfatian apatites rather than wilkeite. In fact, as we shall later show, the name wilkeite is itself superfluous and should be discarded.

Ellestadite was also first described from Crestmore by McConnell (1937), who distinguished it from wilkeite chiefly on the basis of chemical composition. Whereas type wilkeite had 20.85% P₂O₅, McConnell found a specimen with only 3.06% P₂O₅ and called it ellestadite. No difference in paragenesis or space group symmetry was evident for ellestadite and the mineral is visually indistinguishable from wilkeite. In fact, as we shall later show, the name wilkeite is itself superfluous and should be discarded.

The term “hydroxylellestadite” was introduced by Harada et al. (1971) to denote an impure form of Ca₁₀(SiO₄)₃(SO₄)₂(OH)₂, which occurs at Doshinkubo in the Chichibu mining district of Japan. The new mineral was found to be crystallographically and chemically similar to ellestadite, except for the fact that OH > (F + Cl), and the space group was assigned as P6₃/m on the basis of precession photographs. More recently, however, Sudarsanan (1980) has reported natural hydroxylellestadite to be monoclinic-pseudohexagonal with space group P₂₁/m and a = 9.476(2), b = 9.508(2), c = 6.919(1)Å, and γ = 119.53(2)°. The monoclinic cell is not of the same type as that found in monoclinic phosphate apatites, since the latter is a supercell having b = 2a and γ = 120.0° (Young, 1975). Whether all hydroxylellestadites are monoclinic remains an open question. Sudarsanan’s results were obtained from one crystal and it is possible that, like hydroxyapatite, some crystals are monoclinic and others hexagonal.

Trivino Yazquez (1979) reported ellestadite as a constituent of the crustations formed in cement heat-exchange cyclones. He further stated that the thermal decomposition of ellestadite in the presence of potassium yields a “K ellestadite” of probable formula Ca₁₀KSi₃S₂O₂₂F. The existence of this compound remains unproven as of this writing.

Experimental

Chemical analysis of eighteen silicate sulfate apatites including type ellestadite and cotype wilkeite are presented in Table 1. All analyses were performed on an ARLEMSEQ electron microprobe using an operating voltage of 15 kV, a beam current of 0.15 μA, and the following standards: hornblende for Si; fluorapatite for P, Ca, and F; scapolite for Cl; and celestine for S. The data were corrected using Bence–Albee factors. The low summations in Table 1 are due mostly to the fact that CO₂ and H₂O were not determined. Published values for these two components are 2.10% CO₂ and a trace of H₂O in wilkeite (Eakle and Rogers, 1914) and 0.61% CO₂ and 0.63% H₂O in ellestadite (McConnell, 1937). Although McConnell reported minor quantities of MgO, MnO, Al₂O₃, and Fe₂O₃ (<0.5% each with the Fe and Al attributed to admixed vesuvianite) in ellestadite, our specimens show traces of Mn as the only other detectable element of atomic number greater than nine.

Single-crystal fragments of type ellestadite (NMNH #95685) and cotype wilkeite (NMNH #103072) were examined by the precession method.
Table 1. Electron microprobe analyses of silicate sulfate apatites from Crestmore, California

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>CaO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>F</th>
<th>Cl</th>
<th>O=F,Cl</th>
<th>Total</th>
</tr>
</thead>
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<tr>
<td>817219</td>
<td>3.8</td>
<td>55.5</td>
<td>4.2</td>
<td>33.1</td>
<td>2.6</td>
<td>0.5</td>
<td>1.3</td>
<td>98.5</td>
</tr>
<tr>
<td>85256</td>
<td>4.1</td>
<td>55.5</td>
<td>5.1</td>
<td>33.0</td>
<td>2.8</td>
<td>0.6</td>
<td>1.3</td>
<td>99.7</td>
</tr>
<tr>
<td>95685</td>
<td>9.4</td>
<td>55.5</td>
<td>11.7</td>
<td>16.2</td>
<td>1.6</td>
<td>0.8</td>
<td>0.8</td>
<td>96.1</td>
</tr>
<tr>
<td>94033-3</td>
<td>9.6</td>
<td>55.5</td>
<td>12.7</td>
<td>16.1</td>
<td>1.3</td>
<td>0.8</td>
<td>0.6</td>
<td>97.7</td>
</tr>
<tr>
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<td>0.7</td>
<td>0.6</td>
<td>97.5</td>
</tr>
<tr>
<td>94033-2</td>
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<td>14.0</td>
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<td>1.2</td>
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<td>0.6</td>
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<td>1.3</td>
<td>0.7</td>
<td>0.6</td>
<td>96.2</td>
</tr>
<tr>
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<td>1.1</td>
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<td>0.6</td>
<td>96.6</td>
</tr>
<tr>
<td>C0050</td>
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<td>14.9</td>
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<td>1.2</td>
<td>0.7</td>
<td>0.6</td>
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<td>95.9</td>
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<td>17.3</td>
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<td>0.8</td>
<td>0.6</td>
<td>96.4</td>
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<tr>
<td>92917-1</td>
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<td>20.4</td>
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<tr>
<td>92913</td>
<td>16.0</td>
<td>55.4</td>
<td>21.0</td>
<td>4.3</td>
<td>0.4</td>
<td>0.5</td>
<td>97.3</td>
<td></td>
</tr>
</tbody>
</table>

