

are composed of plate-like fragments of tridymite/cristobalite layers, whereas obsidian contains quartz nanocrystals with abundant moganite-like planar faults.

Regarding atmospheric soot particles, a characteristic shift of the first nearest-neighbour interatomic distance was observed. Interatomic distances are proved to be as small as 0.134 nm, much shorter than in graphite (0.142 nm) or in amorphous carbon (0.141–143 nm), but larger than the typical value (0.131–0.132 nm) for a kerogen with significant hydrogen content (H/C=0.61). These results suggest that the first nearest neighbour interatomic distance measurable in soot is the superposition of first-neighbour C–C distances and C–H distances (around 0.143 and 0.11 nm, respectively). Hydrogen is related to the aromatic components in soot which can strongly influence the optical properties of soot particles.

Quantitative electron diffraction has proved to be an efficient method for studying the nanostructures of highly disordered geological materials.

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Compounds AMO_4 (A = Ca, Sr, Ba; M = W, Mo) with scheelite structure: growth, composition, structure peculiarities. Eremín A.^{a)}, Kuz'micheva G.^{a)}, Zharikov E.^{b)}

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Single crystals with scheelite structure ($CaWO_4$), doped by rare earth ions meet very high interest of different scientific groups as active media for solid-state lasers. It is seen from numerous publications, appeared during the last years.

In this paper, we report a results of crystallochemical analysis of AMO_4 (A=Ca, Sr, Ba; M=W, Mo) compounds and a detailed structural study of $CaWO_4$ doped with Na^{1+} and Yb^{3+} .

In the scheelite structure (sp. gr. $I4_1/a$, $z=4$), Ca^{2+} is in a severely distorted dodecahedral oxygen coordination with two sets of bond distances (CN=4+4), W^{6+} is in a slightly distorted tetrahedral coordination, with identical W-O bond distances (CN=4) but different bond angles.

Crystallochemical analysis of structural parameters of well-known AMO_4 (A=Ca, Sr, Ba; M=W, Mo) allowed to ascertain:

- the cell parameter a increases and the cell parameter c decreases in $CaMO_4$ - $SrMO_4$ - $BaMO_4$ and $AMoO_4$ - AWO_4 series,
- the AO_8 dodecahedra are more regular in $AMoO_4$ structures than those in AWO_4 ones,
- the M-O interatomic distances in MO_4 tetrahedra do not depend on cation kind in dodecahedral sites,
- the increasing of A ionic radius leads to the formation of more regular tetrahedra (for AWO_4 appeared to be more than for $AMoO_4$),
- the change of A ionic radius affects only the change of tetrahedra angles (for $AMoO_4$ appeared to be more than for AWO_4),

We studied unannealed (I) and air-annealed (II) single crystals $(Ca_{1-2x}Na_xYb_x)WO_4$ ($x=0.03, 0.10, 0.15$) grown by the Czochralski technique. The crystals were ground into powder and examined by X-ray diffraction (XRD) on a HZG diffractometer (CuK_α radiation, $2\theta = 10-100^\circ$, step

scan mode with a counting time of 10 s per data point and a scan step of 0.05°). Single-crystal structural analysis was carried out on a CAD-4 diffractometer at room temperature (MoK_α radiation, graphite monochromator, ω scan mode) for $(Ca_{0.8}Na_{0.1}Yb_{0.1})WO_4$ microcrystals.

With increasing x value, the lattice parameters of $(Ca_{1-2x}Na_xYb_x)WO_4$ crystals decrease, as would be expected ($r_{Ca}=1.12\text{\AA}$, $r_{Na}=1.18\text{\AA}$, $r_{Yb}=0.99\text{\AA}$). The lattice parameters of the annealed crystal are smaller than those of unannealed for both powder samples and microcrystals, which correlates with the concentration of Na and Yb, as supported by single-crystal XRD data: $(Ca_{0.819}Na_{0.120}Yb_{0.061})WO_{3.970}$ (II) and $(Ca_{0.808}Na_{0.118}Yb_{0.074})WO_{3.978}$ (I)

In the case of unannealed $(Ca_{0.8}Na_{0.1}Yb_{0.1})WO_4$ (I) crystals it was observed that some XRD peaks are split (011, 012, 013, 004, 224 and so on) or their shape is distorted. This can be explained by one of two reasons: the formation of ordered phase (superstructure) or the separation of solid-solution with formation of two isostructural phases of different compositions. The same phenomenon we observed by X-ray study of $(Na_{0.5}Gd_{0.5})WO_4$ and $(Na_{0.5}Gd_{0.5})WO_4:Yb$ crystals that has been explained by superstructure formation.

