MS15-2-10 Supertetrahedra and cation distribution in the strontium aluminium oxonitridophosphate $SrAl_5P_4N_{10}O_2F_3$ by SCXRD and STEM
#MS15-2-10

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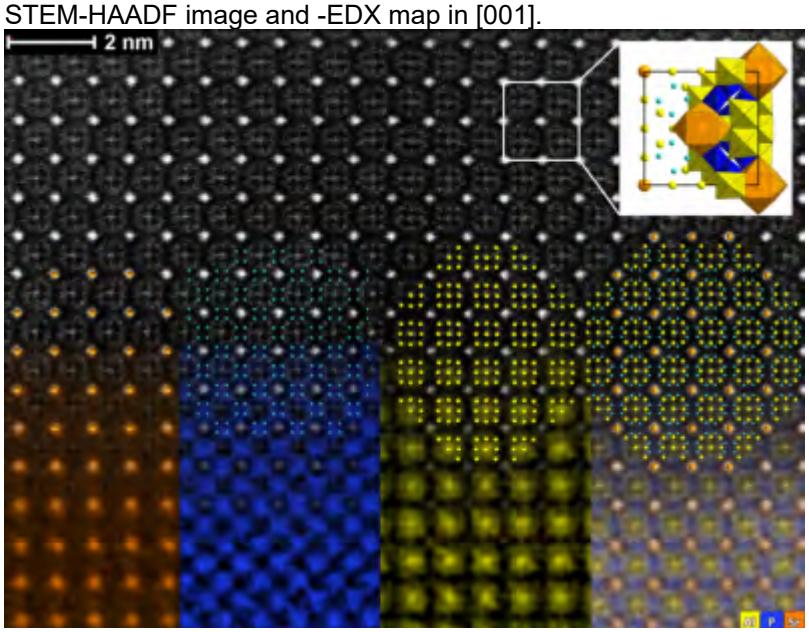
Abstract
Multinary nitrides have received much attention because of their structural diversity and several important applications, e.g. as host lattices for luminescent materials. In addition to the anionic substructure built up from tetrahedra, octahedral building blocks may complement the structural entities like the first nitridic micas $AESi_3P_4N_{10}(NH)_2$ (*AE* = Mg, Ca, Sr), which show typical tetrahedra-octahedra-tetrahedra layers.[1] The strontium aluminium oxonitridophosphate $SrAl_5P_4N_{10}O_2F_3$:Eu^{2+}, which shows green luminescence, was obtained by a mineralizer-assisted high-temperature high-pressure route (1400 °C, 5 GPa) with a Walker-type multianvil press starting from $Sr(N_3)_2$, $SrCO_3$, P_3N_5, AlN, EuF_3 and NH_4F as mineralizer.[2] $SrAl_5P_4N_{10}O_2F_3$ crystallizes in space group *I*-4*m*2 [*a* = 11.179, *c* = 5.148 Å]. The structure was elucidated by single-crystal X-ray diffraction (SCXRD). The metrics were confirmed by a tilt series of selected area electron diffraction patterns. EDX spectra (TEM and SEM) agree with the element ratio suggested by SCXRD, in particular the Al:P ratio of 1.25:1. The structure can be described as a variant of a joint *fcc* packing of all anions and Sr atoms with filled octahedral and tetrahedral voids. Possible disorder of Al and P atoms on these octahedral and tetrahedral sites was investigated by *Z*-contrast imaging (STEM-HAADF) and STEM-EDX mapping with atomic resolution. The corresponding intensities of the *Z*-contrast image as well as the spatial separation of STEM-EDX signals identify the Sr positions and confirm the allocation of Al and P on separate Wyckoff positions. Figure 1 shows a combination of a STEM-HAADF image and the corresponding STEM-EDX maps of the three cation columns Sr, Al and P along [001]. Aluminium exclusively occupies octahedral sites whereas phosphorus occupies the single tetrahedral site. Vertex-sharing PN_4 tetrahedra build up a three-dimensional network together with a new type of supertetrahedra-like building blocks composed of ten edge-sharing $Al(N,O,F)_6$ octahedra (Fig. 2, alternating opaque and transparent supertetrahedra for better visibility). $Sr(N/O/F)_{12}$ cuboctahedra share faces and form chains along [001]. Based on the known cation distribution, BVS calculations suggest the anion distribution in a straightforward way.

References
[1] L. Eisenburger, P. Strobel, P.J. Schmidt, T. Bräuniger, J. Wright, E. Lawrence Bright, C. Giacobbe, O. Oeckler, W. Schnick, *Angew. Chem.* **2022**, *134*, e202114902; *Angew. Chem. Int. Ed.* **2022**, *61*, e202114902.[2] S. Merlino, C. Biagioni, E. Bonaccorsi, N. V. Chukanov, I. V. Pekov, S. V. Krivovichev, V. N. Yakovenchuk, T. Armbruster, *Mineral. Mag.* **2015**, *79*, 145.

STEM-HAADF image and -EDX map in [001].



Interconnected supertetrahedra-like elements.