Accuracy of data: ±1 percent of the amount present for Si, ±3 percent of the amount present for other elements.

Results and discussion

Chemical composition

The chemical formula assigned to ellestadite in most reference books is Ca₅(SiO₄)₂(SO₄)₃(OH,F,Cl) or some variant thereof. All of them are derived from the only published analysis of this mineral by Ellestad in McConnell (1937). A new computation of the unit cell contents using our refined cell parameters and Ellestad's analysis recalculated to 100% after deducting Ca, Mg, Fe, and Al due to vesuvianite yields [Ca₁₀₀₁₉Mg₀₀₅₆]Σ₁₀₀₁₉[Si₇₅₋₅O₄]₂[SO₄]₂₆₄₆(PO₄)₀₄₋₄[CO₃]₀₁₄₂₆ [OH]₀₁₅₋₅₄₁₅₃C₁₀₋₄. Our partial chemical analysis of type ellestadite (Table 1) is consistent with this result. In the above formula all of the carbon has been allotted to the phosphorus site, McConnell's allotment of some to the calcium site as Cr⁺⁺⁺⁺ being chemically unrealistic. Carbonate ion may also be situated in the Z (halide) site according to Young (1975), but this would not alleviate the apparent deficit of 0.7 atom in Σ(OH,F,Cl). The source of the deficit may be an error in the determination of H₂O, or the presence of O²⁻ ions in the Z site as proposed by McConnell (1937), or the existence of atomic vacancies at this site. In fact, a substantial fraction (up to 50%) of the hydroxyl sites may be vacant in biogenic apatites and synthetic hydroxyapatites (Young, 1975).

Table 2. Powder X-ray diffraction data for type ellestadite and wilkeite

<table>
<thead>
<tr>
<th>El Estadite</th>
<th>Wilkeite</th>
<th>El Estadite</th>
<th>Wilkeite</th>
</tr>
</thead>
<tbody>
<tr>
<td>I d₀₂₅</td>
<td>d₀₁₅</td>
<td>h₀₂₀</td>
<td>d₀₁₅</td>
</tr>
<tr>
<td>1 2.88</td>
<td>2.82</td>
<td>2.82</td>
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<td>2 2.75</td>
<td>2.71</td>
<td>2.71</td>
<td>2.70</td>
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<td>3 2.65</td>
<td>2.60</td>
<td>2.60</td>
<td>2.59</td>
</tr>
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<td>4 2.58</td>
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<td>6 2.31</td>
<td>2.28</td>
<td>2.28</td>
<td>2.27</td>
</tr>
<tr>
<td>7 2.08</td>
<td>2.06</td>
<td>2.06</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table 3. Unit cell parameters of several silicate sulfate apatites from Crestmore, California

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt%F</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Vₐᵇ (Å³)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>817219</td>
<td>14.4</td>
<td>9.401</td>
<td>6.896</td>
<td>529.2</td>
<td>0.727</td>
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<tr>
<td>95685</td>
<td>7.8</td>
<td>9.400</td>
<td>6.905</td>
<td>527.5</td>
<td>0.732</td>
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<td>94033-1</td>
<td>4.3</td>
<td>9.498</td>
<td>6.913</td>
<td>540.0</td>
<td>0.728</td>
</tr>
<tr>
<td>100372</td>
<td>1.4</td>
<td>9.503</td>
<td>6.914</td>
<td>543.8</td>
<td>0.755</td>
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</tbody>
</table>

