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(3+1)-incommensurately modulated crystal structure of Cs3ScSi6O15

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(3+1) incommensurately modulated crystal structure of $Cs_3ScSi_6O_{15}$

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S1. Abstract

Abstract Single-crystal X-ray diffraction of $Cs_3ScSi_6O_{15}$ shows the presence of main reflections and satellite reflections up to the fourth order along the **c*** direction. The (3+1)-dimensional incommensurately modulated structure was solved in superspace group $R\bar{3}m1(00g)0s0$ [a = 13.861(1), c = 6.992(1) Å, V = 1163.4(2) Å^3] with a modulation wavevector **q** = 0.14153(2)·**c***. Refinement of three modulation waves for positional and ADP values for all atoms converged to *Ro* values for all, main and satellite reflections of first, second and third order of 0.0200, 0.0166, 0.0181, 0.0214 and 0.0303, respectively. $Cs_3ScSi_6O_{15}$ forms a mixed tetrahedral-octahedral framework with prominent six-membered rings of [SiO_4]-tetrahedra interconnected by [ScO_6]-octahedra. Apart from Sc all atoms are strongly affected by positional modulation with maximum atomic displacements of up to 0.93 Å causing rigid polyhedral arrangements to perform tilt- and twist movements relative to each other, such as a rotation of the Sc-octahedra around the $\bar{3}$ -axis by over 38°. Cs has an irregular coordination environment; however, considering distances up to 3.5 Å the bond-valence sum is changing by no more than 0.02 as a function of t and thus overall kept at a level of ca. 1.075.

S2. Introduction

This document contains supplementary material to the above referenced publication. The structural data can be taken from the accompanying cif file.

S3. Raman spectroscopy

A confocal Raman spectrum was recorded in the range of 100 - 1200 cm^{-1} with a Horiba Jobin Yvon Labram-HR 800 Raman micro-spectrometer from the same single crystal of $Cs_3ScSi_6O_{15}$ as used for the single-crystal X-ray diffraction. The sample was excited 60 seconds by using the 532 nm emission

line of a frequency-doubled 100 mW Nd:YAG laser under an Olympus 100x objective lens. The size of the laser spot on the surface was approximately 1 μm. The scattered light was dispersed by an optical grating with 1800 lines/mm and collected by a 1024 x 256 open electrode CCD detector. Confocal pinhole and spectrometer entrance slit were set to 1000 and 100 μm, respectively. The spectral resolution, determined by measuring the Rayleigh line, was less than 2 cm^{-1}. The spectrum was recorded unpolarised. The accuracy of the Raman line shifts, calibrated by regularly measuring the Rayleigh line, was in the order of 0.5 cm^{-1}. Background and Raman bands were fitted by the built-in spectrometer software LabSpec to second-order polynomial and convoluted Gaussian–Lorentzian functions, respectively.

In the Raman spectra of single-crystalline $Cs_3ScSi_6O_{15}$ (see Figure S1) bands could be detected between 80 and 1145 cm^{-1}. The spectrum can be subdivided into two regions: at low- and medium-wavenumbers up to ca. 800 cm^{-1} a large number of partly overlapping bands were detected. After a gap lacking any bands from 800 to 1000 cm^{-1} the most intense band of the spectrum was observed in the high-wavenumber region at 1143.3 cm^{-1} next to another intense signal at 1053.2 cm^{-1}.

No Raman spectra have been reported for the related structures of $Cs_3DySi_6O_{15}$ and $Cs_{1.86}K_{1.14}DySi_6O_{15}$ or other known alkali silicates containing ring-shaped $[Si_6O_{18}]$-units within a framework structure. The closest proximity can be found in Raman spectra of other mixed tetrahedral-octahedral framework structures containing three- or four-membered rings of $[SiO_4]$-tetrahedra with an A-1 type *PME* of identical coordination sequence up to $k = 3$ such as wadeite-related structures (Chang et al. 2013, Hejny et al. 2012, Sitarz et al. 1997). The Raman spectra of these compounds have split spectra with a 200 cm^{-1} wide gap lacking Raman-bands between the mid- and the high-wavenumber region. Comparison with these spectra allows the following conclusion: The Raman-active bands in the high-wavenumber region above 1000 cm^{-1} can be assigned to Si-O-Si stretching vibrations, those in the mid-wavenumber regions of 300 – 800 cm^{-1} are characteristic for the ring structures and are caused by breathing, stretching and deformation modes for the silicate ring, and bands in the low-wavenumber region are associated with translational modes of the whole ring and the non-ring cations.

S4. Additional figures

In the following additional figures that might help to further illustrate the topics discussed in the text are given. The reciprocal space reconstruction of the *h*0*l* layer in Figure S2 complements Figure 1. In Figures S3 – S8 electron density sections *x*1-*x*4, *x*2-*x*4 and *x*3-*x*4 are given for each atom. The contour lines for Cs, Sc, Si, O1, O2 and O3 are drawn with 2 $eÅ^{-3}$, 1 $eÅ^{-3}$, 5 $eÅ^{-3}$, 0.5 $eÅ^{-3}$, 0.2 $eÅ^{-3}$, and 0.2 $eÅ^{-3}$, respectively. Displacive modulation functions for each atom are given in Figures S9 – S14. In Figure S15 an additional selected section of the (3+1)-incommensurately modulated structure

highlights the infinite column of alternating [ScO_6]-octahedra and six-membered [Si_6O_{18}]-rings along the $\bar{3}$-axis and the inter-column connection via a terminal oxygen atom. Figure S16 is a plot of Cs-O interatomic distances as a function of *t*. Figure S17 plots polyhedral microensembles found in $Cs_3ScSi_6O_{15}$.

