Crystal structure and optical spectroscopy (300 to 2200 nm) of CaCrSi₄O₁₀

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Abstract

Crystals of CaCr²⁺Si₄O₁₀ were synthesized at 1 atm and 1400–1350°C in a closed system with fO₂ < 10⁻¹⁶ bar. CaCrSi₄O₁₀ crystallizes in the space group P4/nnc with a = 7.378(5) Å and c = 15.119(2) Å. The structure was refined to R = 0.026 (Rw = 0.031) based on 546 reflections. CaCrSi₄O₁₀ is a structural analog of gilbertite and other AbSi₄O₁₀ compounds, and although not itself a mineral, has been shown to exhibit structural and compression properties nearly identical to those of gilbertite. The most interesting aspects of the structure are the square-planar coordination of Cr²⁺, and the Si–O–Si bond angle of 176.8°. Apparently, Cr²⁺ is stable in the gilbertite structure because it is readily accepted into the square-planar site, in contrast to other Cr²⁺ compounds that are distorted from type-structures as a result of the Jahn–Teller effect in Cr³⁺. The optical absorption spectrum of CaCrSi₄O₁₀ has bands at 511 and 670 nm polarized ⊥ c and at 453 nm || c, with all absorption occurring only through vibronic coupling. Diamond cell experiments indicate that CaCrSi₄O₁₀ remains tetragonal to at least 50 kbar, with compression behavior identical to that of gilbertite.

Introduction

Until recently, minerals containing divalent chromium were virtually unknown. Cr²⁺ was first observed by Haggerty et al. (1970) in lunar minerals, and by Meyer and Boyd (1972) in terrestrial olivines included in diamonds from kimberlites. The presence of Cr²⁺ in meteorites was established by Keil and Brett (1973) in the mineral later named heideite [(Fe,Cr)₁₋ₓ(Ti,Fe)ₓS₄], and is implied by the formula for brezinaite, Cr₃S₄ (Bunch and Fuchs, 1969). No known terrestrial mineral contains divalent chromium as an essential element. Nevertheless, the presence of small amounts of Cr²⁺ in lunar, and possibly mantle phases, suggests that the mineral chemistry of divalent chromium is a topic worthy of investigation. Furthermore, the electronic configuration of divalent chromium and the resulting Jahn–Teller effect make Cr²⁺ interesting from a purely crystal-chemical viewpoint.

Gasparik (1981) synthesized several Cr²⁺-bearing phases in the system CaO–MgO–CrO₃–Cr₂O₃–SiO₂, including the new compound CaCrSi₄O₁₀. The crystals of CaCrSi₄O₁₀ used in this study were synthesized at 1 atm in an evacuated and closed silica glass tube by cooling from 1400°C to 1350°C in 24 hours. The starting material was a mechanical mix of 3.1 moles of SiO₂, 1.0 CaSiO₃, 0.33 Cr₂O₃, and 0.4 CrO₃. An excess of chromium metal kept the oxygen fugacity below the Cr³⁺–Cr₂O₃ buffer, approximately 10⁻¹⁶ bar at 1300°C. The run produced compact aggregates of subhedral plates separated by small amounts of blue interstitial glass. The crystals are pink to
magenta in color, and show good cleavage perpendicular to the [001] direction.

The ABSiSO₁₀ stoichiometry of CaCrSi₄O₁₀, coupled with its pronounced cleavage, suggested a relationship to gillespite (BaFeSiO₄O₁₀), and to other layer silicates. Such a relationship also implied that Cr²⁺ is present in square-planar coordination, making it an interesting candidate for optical absorption spectroscopy. Preliminary details of the CaCrSi₄O₁₀ structure refinement have been published as an abstract by Belsky et al. (1981).

Data collection

A single cleavage plate, approximately 120 × 70 × 30 μm was chosen for single crystal precession analysis. Zero- and upper-level photographs taken with MoKα radiation at 35 kV and 15 mA for 24 to 48 hours exhibited the following systematic absences: hkl: no conditions; h00: h + k = 2n; 0kl: l = 2n; and hhl: l = 2n. These conditions allow the space group to be chosen as P4/ncc without ambiguity. The minerals gillespite (BaFeSiO₄O₁₀) and cuprorivaite (CaCuSiO₄O₁₀) also crystallize in this space group, as do the synthetic compounds BaMgSiO₄O₁₀, BaCuSiO₄O₁₀, and SrCuSiO₄O₁₀ (cited by Mighell et al., 1977).