Estimated standard deviations in parentheses refer to last digit. NBS silicon internal standard.
A most important feature of the ellestadite formula is the Si:S ratio, which is 28:26 or nearly 1:1. Reference to Figure 1 shows the same to be true of all analyses in Table 1, except perhaps for the silicatian sulfatian apatite B17219. If this specimen is excluded, the average deviation from 1:1 stoichiometry is only 4% and in no case does it exceed 9%. Ignoring the minor CO₂ content and possible Z site vacancies, the correct structural formula for natural ellestadite is therefore Ca₁₀(SiO₄)₃(SO₄)₃(OH,F,Cl)₂, which is in accord with the tetrahedral anion ratio in the synthetic phases of Dihn and Klement (1942). Extending this to the whole solid solution series in Table 1, the general formula is Ca₁₀(SiO₄)₃₋ₓ(SO₄)₃₋ₓ(PO₄)ₓ(OH,F,Cl)₂, where x varies from 0 (ellestadite) to 3 (apatite). The constancy of the Si:S ratio at 1:1 is, of course, a consequence of the necessity to maintain overall electrostatic neutrality in the crystal structure, i.e., the average valence of SiO₄⁻⁴ and SO₄⁻² is the same as the valence of PO₄⁻³. Moreover, the mean bond lengths Si-O = 1.62 Å in silicates (Liebau, 1972) and S-O = 1.47 Å in sulfates (Wuensch, 1972) average to 1.54 Å, which is equal to the mean P-O bond distance in monophosphates (Liebau, 1970).

The presence of SiO₄ and SO₄ groups in consistently equal numbers suggests the possibility of silicon–sulfur ordering in the ellestadite structure if not in its more phosphate-rich congeners. If the space group is really P₆₃ or P₆₅/m as indicated by the precession photographs, no such ordering can occur since all tetrahedrally coordinated atoms must be situated in the same 6-fold equipoint, 6c in P₆₃ or 6h in P₆₅/m, to be consistent with the apatite structure. However, in the structure of monoclinic hydroxyellestadite (Sudarsanan, 1980), the tetrahedrally coordinated atoms (X) are divided among three 2-fold equipoints and from the variation in X-O distances there does appear to be some degree of silicon–sulfur ordering. Whether the same phenomenon obtains in ellestadite, wilkeite, any of the intermediate compositions, or even in all hydroxyellestadites cannot be determined from the data presently available.

Elemental correlations

McConnell (1937) found an unexpected correlation between the elements in the X and Z sites in the silicate sulfate apatites from Crestmore. Specifically, as the phosphorus content decreased toward the ellestadite composition, the fluorine and chlorine contents decreased and increased, respectively. The converse would, of course, be true for the variation of fluorine and chlorine with Σ(Si,S). Reference to Table 1 shows that there is, in fact, no correlation between phosphorus and chlorine contents. Indeed, the latter element remains nearly constant for all specimens analyzed except for #103072, which is type ellestadite. The mean chlorine content, excluding #103072, is 0.7 wt.% with a range of ±0.3 wt.%. There is, however, a strong positive correlation between fluorine and phosphorus as shown in Fig. 2. A linear regression of wt.% F on wt.% P yields the relationship

\[ \text{wt.% F} = 0.03 + 0.18 \times \text{wt.% P} \]

where \( r \) is the correlation coefficient and the numbers in parentheses are the standard errors of the regression coefficients. The two variables go to zero simultaneously, the apparent residual of 0.03% F being statistically insignificant. It is tempting to speculate that the regression line in Fig. 2 might become somewhat nonlinear in the region above 10% P curving upwards to terminate at the composition point for fluorapatite, which is the theoretical limit for fluorine content. In any case, Figure 2 shows that the composition of the Crestmore silicate sulfate apatite series converges toward a fluo-

Fig. 1. Variation of the atomic proportions of silicon with those of sulfur. The slope of the regression line is 0.970 (correlation coefficient \( r = 0.995 \)) indicating that Si:S is essentially 1:1. W and E are composition points of type wilkeite and type ellestadite, respectively.
and FAP are the composition points of type wilkeite, type ellestadite, and pure fluorapatite, respectively.

rine- and phosphorus-free entity, Ca_{10}(SiO_4)_3(SO_4)_3(OH,Cl)_2.

Cell parameter variations

Comparison of the data in Tables 1 and 3 shows some systematic relationships between the unit cell parameters and chemical composition. Both a and c increase linearly as wt.% P decreases (Figs. 3 and 4), although the latter parameter does so at a much slower rate. Vegard’s Law is therefore obeyed by this solid solution series. Here a and c have been plotted against wt.% P for convenience; plots against wt.% (Si+S) and wt.% F are also linear. The regression equations are

\[
\begin{align*}
    a &= 9.543 - 0.0087 \text{ wt.% P} \\
    c &= 6.917 - 0.0014 \text{ wt.% P}
\end{align*}
\]

which at 0% P predict parameters \(a = 9.543\) and \(c = 6.917\AA\) for the hypothetical series member Ca_{10}(SiO_4)_3(SO_4)_3(OH,Cl)_2 mentioned earlier. Unfortunately, these values cannot be compared to those of pure hydroxyellestadite and chlorellestadite, since cell parameters for the latter compound are unavailable.

