The synthetic Cr$^{2+}$ silicates BaCrSi$_4$O$_{10}$ and SrCrSi$_4$O$_{10}$: The missing links in the gillespite-type ABSi$_4$O$_{10}$ series

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ABSTRACT

The new Cr$^{2+}$-containing silicate compounds BaCrSi$_4$O$_{10}$ and SrCrSi$_4$O$_{10}$ were synthesized both from alkali-borate fluxes and by high-T subsolidus solid-state reactions. The gillespite-type crystal structures (space group $P4/ncc$, $Z = 4$) were determined from single-crystal X-ray diffraction data. The unit-cell parameters are $a = 7.4562(4)$, $c = 15.5414(4)$ Å for SrCrSi$_4$O$_{10}$, and $a = 7.5314(3)$, $c = 16.0518(4)$ Å for BaCrSi$_4$O$_{10}$. Comparison with previously published data shows that A (Ba, Sr, Ca) cation substitution in ABSi$_4$O$_{10}$ gillespite-type compounds mainly affects the $c$ lattice parameter whereas the substitution of the B (= Cu, Cr, Fe) site leads to only small changes, mainly in $a$. The Cr$^{2+}$ cation occupies a square-planar coordinated site unique in oxide crystal chemistry, with a Cr−O bond length of 1.999 ± 0.002 Å in all three Cr compounds. The rigidity of these bonds leaves the CrSi$_4$O$_{10}$ layers within the structure with only one significant degree of freedom, that of rotation of the four-membered Si$_4$O$_{10}$ rings in response to substitution on the A cation site. The magnitudes of these rotations are independent of the identity of the B cation. In addition the AO$_8$ polyhedron becomes more elongated // $c$ with increasing radius of the A cation. The increasing aplanarity of the O(3)X$_3$ configuration is almost exclusively determined by occupational changes on A, whereas the aplanarity of the square-planar BO(3)$_4$ group can be related to the positional shifts induced by the individual substitutions on both A and B sites. Polarized optical absorption spectroscopy was conducted on ($hk0$) sections of SrCrSi$_4$O$_{10}$ and BaCrSi$_4$O$_{10}$. Absorption bands at ~19500, ~14900, and ~22070 cm$^{-1}$ could be assigned to $^3B_{1g} \rightarrow ^3B_{2g}$, $^3B_{1g} \rightarrow ^3A_{1g}$ ($E \perp c$), and $^3B_{1g} \rightarrow ^3E_{cq}$ ($E // c$) spin-allowed d-d transitions for Cr$^{2+}$ in a square-planar configuration. The crystal-field stabilization energies of 13110 ± 150 and 13220 ± 180 cm$^{-1}$ are indistinguishable for both compounds reflecting the very similar CrO$_6$ geometries.

INTRODUCTION

Natural and synthetic gillespite undergo a pressure-induced, reversible first-order phase transition variously reported to occur between 1.2 and 1.8 GPa (Hazen and Burnham 1974; Huggins et al. 1975, 1976; Hazen 1977; Hazen and Finger 1983). The relative size of the A cation (that is Ba in gillespite), for which the number of coordinating O atoms increases from eight to ten, plays a key role in the phase transition (Hazen and Finger 1983). In addition, the phase transition is accompanied by, among other structural changes, a change from an unusual square-planar fourfold coordination to a more normal distorted (4 + 2) octahedral coordination. The color change at the phase transition was also the subject of speculation and was originally attributed by Strens (1966) to spin-pairing accompanying a change in the crystal field from a high-to-low spin state. However, Abu-Eid et al. (1973) later showed that the changes of the Fe$^{2+}$ coordination and polyhedral distortion explain the transition-induced change in optical absorption.

As the square-planar coordination geometry is an extreme version of a uniaxially elongated octahedron, which is expected to be favored by Jahn-Teller–active cations like Cu$^{2+}$ and Cr$^{2+}$, the existence of an isostructural ABSi$_4$O$_{10}$ series (A = Ba, Sr, Ca; B = Cu$^{2+}$, Cr$^{2+}$) is to be expected. Although all three Cu compounds are known to exist, both as synthetic phases (Janzcak and Kubíak 1992; Lin et al. 1992; Chakoumakos et al. 1993) and as the natural minerals effenbergerite, wesselsite, and cupro-prite (Giester and Rieck 1994, 1996; Pabst 1959), the existence of only one Cr$^{2+}$ analog, CaCrSi$_4$O$_{10}$, was reported previously (Gasparik 1981; Belsky et al. 1984). To determine the influence of the type B cations on the gillespite-type crystal structure, we synthesized the two missing Cr$^{2+}$ phases and determined their crystal structures from single-crystal X-ray diffraction data. The seven known compounds with the gillespite structure type were compared to identify the mechanisms of structural changes induced by the substitution on the two cation