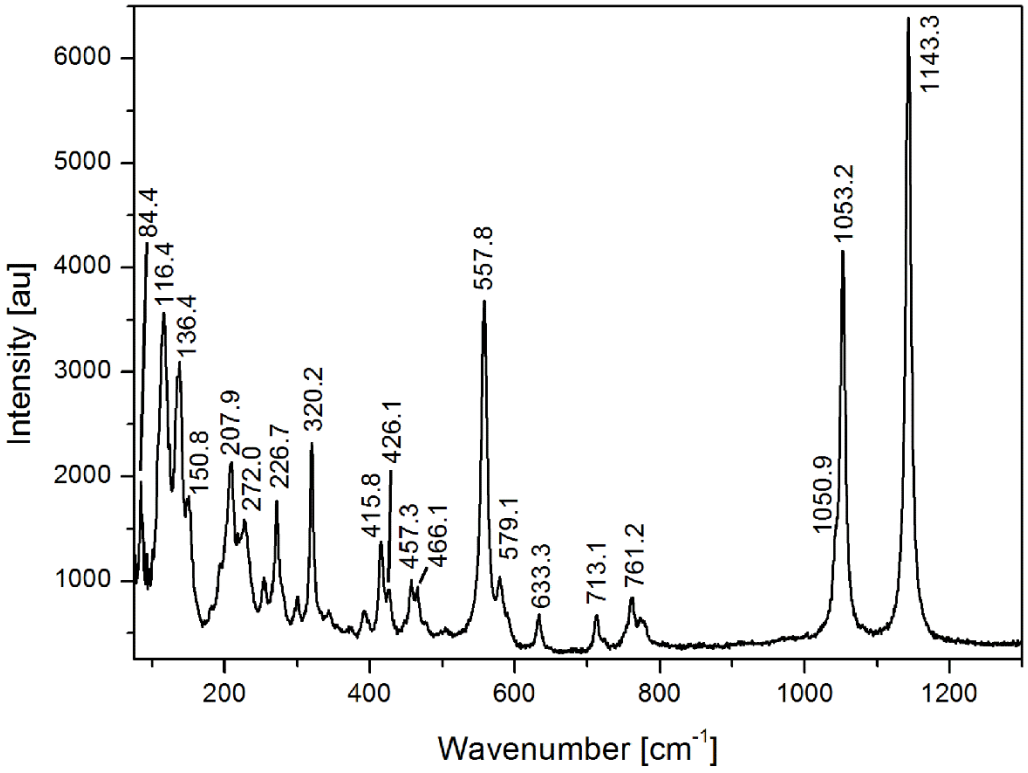

Figure S1 Raman spectrum of $Cs_3ScSi_6O_{15}$.

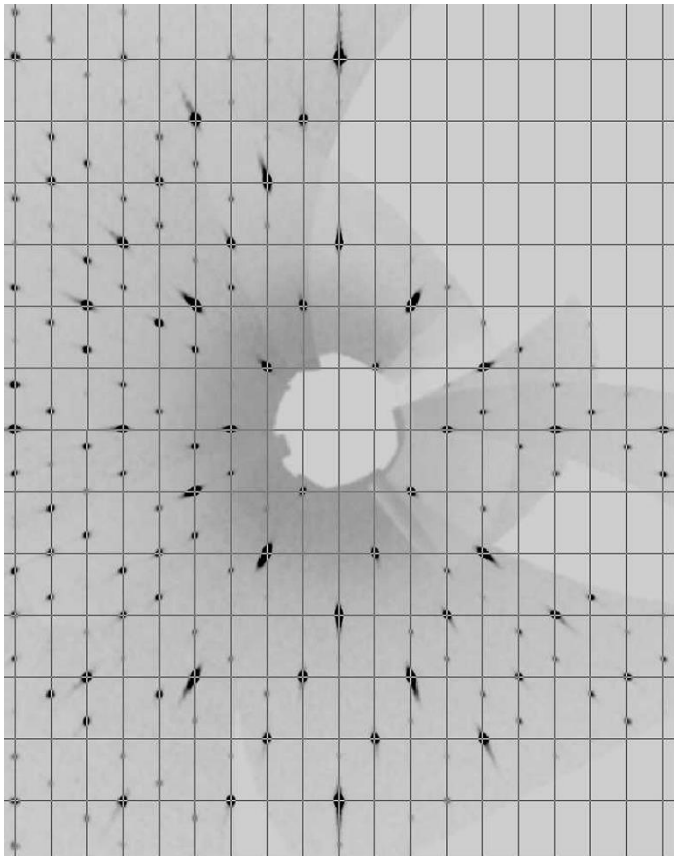

Figure S2 Reconstruction of reciprocal space layer *h*0*l*, **a*** pointing to the left, **c*** to the top.

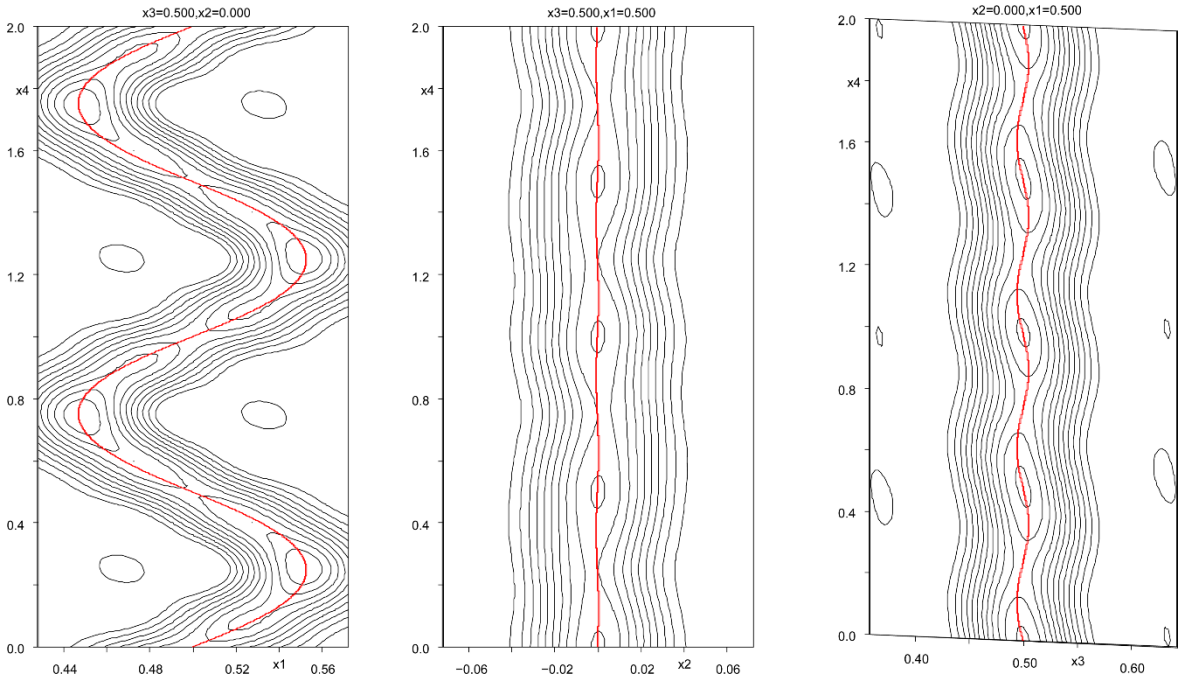

Figure S3 Electron density sections for Cs.

