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The synthetic Cr^{2+} silicates $BaCrSi_4O_{10}$ and $SrCrSi_4O_{10}$: The missing links in the gillespite-type $ABSi_4O_{10}$ series

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ABSTRACT

The new Cr^{2+}−containing silicate compounds $BaCrSi_4O_{10}$ and $SrCrSi_4O_{10}$ 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 $SrCrSi_4O_{10}$, and $a = 7.5314(3)$, $c = 16.0518(4)$ Å for $BaCrSi_4O_{10}$. Comparison with previously published data shows that A (= Ba, Sr, Ca) cation substitution in $ABSi_4O_{10}$ 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 $CrSi_4O_{10}$ layers within the structure with only one significant degree of freedom, that of rotation of the four-membered Si_4O_{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 $SrCrSi_4O_{10}$ and $BaCrSi_4O_{10}$. Absorption bands at ~19500, ~14900, and ~22070 cm^{-1} could be assigned to ${}^5B_{1g} \rightarrow {}^5B_{2g}$, ${}^5B_{1g} \rightarrow {}^5A_{1g}$ ($\mathbf{E} \perp c$), and ${}^5B_{1g} \rightarrow {}^5E_g$, ($\mathbf{E}$ // 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_4 geometries.