The crystal fragment was then mounted on a computer-controlled Picker four-circle diffractometer, and intensity data were collected in one octant of reciprocal space from 4° ≤ 2θ ≤ 70° (k, l ≥ 0). The diffractometer was operated in the constant precision mode using graphite monochromated MoKα radiation. The total scan width was computed from the formula 2 + 0.7 tan θ°. A reflection was flagged if ωl > 0.01, and background counts were measured for a maximum of twenty seconds. All reflection data were corrected for Lorentz and polarization effects during the collection procedure. In all, 2117 reflections (including those that should be absent for space group P4/ncc) were collected.

Cell parameters were determined from eight automatically centered reflections using the method of least squares. Final cell parameters for CaCrSi₄O₁₀ are a = 7.378(5) Å, c = 15.119(2) Å, and V = 823.0(6) Å³, corresponding to a calculated density D = 2.94 g/cm³ with Z = 4. This value is in agreement with the specific gravity D (meas.) = 2.937 g/cm³, measured by heavy liquid techniques. More precise cell parameters could not be measured, because there are no strong, high-angle general reflections produced by CaCrSi₄O₁₀.

Structure refinement

The structure refinement was initiated using the program RADY (Sasaki, pers. comm.), a modification of RADIEL (see Coppens et al., 1979). Atomic coordinates for gillespite (Hazen and Burnham, 1974) were used as initial values. Atomic scattering factor curves for Ca²⁺, Cr²⁺, and Si⁴⁺ were obtained from Ibers and Hamilton (1974), and that for O²⁻ was obtained from Tokonami (1965).

Of the 2117 reflections, 365 were confirmed to obey the systematic absence conditions for the space group P4/ncc and were deleted from the data set. The remaining data were corrected for absorption and the structure refined, followed by an isotropic extinction correction. The data were then averaged and the structure re-refined, converging to R = 0.026 (Rw = 0.031) after four cycles of the final refinement, based on 545 reflections, using an anisotropic thermal model. The observed and calculated structure factors are listed in Table 1.

Discussion of the structure

CaCrSi₄O₁₀ (Fig. 1) is a structural analog of gillespite, BaFeSiO₄O₁₀ (Hazen and Burnham, 1974). As with barium in gillespite, calcium occupies the site with 4 symmetry and is in irregular cubic coordination. Chromium occupies the site with four-fold symmetry and is in nearly ideal square-planar coordination. There are three distinct oxygen atoms in the CaCrSi₄O₁₀ structure.

The structure consists of layers of four-member rings of SiO₄ tetrahedra perpendicular to c. Each ring is linked to four others by a bridging O1 atom making an Si–O1–Si bond angle of 176.8°. This linking of rings results in an infinite Si₈O₂₂ sheet perpendicular to c. Each chromium atom, coordinated to four O3 atoms in a nearly square-planar arrangement, lies within a given sheet. Calcium is bonded to four O2 atoms and four O3 atoms in distorted cubic coordination, and serves as a link between upper and lower sheets. The atomic coordinates for CaCrSi₄O₁₀ are presented in Table 2, with anisotropic temperature factors listed in Table 3.

1 To receive a copy of Table 1, order document AM-84-244 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $5.00 in advance for the microfiche.
In the CaO₈ polyhedron, the four Ca–O₃ bonds (2.630Å) are shorter than the four Ca–O₂ bonds (2.698Å), resulting in a distorted cubic coordination. The shortening of the Ca–O₃ bonds is consistent with the fact that O₃ is underbonded relative to O₂.

In the square-planar group, the chromium atom is only 0.0025Å out of the plane of the four bonding O₃ atoms. The Cr–O₃ bond distance is 2.000Å, close to the 1.995Å bond distance determined for square-planar Fe²⁺ in gillespite (Hazen and Burnham, 1974).

In the SiO₄ tetrahedra, the average Si–O bond distance is 1.609Å. Again, underbonding of the O₃ arom may explain why the Si–O₃ bond length (1.581Å) is the shortest, and similar reasoning can be used to explain the relative Si–O₂ and Si–O₃ bond distances.

The Si–O₁–Si bond angle of 176.8° is unusually large, although angles of such magnitude have been reported for gillespite, 177.7° (Hazen and Burnham, 1974), liebauite (1961) argued that such high-angle bonds are energetically unfavorable, but Gibbs et al. (1981) concluded that only at angles below about 120° are Si–O–Si bonds highly unstable. A summary of bond lengths and bond angles appears in Table 4.

Table 5 lists the magnitude and orientation of the ellipsoids of thermal vibration for each atom. As expected, the O₁ atom, bonded only to two cations, shows the

* Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left.
highest degree of displacement, which is in the direction perpendicular to the Si–O1–Si bond. For square-planar Cr$^{2+}$, the direction of maximum thermal vibration is, as expected, perpendicular to the four bonding O3 atoms.