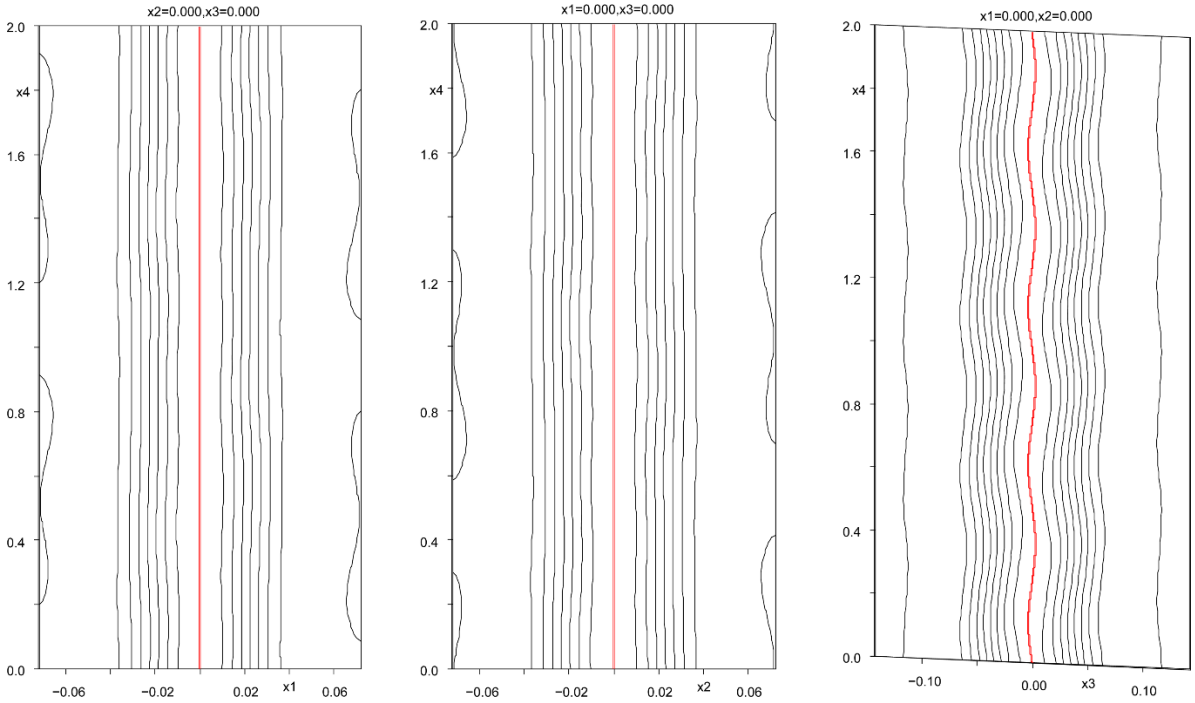

Figure S4 Electron density sections for Sc.

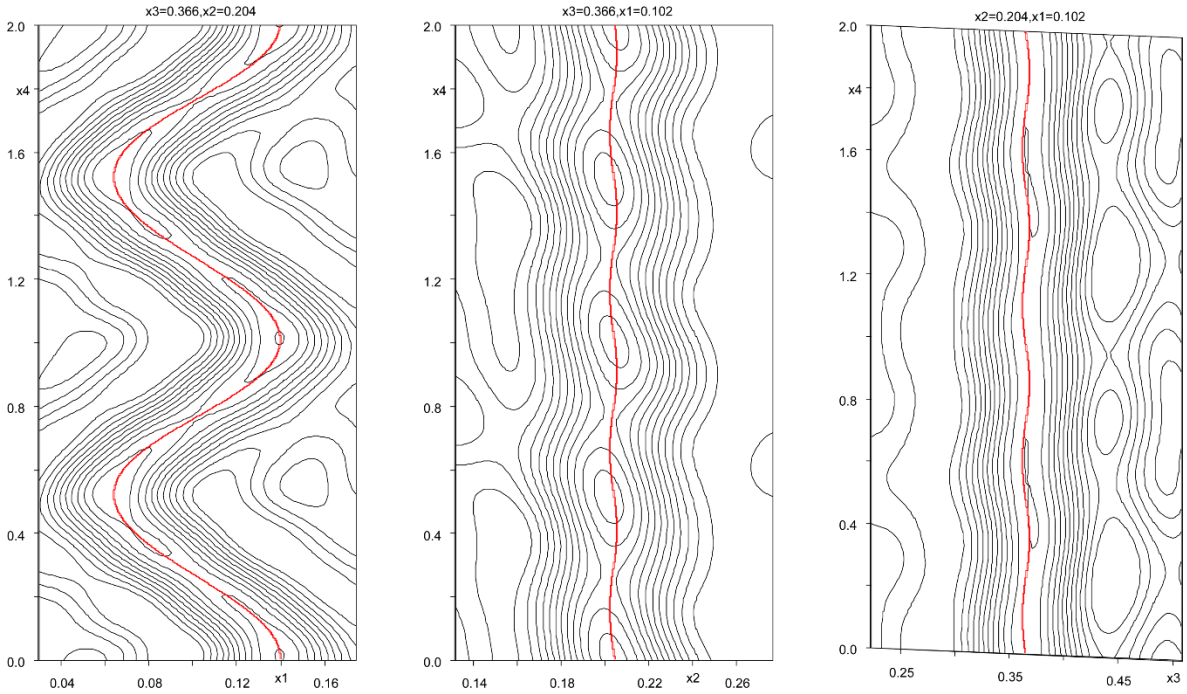

Figure S5 Electron density sections for Si.

