

MS15-1-7 Isolated $[\text{SiO}_4]^{4-}$ tetrahedra in the chloride-poor oxosilicate $\text{Ce}_3\text{Cl}[\text{SiO}_4]_2$
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Abstract

In an attempt to synthesize $\text{CeSb}_2\text{O}_4\text{Cl}$, rod-shaped colourless single crystals with the composition $\text{Ce}_3\text{Cl}[\text{SiO}_4]_2$ were obtained as a by-product from glassy silica ampoules. $\text{Ce}_3\text{Cl}[\text{SiO}_4]_2$ crystallizes isotypically to the A-type $\text{Ln}_3\text{Cl}[\text{SiO}_4]_2$ series with $\text{Ln} = \text{La}, \text{Pr}$ and $\text{Nd}^{(\text{I}-\text{IV})}$ in the monoclinic space group $C2/c$ with $a = 1439.13(9)$ pm, $b = 646.24(4)$ pm, $c = 877.96(6)$ pm and $\beta = 98.341(3)^\circ$ for $Z = 4$ (CSD-2124078).

The crystal structure of $\text{Ce}_3\text{Cl}[\text{SiO}_4]_2$ contains isolated $[\text{SiO}_4]^{4-}$ tetrahedra (Figure 1) as the defining building blocks, showing a slight distortion with angles O–Si–O in the range from $105.9(2)$ to $118.4(2)^\circ$. The Si–O distances reside between $160.6(5)$ and $164.2(4)$ pm, which are quite typical oxosilicate values. Furthermore, two crystallographically distinct Ce^{3+} cations are present with $(\text{Ce}1)^{3+}$ being surrounded by one Cl^- anion plus another more distant Cl^- one as well as eight oxygen atoms forming a 9+1-fold coordination sphere. The $(\text{Ce}2)^{3+}$ cations show a tricapped trigonal prismatic coordinative environment, built up by one Cl^- anion and eight oxygen atoms. The distances $d(\text{Ce}-\text{O}) = 243.2(4) - 290.8(4)$ pm and $d(\text{Ce}-\text{Cl}) = 287.6(1) - 295.4(2)$ pm plus $350.8(1)$ pm range in common intervals, when compared with PbFCl -type $\text{CeOCl}^{(\text{b})}$ ($d(\text{Ce}-\text{O}) = 237$ pm ($4\times$) and $d(\text{Ce}-\text{Cl}) = 312$ pm ($1\times$) and 319 pm ($4\times$)) for example. The Cl– Ce^{3+} partial structure with infinite chains $1\text{D}-\{[\text{ClCe}_{2/1}^{\text{t}}\text{Ce}_{2/2}^{\text{v}}]^{8+}\}$ of *trans*-vertex linked kites $[\text{ClCe}_{3+1}]^{11+}$ propagating along $[010]$ is shown in Figure 2 displaying one short and one long $(\text{Ce}1)^{3+}$ –Cl distance.

References

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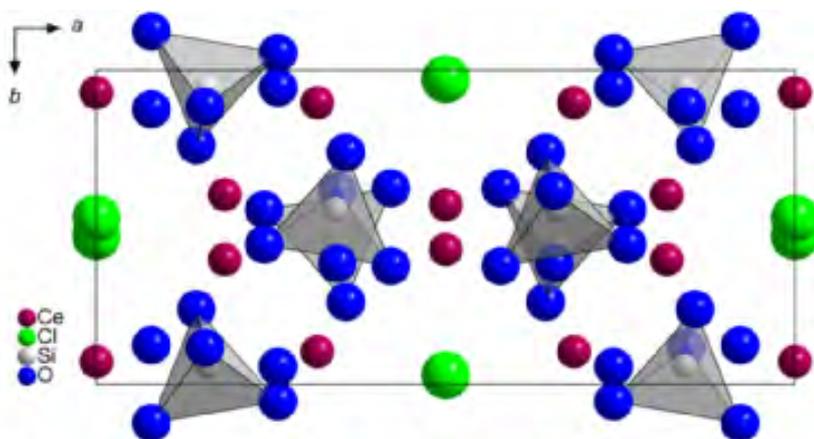


Figure 1. Projection of the monoclinic crystal structure of $\text{Ce}_3\text{Cl}[\text{SiO}_4]_2$ onto (001) emphasizing the isolated $[\text{SiO}_4]^{4-}$ tetrahedra.



Figure 2. Cl– Ce^{3+} partial structure of $\text{Ce}_3\text{Cl}[\text{SiO}_4]_2$ with infinite chains $1\text{D}-\{[\text{ClCe}_{2/1}^{\text{t}}\text{Ce}_{2/2}^{\text{v}}]^{8+}\}$.