

[o.m2.p13] Crystal Structure of $\text{Ca}_{4.78}\text{Cu}_6\text{O}_{11.60}$. Ph. Galez, M. Lomello-Tafin, Th. Hopfinger, *LAIMAN, Université de Savoie, 9 rue de l'Arc-en-Ciel, BP240, F-74942 Annecy-le-Vieux cedex, France.*

Keywords: $\text{Ca}_{4.78}\text{Cu}_6\text{O}_{11.60}$, crystal structure, substitution effects.

The crystal structure of $\text{Ca}_{4.78}\text{Cu}_6\text{O}_{11.60}$ (space group : $P2/c$, $Z = 4$, $\rho = 4.48(2) \text{ g/cm}^3$, $a = 10.9456(4) \text{ \AA}$, $b = 6.3192(2) \text{ \AA}$, $c = 16.8408(5) \text{ \AA}$ and $\beta = 104.952(2)^\circ$) has been solved and refined using X-ray and neutron powder diffraction combined with Rietveld analysis. It is closely related to the NaCuO_2 -type structure. The phase stoichiometry and the displacements of atoms with respect to their positions in the previously reported substructure [1] ($Fmmm$, $a = 2.807(1) \text{ \AA}$, $b = 6.351(2) \text{ \AA}$ and $c = 10.597(3) \text{ \AA}$) are explained by the minimization of Ca-Ca repulsion and by a relaxation towards a more regular octahedral environment for Ca atoms.

Bond valence sum calculations indicate that the individual valences for Cu atoms lie between 1.3 and 3. These results could give additional clues for the understanding of the low-temperature magnetic properties of the phase (and more generally of linear chains of edge-shared CuO_4 squares also present in $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$) which have been interpreted in terms of the presence of Cu^{3+} ions [2] or Zhang-Rice singlets [3].

The substitution of Tl atoms for Ca atoms results in an increased thermal stability and in incommensurate structures with modulation vectors depending strongly on the Tl content.

The substituted phase plays an important role in phase equilibria in the superconducting $\text{TlO}_{1.5}\text{-BaO-CaO-CuO}$ system. It is an endmember of an equilibrium three phase field ($\text{Tl-2212} - \text{Tl}_2\text{Ca}_3\text{O}_6 - (\text{Ca,Tl})_{1-x}\text{CuO}_2$) which prevents the formation of the Tl-2223 phase when the Tl content exceeds 2 atoms per formula unit [4].

[o.m2.p14] Ferroelastic phase of $\text{Pb}_5\text{Al}_3\text{F}_{19}$. G. Bravic, R. Von der Mühl, J. Ravez. *Institut de Chimie de la Matière Condensée de Bordeaux. 87, av. du Dr Albert Schweitzer. F-33608 PESSAC (France).*

Keywords: ferroelastic, phase, structure.

$\text{Pb}_5\text{Al}_3\text{F}_{19}$ shows three phase transitions between 100K and 400K. The crystal structures of three phases among four have been reported yet, there are tetragonal^{1,2,3}. The crystals of the last one, stable between 320K and 360K, present ferroelastic domains and so are not suitable for single crystal X-ray diffraction study.

The incorporation of a slight quantity of Cr^{3+} ions stabilizes this phase at room temperature. We have obtained a very small single-domain crystal of $\text{Pb}_5\text{Al}_{2.96}\text{Cr}_{0.04}\text{F}_{19}$ (0.05 x 0.04 x 0.015 mm). X-ray diffraction measurements were performed on an Enraf-Nonius CAD4 diffractometer with the $\lambda\text{K}\alpha(\text{Mo})$ radiation (0.71 \AA). The parameters of the $P\bar{1}$ triclinic cell are: $a = 10.72(3) \text{ \AA}$, $b = 10.67(3) \text{ \AA}$, $c = 7.24(2) \text{ \AA}$, $\alpha = 109.27(5)^\circ$, $\beta = 110.14(5)^\circ$, $\gamma = 83.33(5)^\circ$.

However a better description consists in the non-conventional centered cell $I\bar{1}$ whose parameters are close to those of a tetragonal cell: $a = 14.26(5) \text{ \AA}$, $b = 14.22(4) \text{ \AA}$, $c = 7.24(2) \text{ \AA}$, $\alpha = 89.30(6)^\circ$, $\beta = 89.89(3)^\circ$, $\gamma = 89.99(8)^\circ$. So, we can easily compare the ionic packing with those of the adjacent phases^{1,3} in terms of weak displacements, e. g., rotation of AlF_6^- octaedra and break of the Pb^{2+} alignment along the c crystal axis. These characteristics explain the loss of the 4-fold symmetry which leads to the triclinic cell and the appearance of crystal ferroic domains.

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