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Chemical, Structural and Electrical Studies of Layered Alkali Uranyl Vanadates.

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In recent works [1-4] we have studied different alkali uranyl vanadates and shown that the nature of the alkaline salt used for the synthesis is a determining factor for the crystal structure stability. Thus, the size of the anion associated with the alkaline element plays a significant role in this stability.

Reaction of various alkaline salts with the pentahydrated uranyl ortho-vanadate compound $(UO_2)_3(VO_4)_2$. $5H_2O$, recently characterized in our laboratory, leads to the synthesis of single crystals of different alkali uranyl vanadates, **Fig. a**. All these new compounds are characterized by layered structures, the layers are formed by the association of the uranyl and vanadate ions.

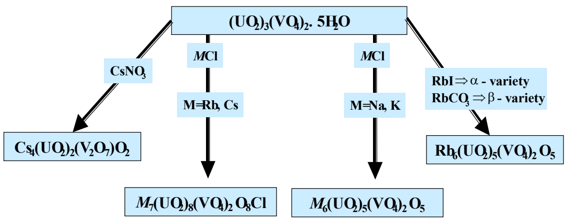

Fig. a : *Synthesis of the uranyl vanadates single crystals*

$Cs_4[(UO_2)_2(V_2O_7)O_2]$ crystallizes in the orthorhombic system with space group Pmmn and cell parameters : a = 8.4828(15)Å, b = 13.426(2)Å, c = 7.1366(13)Å and Z = 2. The crystal structure is characterized by $[(UO_2)_2(V_2O_7)O_2]^{4-}$ corrugated layers parallel to (001) and the cohesion of this structure is assured by interlayer Cs^+ ions, **Fig. b**. Uranyl tetragonal bipyramids $(UO_2)O_4$ are linked by corners to form infinite chains $(UO_5)_\infty$ parallel to the **a** axis. These chains are linked together by symmetrical divanadate units V_2O_7 sharing two corners with each chain $(UO_5)_\infty$, to form $[(UO_2)_2(V_2O_7)O_2]^{4-}$ layers, **Fig. c**.

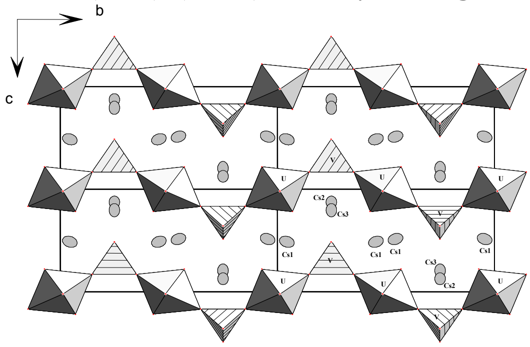

Fig. b : *Structure of $Cs_4[(UO_2)_2(V_2O_7)O_2]$*

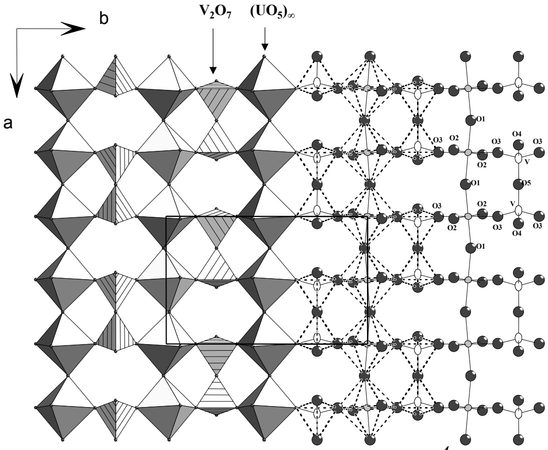

Fig. c : *Vue of $[(UO_2)_2V_2O_7O_2]^{4-}$ layer*

The oxychlorides $M_7[(UO_2)_8(VO_4)_2O_8Cl]$ with *M*=Rb and Cs, crystallize in the orthorhombic system with space groups Pmcn and Pmmn, respectively. The a and b unit cell parameters are almost identical in both compounds while the c parameter in the Rb compound is doubled : **Rb :** a = 21.427(5)Å, b = 11.814(3)Å, c = 14.203(3)Å, Z = 4; and **Cs :** a = 21.458(3)Å, b = 11.773(2)Å, c = 7.495(1)Å, Z = 2. Both structures are characterized by $[(UO_2)_8(VO_4)_2O_8Cl]^{7-}$ layers parallel to the (001) plane. The layers are built up from VO_4 tetrahedra, UO_7 and UO_6Cl pentagonal bipyramids, and UO_6 tetragonal bipyramids, **Fig. d**. Uranyl tetragonal bipyramids $(UO_2)O_4$ are linked by corners to form infinite chains $(UO_5)_\infty$ parallel to the **a** axis. These chains are linked together by symmetrical divanadate units V_2O_7 sharing two corners with each chain $(UO_5)_\infty$, to form $[(UO_2)_2(V_2O_7)O_2]^{4-}$ layers, **Fig. c**.

