



# New insights into structural diversity of open-framework silicates inspired by the exploration of the Cs<sub>2</sub>O–CaO–SiO<sub>2</sub> system

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The structural chemistry of silicates is extremely diverse because of many specific ways SiO<sub>4</sub> tetrahedra can condense with the formation of different types of tetrahedral units (Liebau, 1985). Among them, the microporous framework silicates attract interest due to their unique structural topologies with many possible derivatives within the same stoichiometry, *i.e.* the large family of natural and synthetic zeolites with tetrahedral frameworks (Baerlocher & McCusker, 2007). This number of tetrahedral frameworks is enriched by open-framework silicates (Krivovichev, 2005), where the four- and three-connected silicate tetrahedra are simultaneously present (Day & Hawthorne, 2020). These materials exhibit unique structural features, such as partial connectivity of the tetrahedra, which introduces flexibility in their chemical composition and potential for novel properties.

The exploration of alkali and alkaline-earth silicates has historically focused on systems involving lighter cations (*e.g.* Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>), driven by their abundance in natural minerals and industrial relevance (*e.g.* in glass and cement production) (Xu & Van Deventer, 2000; Richardson, 2008). In contrast, heavier alkali metals like caesium (Cs<sup>+</sup>) have received less attention, despite their potential to stabilize unconventional silicate frameworks due to their large ionic radii. In contrast to Na<sub>2</sub>O–CaO–SiO<sub>2</sub> and K<sub>2</sub>O–CaO–SiO<sub>2</sub> systems, the corresponding Cs<sub>2</sub>O–CaO–SiO<sub>2</sub> system was unexplored and the synthesis and crystal structure of the first caesium calcium silicate, Cs<sub>2</sub>Ca<sub>4</sub>Si<sub>6</sub>O<sub>17</sub>, with the clinotobermorite-type structure recently published (Kahlenberg, 2025a).

The detailed analysis by Professor Kahlenberg of the phases in the Cs<sub>2</sub>O–CaO–SiO<sub>2</sub> system led to the discovery of a new compound, Cs<sub>4</sub>Ca[Si<sub>8</sub>O<sub>19</sub>] (Kahlenberg, 2025b), which belongs to the group of interrupted framework silicates. This new compound, Cs<sub>4</sub>Ca[Si<sub>8</sub>O<sub>19</sub>], was synthesized from a mixture of Cs<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub> and SiO<sub>2</sub> (dried at 673 K) in a molar ratio of Cs<sub>2</sub>O: CaO: SiO<sub>2</sub> = 4:1:10 heated from 294 K to 1373 K in a platinum container.

The crystal structure of the new compound, recently published in *Acta Crystallographica Section B* (Kahlenberg, 2025b), is unique and is based on the tetrahedral framework which can be described by the condensation of tetrahedral layers parallel to (010). These layers are characterized by the presence of three- and nine-membered rings and the net topology (Hawthorne, 2015; Blatov *et al.*, 2010) can be denoted as (3.9<sup>2</sup>)<sub>6</sub>(9<sup>3</sup>)<sub>2</sub>, corresponding to *hnb* net type (O’Keeffe *et al.*, 2008). The single crystallographically-independent calcium cation exhibits an octahedral coordination with only minor deviation from regularity and is inserted into the silicate tetrahedral framework forming the mixed octahedral–tetrahedral (heteropolyhedral) framework. The wide cavities are filled by the caesium cation balancing the negative charge of the heteropolyhedral framework. The topological features of the heteropolyhedral framework were analysed using *ToposPro* software (Blatov *et al.*, 2014). It was found that the cation net contains two types of natural tiles, a very simple tile [4<sup>3</sup>] (frequently observed in zeolites) and a complex one [3<sup>4</sup>.4<sup>6</sup>.6<sup>2</sup>.7<sup>8</sup>], which has not been observed before.

Within the family of silicates containing [Si<sub>8</sub>O<sub>19</sub>] anions, Cs<sub>4</sub>Ca[Si<sub>8</sub>O<sub>19</sub>] is the second member after Na<sub>12</sub>Th<sub>3</sub>[Si<sub>8</sub>O<sub>19</sub>]<sub>4</sub>·18H<sub>2</sub>O (Li *et al.*, 2000) containing an interrupted framework. Comparing Cs<sub>4</sub>Ca[Si<sub>8</sub>O<sub>19</sub>] with related phases, helps identify the key factors governing framework interruption, including the presence of large cations, the size of

tetrahedrally coordinated cations, and the presence of larger (molecular) clusters in the channels.

The work of Professor Kahlenberg not only expands the known structural diversity of interrupted silicates but also provides insights into the design principles for synthesizing analogous materials. In particular, the large family of alkaline microporous rare-earth silicates are also characterized by the silicate tetrahedral open frameworks, where the insertion of the additional octahedra filled by rare-earth cations result in formation of the heteropolyhedral frameworks of different topologies (Aksenov *et al.*, 2013, 2019). New compound  $\text{Cs}_4\text{Ca}[\text{Si}_8\text{O}_{19}]$  contributes to the broader understanding of structure–property relationships in open-framework silicates (as well as silicates with mixed octahedral–tetrahedral frameworks), with potential implications for ion-exchange, catalysis, and materials with tailored thermal expansion.

Moreover, the discovery of caesium calcium silicates raises the search for possible phosphors as  $\text{Ca}^{2+}$  can be easily substituted by rare-earth elements. Such caesium calcium silicate materials activated by rare-earth cations could potentially combine the structural stability of silicate hosts with efficient luminescence, making them promising candidates for solid-state lighting or radiation detection applications. The unique framework topology, with its tailored cavity sizes and mixed connectivity, may offer distinct crystal field environments that could enable fine-tuning of optical properties through selective rare-earth doping.

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