The cell constants of the apatite group are known to be affected by substitutions in the A (cation), X (tetrahedral), and Z (halide) sites. According to McConnell (1973), an increasing chlorine content increases a but decreases c, while increasing hydroxyl increases both parameters. LeGeros (1965) found that increasing the amount of carbonate ion in the X site shortens a by about 0.01Å for each 1.66 wt.% CO_3 but lengthens c only slightly. Among the apatite isotypes listed in Table 1, chlorine remains approximately constant and will therefore contribute negligibly to the observed systematic changes in a and c. The only available values for CO_2 (0.61% in type ellestadite and 2.10% in type wilkeite) correspond to decreases of 0.005 and 0.017Å in a relative to the same compositions without carbonate. Since two CO_2 determinations are not enough to establish any systematic changes, if any exist, in the carbonate content of the Crestmore silicate sulfate apatites, the effect of CO_3 ion on their cell dimensions cannot be evaluated at this time.

As noted previously, the Si:S ratio is essentially constant at 1:1 and the mean of the effective radii of SiO_4 and SO_4 is equal to the effective radius of PO_4. Thus changes in the (Si,S):P ratio should not affect the size of the unit cell. Moreover, substitutions for calcium in the A site are negligible in the specimens analyzed. This leaves only the increasing degree of OH for F substitution in the Z site and a possible, but unproven, systematic decrease in carbonate content as the principal causes of the increase in a and c as the ellestadite composition is approached.
**Nomenclature revisions**

From the foregoing discussion it is apparent that ellestadite and wilkeite are members of several solid solution series involving (Si,S,P,C) and (OH,F,Cl,O?). Neglecting the two minor components, the carbonate and oxide ions (the presence of the latter is problematical), the solid solution relationships among the calcium silicate sulfate apatites are best displayed on a trigonal prismatic composition diagram. The upper triangular face consists of the three pure end-members Ca_{10}(SiO_4)_3(SO_4)_3Z_2, where Z = OH (hydroxyellestadite), F (fluorellestadite), or Cl (chlorellestadite), while the lower triangular face consists of the end-members Ca_{10}(PO_4)_6Z_2, where Z = OH (hydroxyapatite), F (fluorapatite), or Cl (chlorapatite).

Since the atomic ratios in type ellestadite are Si:S:P = 28:26:4 and OH:F:Cl = 5:3:5, the composition of this mineral falls just below the approximate center of the ellestadite face of the composition prism. The tetrahedral atom ratio in type wilkeite is Si:S:P = 16:15:30 (F and Cl were not determined by Eakle), which places this material somewhat in the median plane of the prism. Note that the composition of wilkeite does not approach that of any of the end-members defined above. Wilkeite is, in fact, merely one of numerous compositions intermediate between the ellestadite and apatite faces. There is therefore no chemical justification for regarding this compound as a distinct mineral species. Moreover, the single-crystal and powder diffraction data indicate that there is nothing in the known crystallography of wilkeite to set it apart from other intermediate compositions in the series. Its cell parameters follow the same trends illustrated in Figures 3 and 4 as those of other compositions.

There is one additional difficulty with attempting to maintain the validity of wilkeite as a distinct species. Whereas in the case of ellestadite the type material is well-defined, there exists no exact type specimen of wilkeite. The one designated as the type in Table 1 (NMNH #94463) is only one specimen from the type lot. Documentation of the type status of #94463 is inadequate and the correspondence between our chemical analysis of this specimen and the analysis in Eakle and Rogers (1914) is poor. The composition of NMNH #95685 is in better agreement with Eakle’s analysis, but the connection between this specimen and his is very tenuous.

In view of the foregoing arguments, it may be asked whether the term “ellestadite” should not also be discarded in favor of fluorellestadite, hydroxyellestadite, and chlorellestadite. We believe that “ellestadite” still has utility as a group name for all of the apatite isotypes of composition (Ca,...)[(Si,S,P,C)O_4]_3(OH,F,Cl) when that composition does not approximate any of the pure end-members named above. The only restriction is that Σ(Si,S,P) must exceed P in atomic percent. Specimens having Σ(Si,S) ≤ P are best termed silicatian sulfatian apatites.

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Schwarz, H. (1967b) Verbindungen mit Apatitstruktur. II. Apatite des Typs Pb_5K_4(XO_4)_6(X_1+X_2O_3)_2 (X^V = P, As; X^VI =

Schwarz, H. (1967c) Verbindungen mit Apatitstruktur. III. Apatite des Typs $M^{II}_3(X^{VI}O_4)_3(X^{IV}O_4)_2F_2$ ($M^{II}$ = Sr, Pb; $X^{VI}$ = S, Cr; $X^{IV}$ = Si, Ge). Zeitschrift für Anorganische und Allgemeine Chemie, 356, 36-45.


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