The theorem of Jahn and Teller predicts that Cr$^{2+}$ will be stabilized in distorted octahedral environments. Such distortions presumably occur in the Cr$^{2+}$ unit in Cr$_2$SiO$_4$ (Scheetz and White, 1972; Belsky et al., 1981). No major distortion of the gillespite-type structure occurs when Cr$^{2+}$ is present, suggesting that Cr$^{2+}$ enters the gillespite structure because the square-planar site is already favorable. This is reasonable because the square-planar environment can be viewed as the limiting case to which an octahedron can be distorted by the elongation of the metal–oxygen bonds along the c axis. The square-planar coordination of Cr$^{2+}$ in CaCrSi$_4$O$_{10}$ is unique among silicate structures, although it has also been reported in the organometallic chromous phthalocyanine (cited by Lever, 1968).

**High pressure behavior**

A crystal CaCrSi$_4$O$_{10}$, approximately $80 \times 60 \times 30$ $\mu$m, was mounted in a gasketed diamond-anvil pressure cell using a 4:1 methanol:ethanol mixture as the pressure medium. Ruby chips of approximately 10 $\mu$m were included for pressure calibration. The crystal was mounted with the c axis perpendicular to the flat faces of the diamonds. Crude optical examination revealed a distinct but gradual change in color from magenta to yellow through 25 kbar.

In a continuation of the experiments, an elongated crystal of CaCrSi$_4$O$_{10}$, approximately $130 \times 50 \times 40$ $\mu$m, was mounted for optical and X-ray examination according to the methods outlined above (see Hazen and Finger, 1982). The crystal was mounted with the tetragonal e axis parallel to the diamond faces, so that both the e (deep magenta at room conditions and o (orange at room conditions) optical directions could be observed under a polarizing microscope at high pressure. Between room pressure and 50 kbar, dramatic but gradual color changes were observed in both directions. The direction changed from deep magenta through red to orange, with a distinct decrease in color intensity over this pressure range. The color also shifted to higher energy, from orange to deep yellow at 50 kbar. The changes in pleochroism at high pressure, although striking, are distinct in character from the discontinuous red-to-blue change observed at high pressure in gillespite, which undergoes a first-order phase transition at 18 kbar (Huggins et al., 1976).

A second crystal, approximately $100 \times 100 \times 40$ $\mu$m, was mounted in a diamond cell with the e axis perpendicular to the flat diamond faces. Unit cell parameters of this crystal were measured at 15.0, 25.9, and 40.3 kbar, as well as at room pressure (all at 24°C), and are listed in Table 6. The crystal remained tetragonal to the highest pressure studied, and changes in cell edges and volume are continuous versus pressure. Therefore, a phase transition to an orthorhombic form of CaCrSi$_4$O$_{10}$, if it occurs, must take place above 40 kbar. Linear compressibility of the c axis ($\beta_c = \Delta c / \Delta P = 6.0 \times 10^{-4}$ kbar$^{-1}$) is more than twice that of the a axis ($\beta_a = 2.5 \times 10^{-4}$ kbar$^{-1}$). This compression behavior is identical to that of gillespite below 18 kbar; in gillespite, $\beta_c = 3.7 \times 10^{-4}$ kbar$^{-1}$, and $\beta_a = 8.7 \times 10^{-4}$ kbar$^{-1}$. Thus, the axial compression ratio in both BaFeSi$_4$O$_{10}$ and CaCrSi$_4$O$_{10}$ is $\beta_c / \beta_a = 2.4$. It may be assumed therefore, that structural changes in CaCrSi$_4$O$_{10}$ are similar to those determined by Hazen and Finger (1983) for gillespite. Specifically, the eight-coordinated Ca site, like the Ba site in gillespite, undergoes significant compression, thus primarily reducing the c dimension. The square-planar site undergoes moderate compression, comparable to bulk compression in the (001) plane. The silicon tetrahedron undergoes little, if any volume change, although some bending of Si–O–Si angles (in particular, the Si–O1–Si angle) is observed.

The magnitudes of CaCrSi$_4$O$_{10}$ linear compressibilities are approximately 30% less than in gillespite because of the smaller polyhedral compressibility of calcium compared to barium (Hazen and Finger, 1982). Nevertheless, in all major aspects CaCrSi$_4$O$_{10}$ below 50 kbar responds to pressure in the same way as gillespite below 18 kbar.