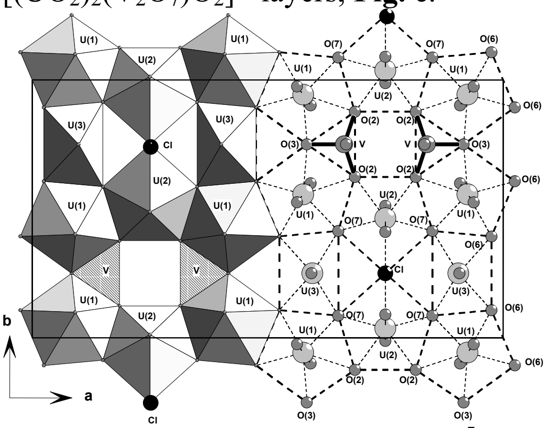

Fig. d : *Vue of the* $[(UO_2)_8(VO_4)_2O_8Cl]^{7-}$ *layer*

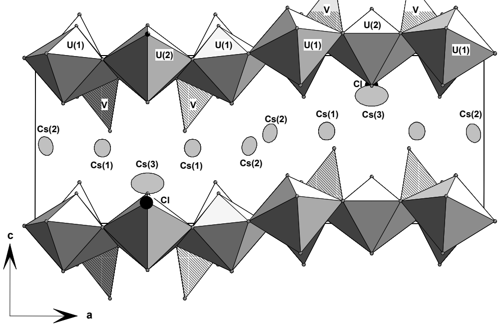

Fig. e : *Structure of* $Cs_7[(UO_2)_8(VO_4)_2O_8Cl]$

$M_6(UO_2)_5(VO_4)_2O_5$ adopt two types of structures. Both structures are characterized by parallel $[(UO_2)_5(VO_4)_2O_5]^{6-}$ layers which are flat in α-Rb variety, **Fig. f**, and corrugated in the Na, K and β-Rb compounds, **Fig. g**. The layers are built up from VO_4 tetrahedra and UO_7 pentagonal bipyramids. The UO_7 pentagonal bipyramids are associated by sharing opposite equatorial edges to form zig-zag infinite chains $(UO_5)_\infty$. These chains are linked together on one side by VO_4 tetrahedra and on other side by UO_7 pentagonal bipyramids sharing corner and opposite edges in α variety, and in the three other structures by UO_6 tetragonal bipyramids. In the α variety, the layers are flat according to the rows of VO_4 tetrahedra parallel to the b axis whose apical oxygen atoms are alternatively pointing on the both sides in each row whereas in the other compounds, they are all pointing in the same side in a row and in opposite side in the next row, yielding to corrugated layers.

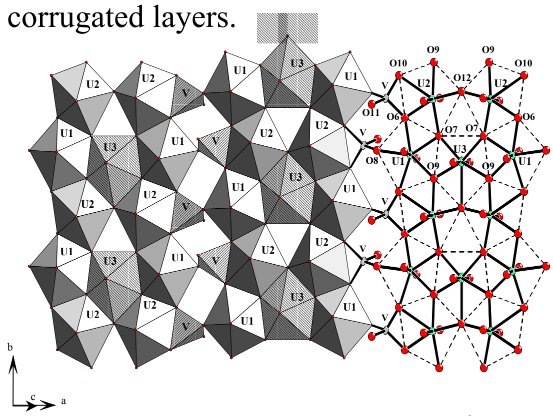

Fig. f : *Vue of the* α-$[(UO_2)_5(VO_4)_2O_5]^{6-}$ *layer*

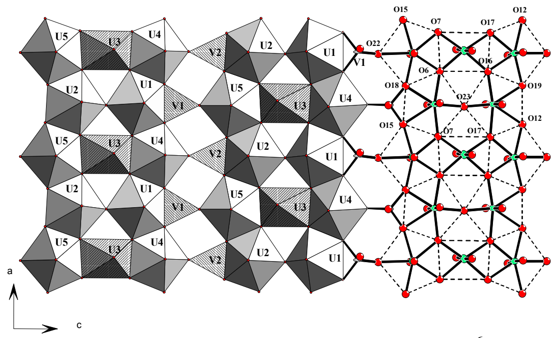

Fig. g : *Vue of the* β-$[(UO_2)_5(VO_4)_2O_5]^{6-}$ *layer*

For all materials , the conductivity measurements, ***logσ*** vs ***10^3/T***, between 200 and 800 °C, shown an Arrhenius law evolution.

References

[1]-Synthesis, Crystal Structure, and Comparison of Two New Uranyl Vanadate Layered Compounds : $M_6(UO_2)_5(VO_4)_2O_5$ with M = Na, K,.C. Dion, S. Obbade, E. Raekelboom, F. Abraham, and M. Saadi, *J. Solid State Chem*. 155, 342 (2000).

[2]-Synthesis and Crystal Structure of Two New Uranyl Oxychloro - Vanadate Layered Compounds: $M_7(UO_2)_8(VO_4)_2O_8Cl$ with M= Rb, Cs, I. Duribreux, M. Saadi, S. Obbade, C. Dion and F. Abraham, *J. of Solid State Chem., (2003,) In Press, corrected proof.*

[3]- Synthesis and Crystal Structure of α and β-$Rb_6U_5V_2O_{23}$, a New Layered Compound, S. Obbade, C. Dion, L. Duvieubourg, M. Saadi and F. Abraham, *J. of Solid State Chem., (2003) In Press, corrected proof.*

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