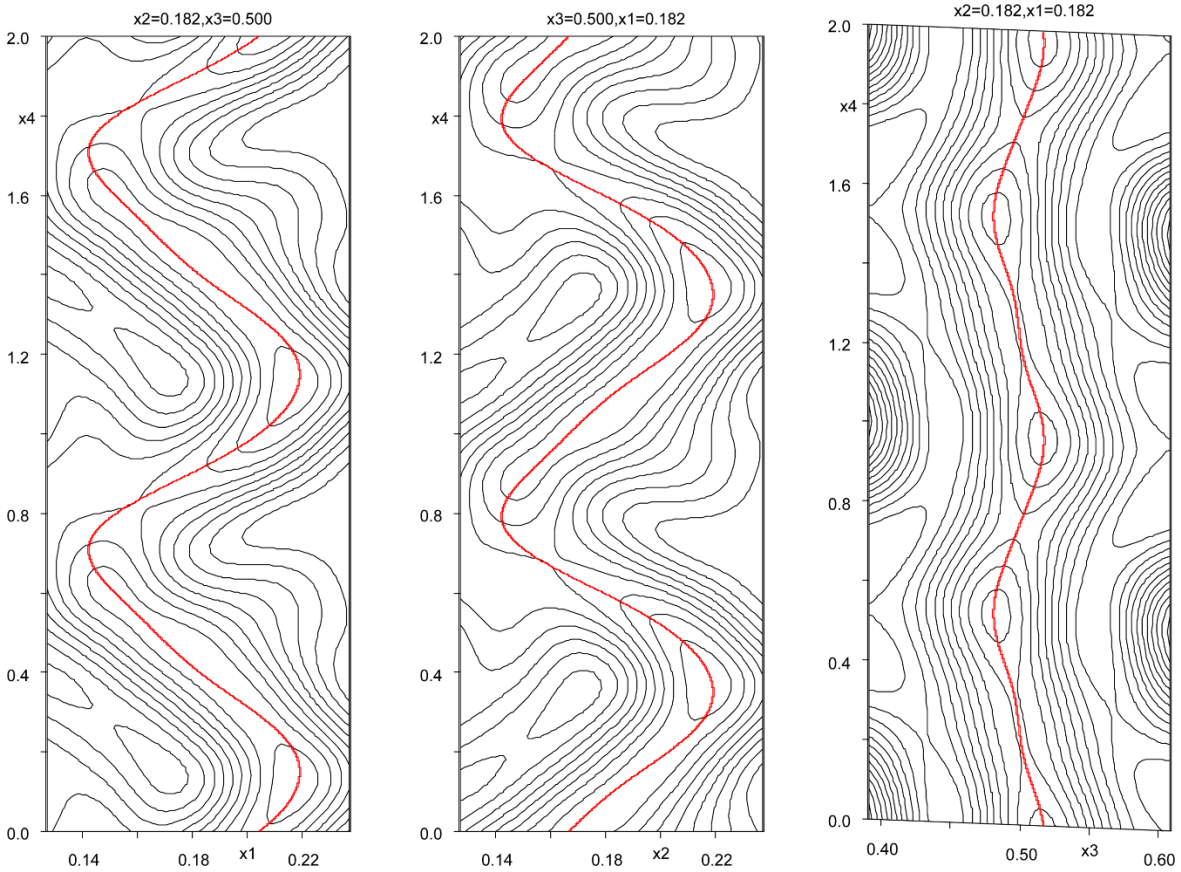

Figure S6 Electron density sections for O1.

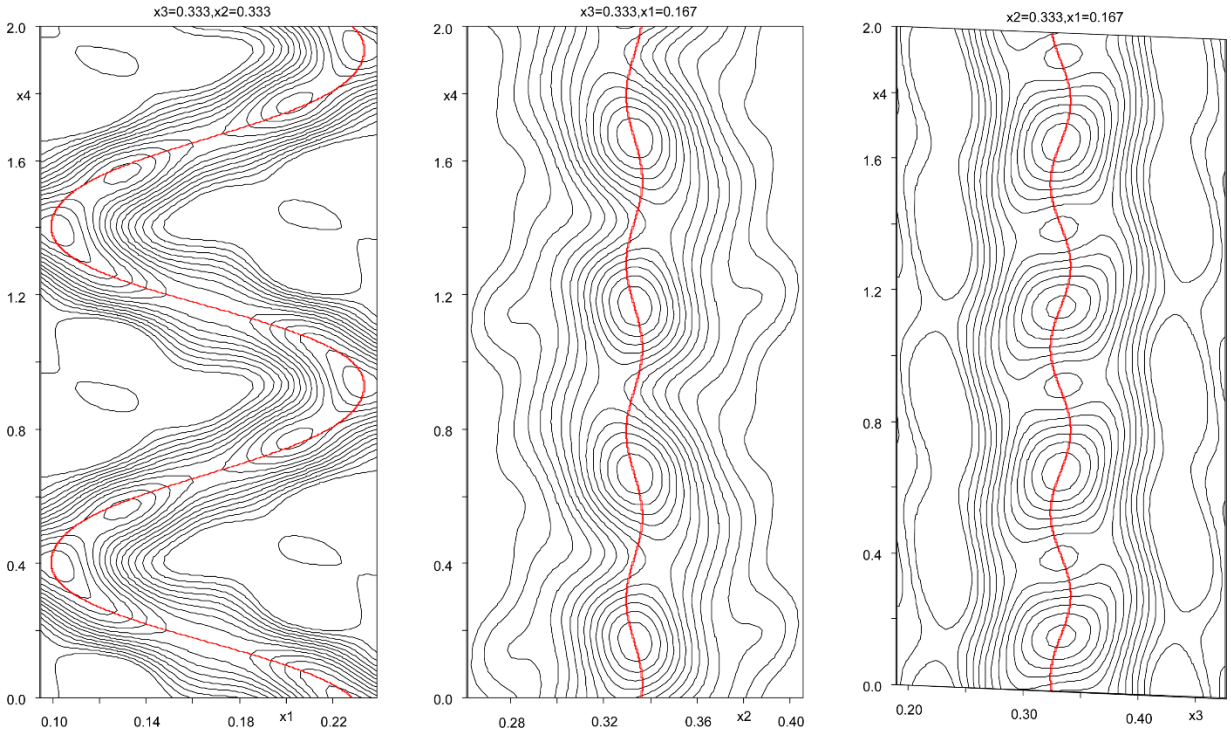

Figure S7 Electron density sections for O2.