**Optical spectroscopy**

The optical absorption spectrum of an oriented section of CaCrSi$_4$O$_{10}$ examined between 300 and 2200 nm shows two prominent absorption bands (Fig. 2). The most intense absorption reaches a maximum at 511 nm for light polarized in (001). Additional structure on the main band occurs at 530, 540, and 551 nm. For light polarized parallel to the e axis, an absorption maximum occurs at 453 nm. A broad, weak absorption also occurs centered at $\sim 670$ nm in (001). When the sample is at 78 K, the 511 nm absorption becomes sharper, the various components move to slightly shorter wavelengths, the 453 nm band decreases in intensity, but no significant new features are revealed. The intensity of the absorption is moderate; the

Table 6. Unit cell parameters for CaCrSi$_4$O$_{10}$ at several pressures. (High pressure data were measured by R. M. Hazen, Geophysical Laboratory, Washington, D. C.)

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>y (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>7.376(2)</td>
<td>15.113(3)</td>
<td>822.3(7)</td>
</tr>
<tr>
<td>15.0</td>
<td>7.348(2)</td>
<td>14.961(8)</td>
<td>807.8(10)</td>
</tr>
<tr>
<td>25.9</td>
<td>7.327(1)</td>
<td>14.881(8)</td>
<td>798.9(5)</td>
</tr>
<tr>
<td>40.3</td>
<td>7.301(2)</td>
<td>14.71(2)</td>
<td>784.5(15)</td>
</tr>
</tbody>
</table>
Fig. 2. Linear and volume compression of CaCrSi$_4$O$_{10}$ and BaFeSi$_4$O$_{10}$ (gillespite). In both compounds, the c axis is 2.4 times more compressible than the a axis. The barium compound is approximately 50% more compressible than the calcium analog because Ba polyhedra are more compressible than Ca polyhedra.

The general appearance of the spectrum is distinct from that of Cr$^{3+}$ in octahedral coordination. No other relevant spectra of Cr$^{2+}$ in square planar coordination are available for comparison. Because of the Jahn–Teller effect, the environment around Cr$^{2+}$ in six-fold coordination may distort to D$_{4h}$ local symmetry by elongation of two axial Cr–O bonds. The spectra of Cr$^{2+}$ in such environments (Clark, 1964; Fackler and Holah, 1965) differs from that of CaCrSi$_4$O$_{10}$. The spectrum does bear some resemblance to that of Cr$_2$SiO$_4$ (Scheetz and White, 1972) which has an absorption maximum near 546 nm with conspicuous structure on the sides.

From the analysis of the spectrum of high spin Cr$^{2+}$ in D$_{4h}$ local symmetry following a procedure similar to that followed by Burns et al. (1966) for gillespite, and by Clark and Burns (1967) for BaCuSi$_4$O$_{10}$, it can be shown that despite electronic d–d orbital transitions are forbidden, absorption can occur only through vibronic coupling.

Conclusions

The structure of CaCrSi$_4$O$_{10}$ has been refined to $R = 0.026$ ($R_w = 0.031$) in the space group P4/ncc. CaCrSi$_4$O$_{10}$ is isostructural with gillespite (BaFeSi$_4$O$_{10}$) and other ABSi$_4$O$_{10}$ compounds.

The average Si–O bond distance in the SiO$_4$ tetrahedra is 1.609 Å. Summation of Pauling bond strengths can be used to explain the relative lengthening and shortening of the Si–O and Ca–O bonds.

The most interesting aspects of the CaCrSi$_4$O$_{10}$ structure are (1) the square-planar coordination of Cr$^{2+}$, and (2) the Si–O–Si bond angle of 176.8°. It appears that Cr$^{2+}$ is stable in the gillespite structure because the square-planar site is already distorted (relative to an octahedron).

This is in contrast to other Cr$^{2+}$ compounds in which the structure distorts as a result of the presence of Cr$^{2+}$. CaCrSi$_4$O$_{10}$ is the only known silicate that contains square-planar coordinated Cr$^{2+}$.

Analysis of the spectrum of high spin Cr$^{2+}$ in CaCrSi$_4$O$_{10}$ examined between 300 and 2200 nm shows that absorption occurs solely through vibronic coupling. Although no other relevant spectra of Cr$^{2+}$ in square-planar coordination are available for comparison, the spectrum does bear some resemblance to that of Cr$_2$SiO$_4$.

CaCrSi$_4$O$_{10}$ remains tetragonal to at least 50 kbar. However, striking changes in pleochroism are observed as pressure is increased. The compression behavior is identical to that of gillespite, suggesting that the structural changes in CaCrSi$_4$O$_{10}$ are similar to those observed in gillespite.

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