PRELIMINARY DATA ON A NEW NATURAL Ca-Ce^{4+}-ARSENATE AND ITS CRYSTAL STRUCTURE

Kolitsch, U.[1,2], Ciriotti, M.E.[3] & Blaß, G.[4]

[1]Mineralogisch-Petrographische Abt., Naturhistorisches Museum, Burgring 7, A-1010 Wien, Austria
[2]Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstr. 14, A-1090 Wien, Austria
[3]Associazione Micromineralogia Italiana, via San Pietro, 55, I-10073 Devesi-Cirié, Italy
[4]Merzbachstr. 6, D-52249 Eschweiler, Germany
e-mail: uwe.kolitsch@nhm-wien.ac.at

At the abandoned Fe-Mn Montaldo mine, Montaldo di Mondovì, Cuneo province, Piedmont, Italy (KOLITSCH et al., 2011), a new Ca-Ce^{4+}-arsenate mineral was recognised. It forms very small, pale yellow to brown-yellow pseudo-octahedral crystals embedded in matrix. The Montaldo mine is also known for unnamed $LaAsO_4$ and $NdAsO_4$ (both occurring as tiny grains) (CABELLA et al., 1999) and an unnamed Ca-Na-Mn^{3+}-arsenate (KOLITSCH, 2008).
The crystal structure was solved from single-crystal X-ray intensity data (CCD area detector; T = 293 K) and refined in space group $I4_1/a$ [a = 10.479(2), c = 12.030(2) Å, V = 1390.0(4) $Å^3$, Z = 4] to $R1(F)$ = 2.34 % and $wR2_{all}$ = 5.54 % for 1275 'observed' reflections with $F_o > 4\sigma(F_o)$. In the asymmetric unit there is one Ca, one Ce, one As and four O sites. Additionally, the structure hosts, in a void, a partially occupied, disordered water(?) site [O occupancy ~0.32; O-O' = 0.720(14) Å], but this has not been confirmed yet by supplementary methods. A three-dimensional framework is built of AsO_4 tetrahedra (<As-O> = 1.688 Å), Ca-O polyhedra [(6+3)-coordination with six ligands within 2.51 Å and three additional ligands between 2.775(18) and 3.064(3) Å] and CeO_8 polyhedra (<Ce-O> = 2.368 Å).
Semiquantitative SEM-EDS analyses and occupancy refinements indicate that Ca is partly replaced by Y, Nd and/or Ce, and that Ce^{4+} is partly replaced by Zr, Th, Y, Nd and/or Ca(?). Minor amounts of Si replace As. The derived simplified formula is $Ca_4Ce^{4+}(AsO_4)_4 \cdot \sim 1.3H_2O$. The Ce valency has been confirmed by bond-valence calculations (ROULHAC & PALENIK, 2003).
The structure of the new Ca-Ce^{4+}-arsenate is derivable from that of scheelite and isotypic with synthetic $Na_{3.68}Dy_{1.44}(SeO_4)_4$ and several molybdates and tungstates $M_5REE(Mo/WO_4)_4$. The water(?) site of the new mineral is equivalent to one of two alkali sites in these compounds.
Additional studies (EPMA, Raman spectroscopy, polarised-light microscopy) are underway

CABELLA, R., LUCCHETTI, G., MARESCOTTI, P. (1999): Can. Mineral., 37, 961-972.
KOLITSCH, U. (2008): Geochim. Cosmochim. Acta 72, Special Supplement 12S, A487.
KOLITSCH, U., CIRIOTTI, M.E., CADONI, M., ARMELLINO, G., PICCOLI, G.C., AMBRINO, P., BLASS, G., ODICINO, G., CIUFFARDI, M. (2011): Micro, 9, 4-21.
ROULHAC, P.L., PALENIK, G.J. (2003): Inorg. Chem., 42, 118-121.