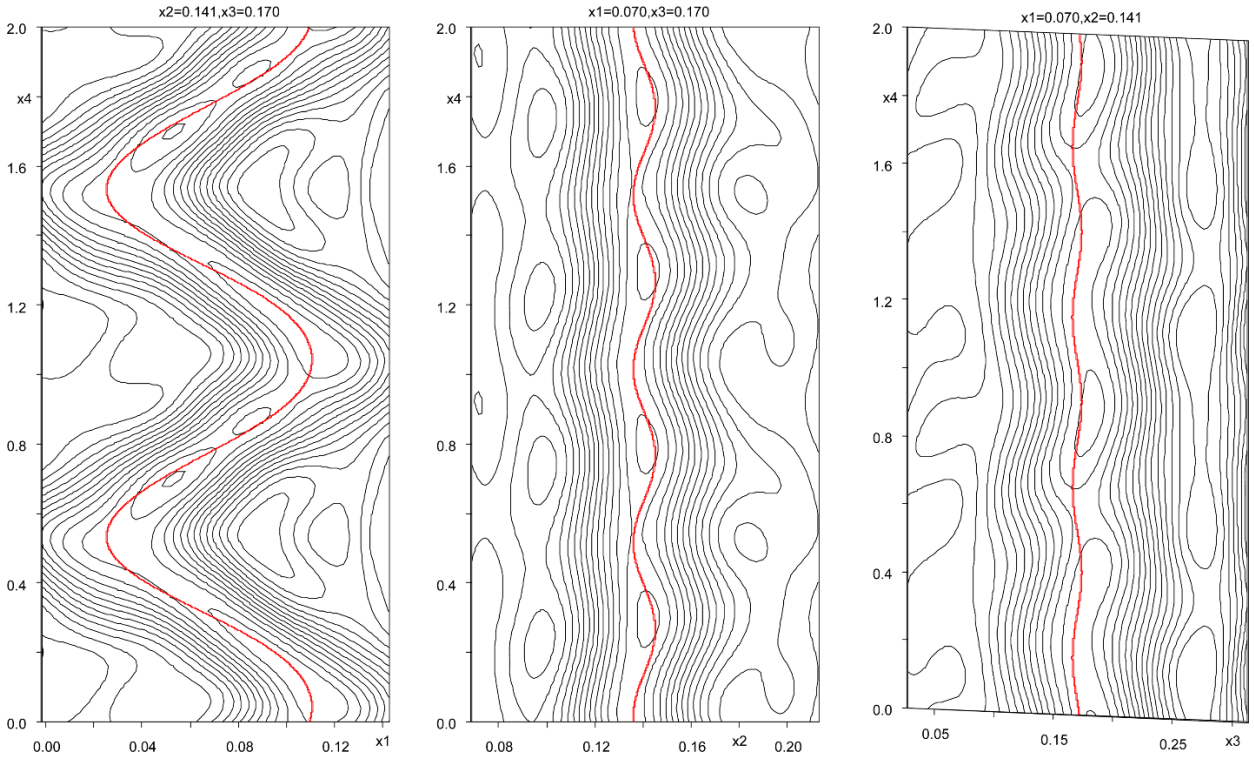

Figure S8 Electron density sections for O3.

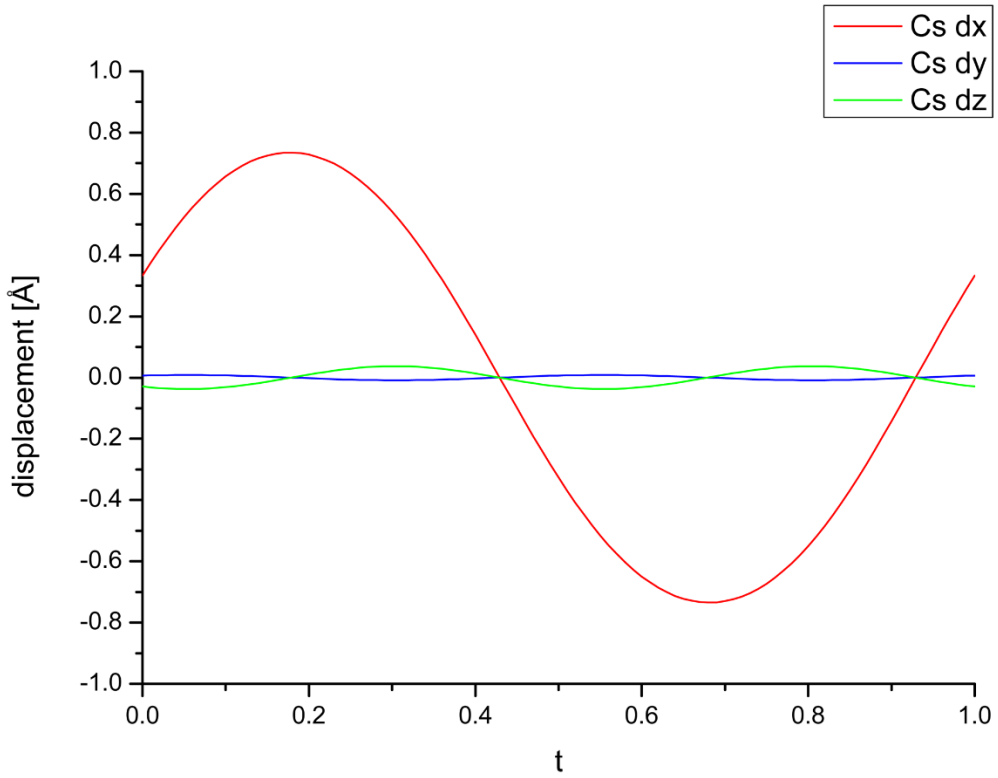

Figure S9 Displacements of Cs.

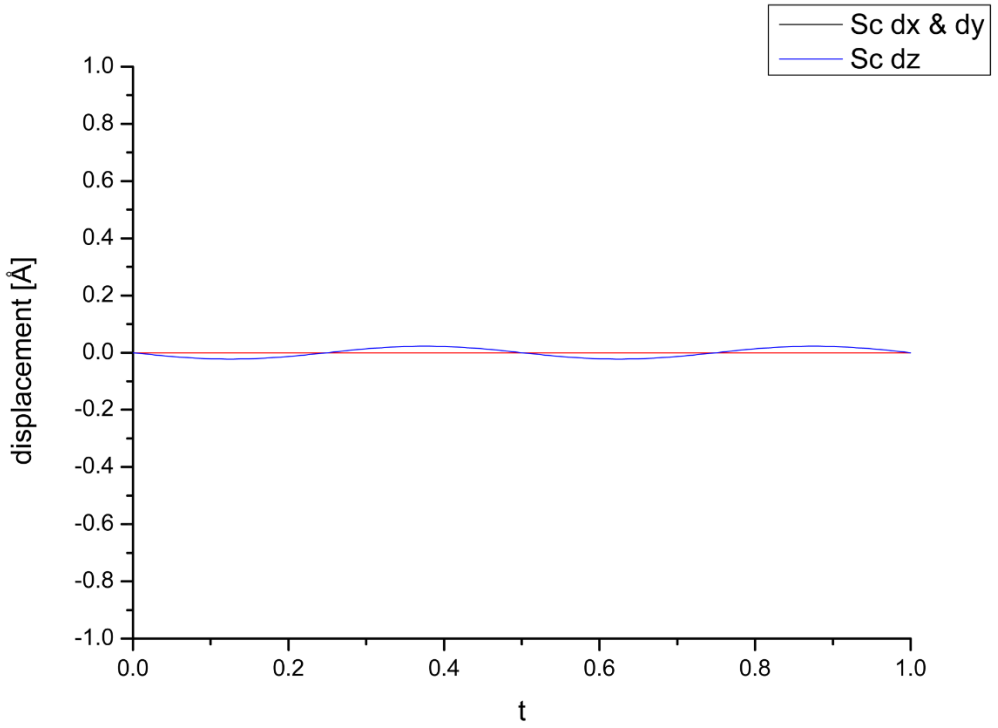

Figure S10 Displacements of Sc.

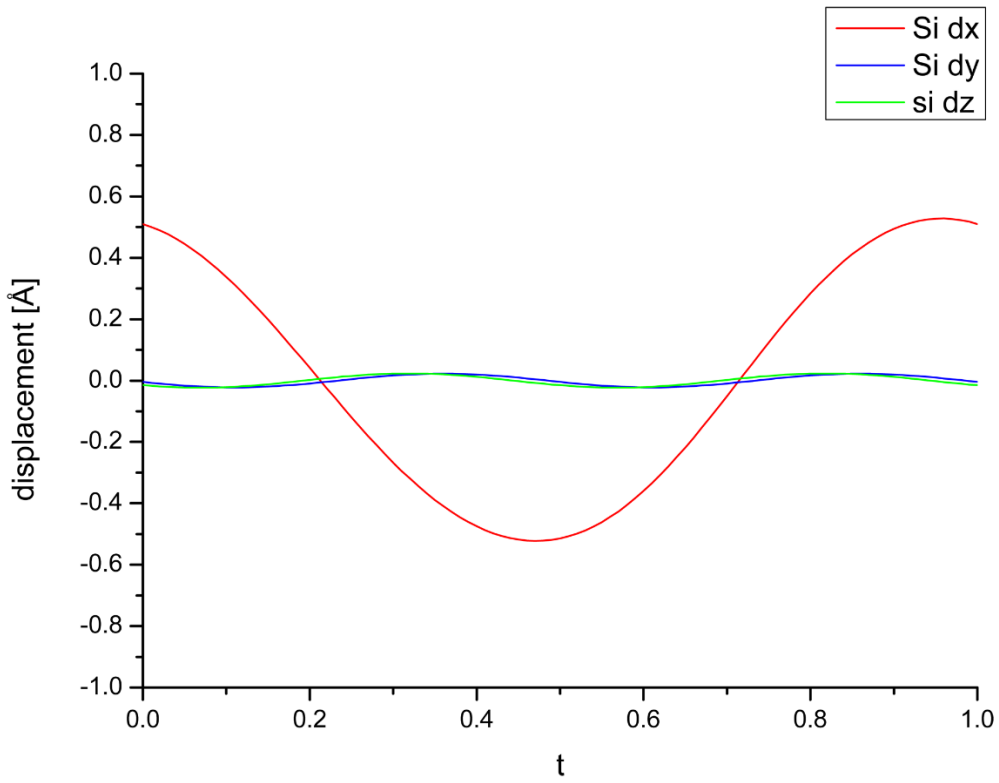

Figure S11 Displacements of Si.

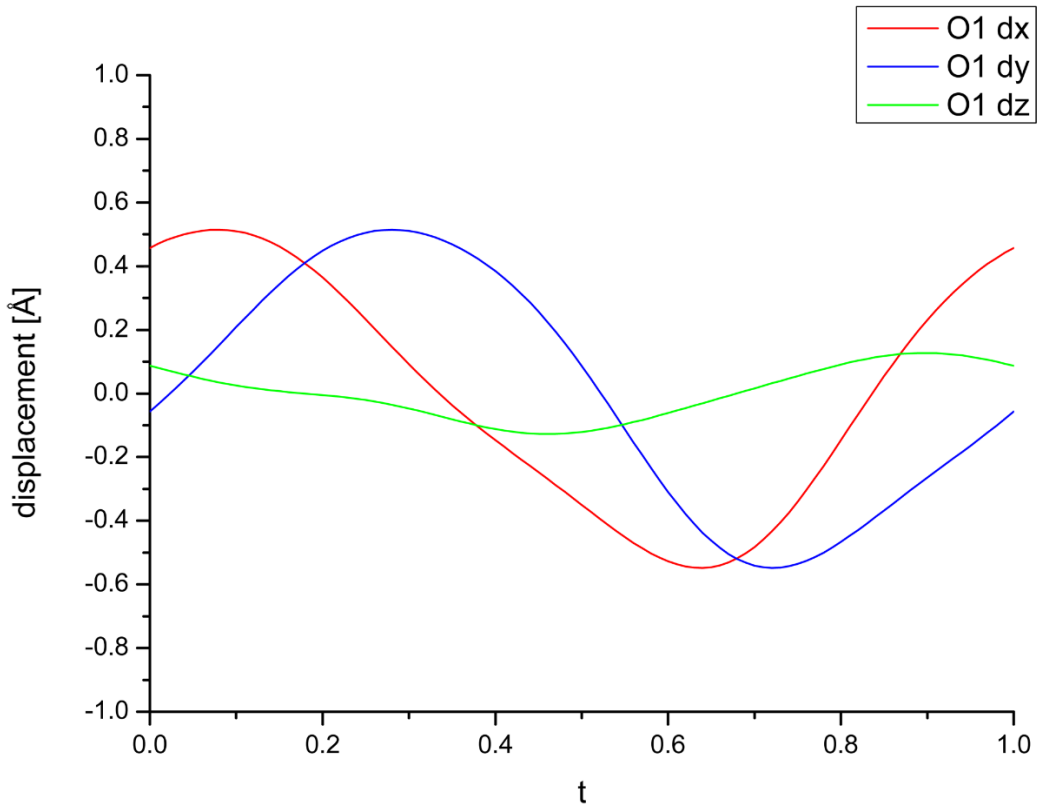

Figure S12 Displacements of O1.

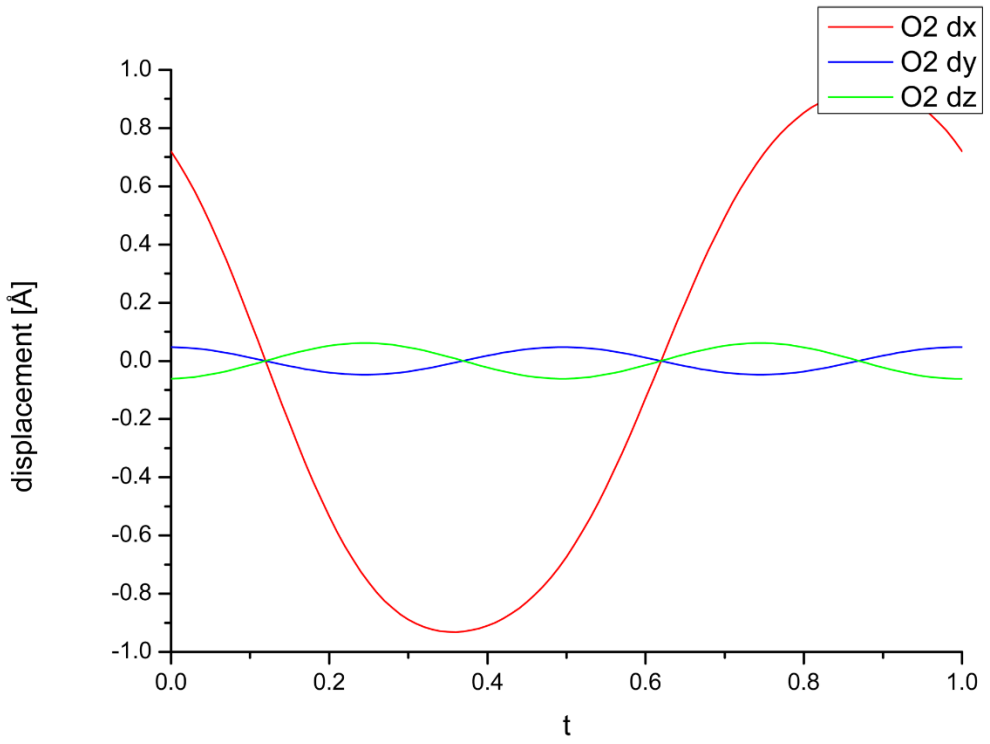

Figure S13 Displacements of O2.

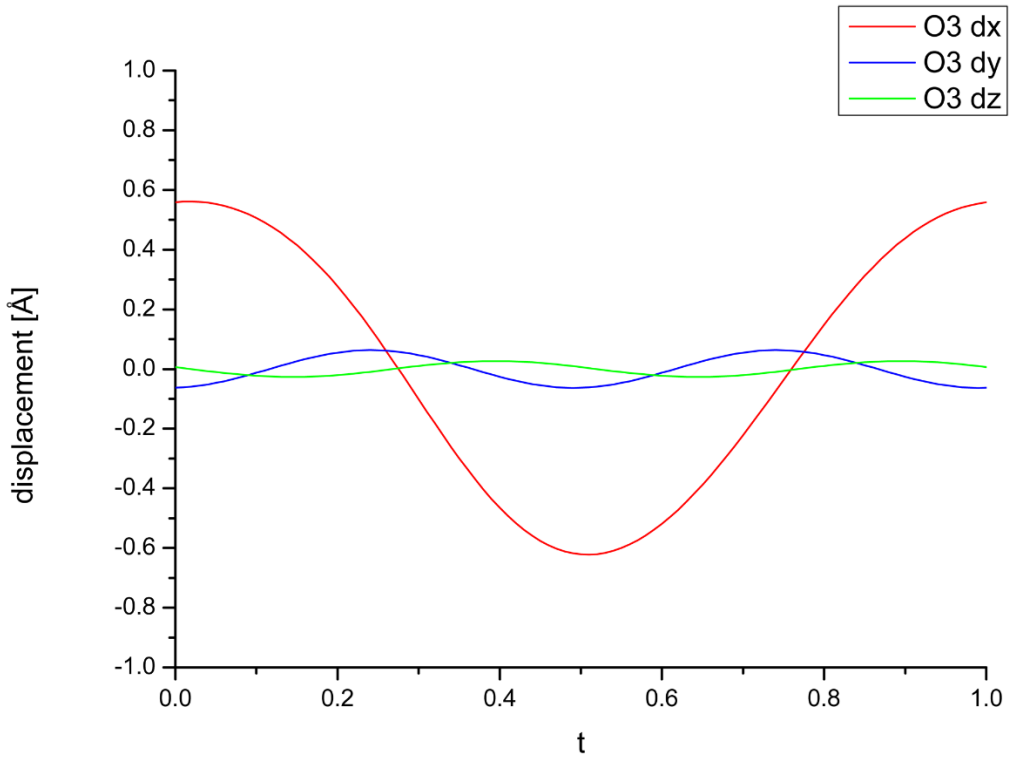

Figure S14 Displacements of O3.

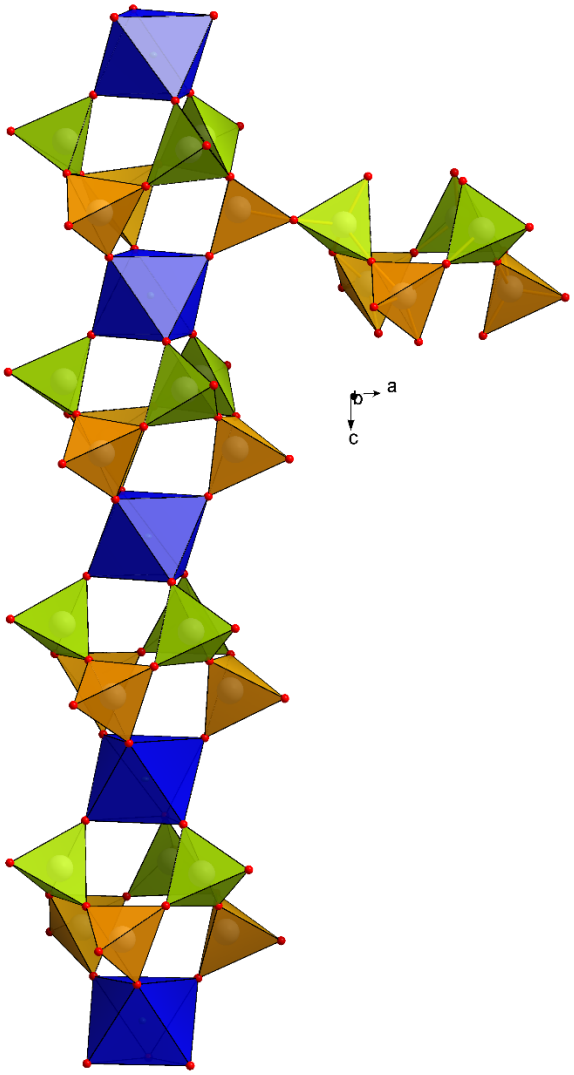

Figure S15 A section of the infinite column of alternating [ScO_6]-octahedra and six-membered [Si_6O_{18}]-rings along the $\bar{3}$-axis in the (3+1)-incommensurately modulated structure of $Cs_3ScSi_6O_{15}$. Each [ScO_6]-octahedron is rotated relative to its adjacent [ScO_6]-octahedron. Notice, that the selected part of the modulated structure does not repeat translationally.

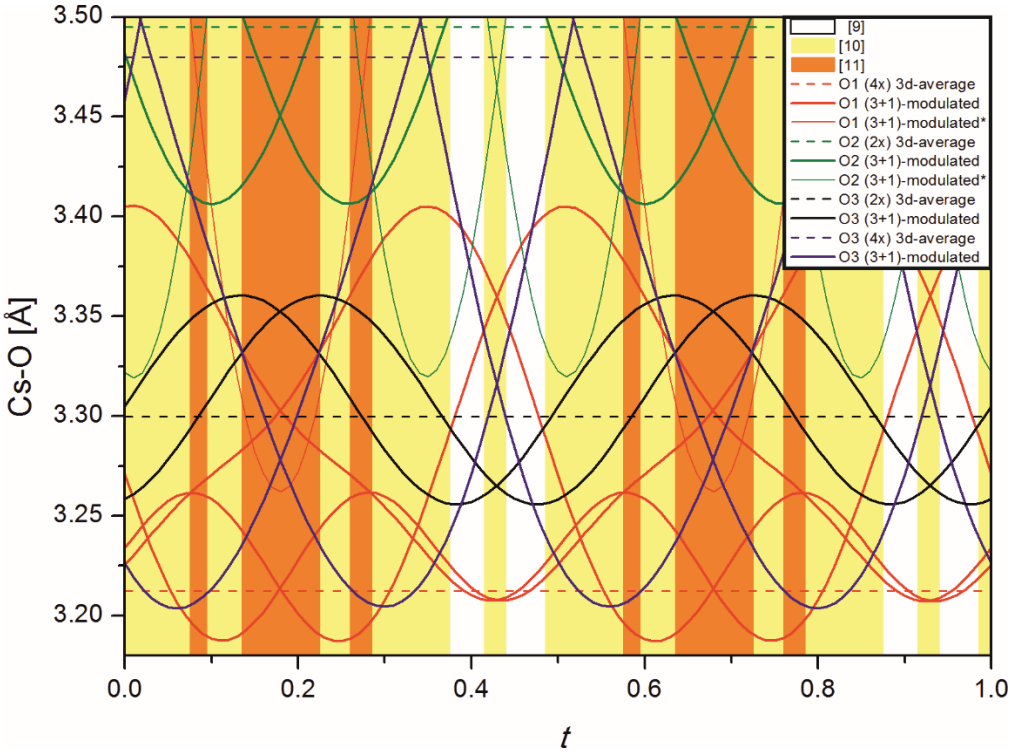

Figure S16 Cs-O distances as a function of *t*. Cs-O distances that are symmetrically equivalent in the average structure diversify in the modulated structure for different values of *t*; e.g. 4x Cs-O1 (broken red line) has an interatomic distance of 3.212(1) Å in the average structure whereas the corresponding interatomic distances in the modulated structure (think solid red line) ranging from 3.187(5) – 3.405(5) are represented by four individual lines. Thin solid lines represent interatomic Cs-O distances in the (3+1)-dimensionally modulated structure that correspond to a non-bonding distance in the average structure, i.e. distances that are larger than 3.5 Å in the 3d-average structure. The underlying background colour indicates the number of coordinating oxygen atoms in the modulated structure; white for nine-fold coordination, yellow for ten-fold coordination and orange for eleven-fold coordination.

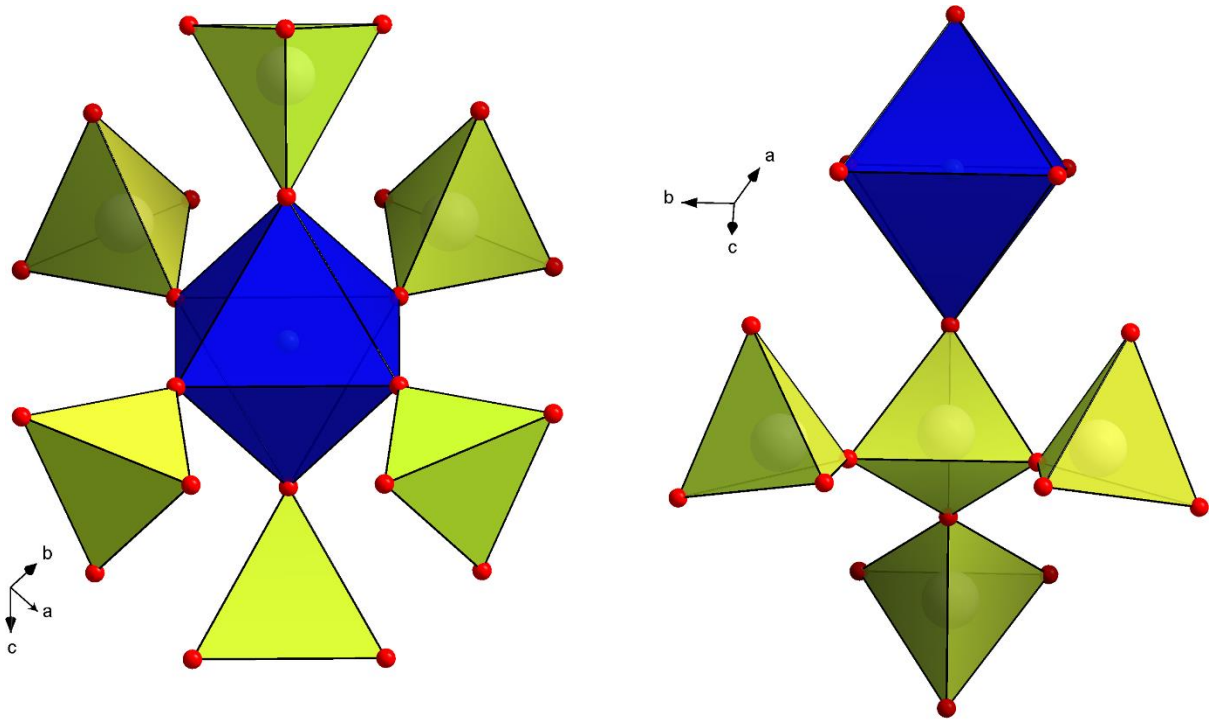

Figure S17 Polyhedral microensembles (*PME*) of (a) the [ScO_6]-octahedron (left) and (b) the [SiO_4]-tetrahedron (right).