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Structure in layers or in tunnels to basis of uranyl - vanadate M. Saadi^{a)}, S. Obbade^{b)}, C. Dion^{b)}, S. Yagoubi^{b)}, C. Renard and F. Abraham^{b)} ^{a)Laboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Université Mohammed V Agdal, Rabat, Maroc} ^{b)Laboratoire de Cristalochimie et Physicochimie du Solide, UMR CNRS 8012, ENSCL - USTL, Villeneuve d'Ascq Cedex, France.} E-mail : saadi@fsr.ac.ma

Keywords: Layered structure -1, Uranyl -2, vanadate -3

The study of the association of uranyl ions and oxyanions presents an interest at the same time environmental, mineralogical, geological, structural and physical. From the physical property point of view these compounds are particularly interesting because they frequently generate original, two-dimensional structures (2D) by the formation of infinite layers, or the structures known as monodimensional by the formation of tunnels. These structures favours the mobility of the cations present in the tunnels or in spaces inter layers as well as the possibilities of intercalation and desintercalation of these cations. Within the framework of the search for new uranyl $(UO_2)^{2+}$ and oxyanions $X_mO_n^{p-}$ based materials, we began our study with uranyl vanadates of the type carnotite $M_2(UO_2)_2V_2O_8 \cdot nH_2O$ ($V/U = 1$) of the monovalent cations ($M = Na, K, Rb, Cs, Tl, Ag, NH_4$). Their crystalline structure is formed by a stacking up of infinite layers $[(UO_2)_2V_2O_8]^{2-}$, resulting from the association of uranyl ions UO_2^{2+} and $V_2O_8^{6-}$ entities. The field of investigations then was widened to the compounds of report/ratio $V/U = 3$. This work allowed the focusing of the $CsUO_2(VO_3)_3$ phase whose the structure is formed by layers $[UO_2(VO_3)_3]$. The layers join per pairs without direct connection between them [1]. At the time of the tests of synthesis of the acid $(H_3O)_2(UO_2)_2V_2O_8 \cdot nH_2O$ whose derives the carnotites family, a new compound of formula $(UO_2)_3(VO_4)_2 \cdot 5H_2O$ was highlighted. Its structure is constituted by layers $[UO_2VO_4]$ interconnected by other uranyl ions UO_2^{2+} and the water molecules [2]. This

compound $(\text{UO}_2)_3(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$ is used then as precursor for the synthesis of the following phases :

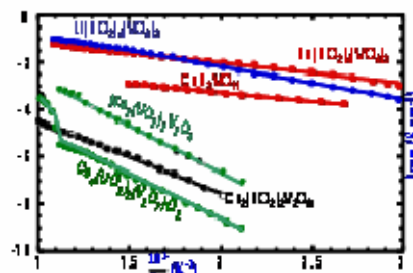
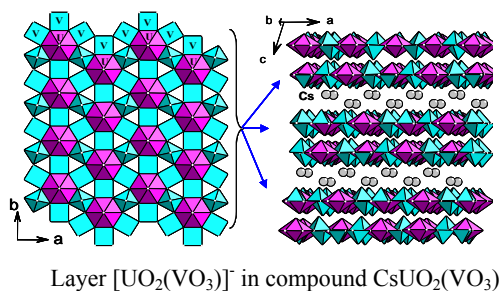
- Compounds $\text{M}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$ with $\text{M} = \text{Na}$ and K who crystallizes in a monoclinic system with the same space group $\text{P}2_1/\text{c}$. Their structure consists of infinite layers $[(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5]^{6-}$ [3].

- Compounds α and β $\text{Rb}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$, for which the structures were respectively resolved in space groups $\text{C}2/\text{c}$ and $\text{P}2_1/\text{n}$. In the form $\alpha\text{-Rb}_6\text{U}_5\text{V}_2\text{O}_{23}$, the ribbons $[(\text{UO}_2)_5\text{O}_{11}]^{6-}$ are connected the ones to the others by VO_4 tetrahedrons,

- For the form $\beta\text{-Rb}_6\text{U}_5\text{V}_2\text{O}_{23}$, the ribbons $(\text{UO}_5\text{O}_{21})_\infty$ are interconnected by tetrahedrons $\text{V}(1)\text{O}_4$ and $\text{V}(2)\text{O}_4$. In both cases the association of $(\text{UO}_5\text{O}_{21})_\infty$ ribbons and VO_4 tetrahedrons gives $[(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5]^{6-}$ layers [4].

- The $\text{Cs}_4(\text{UO}_2)_2\text{V}_2\text{O}_7\text{O}_2$ phase which crystallizes in the space group Pmmn and from which the structure is formed by stacking up of the layers with wrinkled characters $[(\text{UO}_2)_2(\text{V}_2\text{O}_7)\text{O}_2]^{4-}$ [5].

-The phases $\text{M}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ ($\text{M} = \text{Rb}, \text{Cs}$) [6], in which, the association of vanadium polyhedrons and of the uranium leads to a particularly dense layer, $[(\text{UO}_2)_2(\text{UO}_2)_6\text{O}_8\text{Cl}(\text{VO}_2)_2]^{7-}$ parallel to the (\bar{a}, \bar{b}) plan. The structural study of $\text{M}(\text{UO}_2)_4(\text{VO}_4)_3$ ($\text{M} = \text{Na}, \text{Li}$) shows that the structure of these compounds is formed by three dimensional framework $[(\text{UO}_2)_4(\text{VO}_4)_3]^{2-}$ which makes a tunnels in an alternate way along the a and b axis . These tunnels are half occupied by the alkaline cations [7].



Linear conductivity evolution agrees with Arrhenius law

[1] $\text{CsUO}_2(\text{VO}_3)_3$ a new uranyl vanadate with a layered structure, I. DURIBREUX, C. DION, F. ABRAHAM, M SAADI, *Journal of Solid State Chem.*, 146, 258-265, 1999.

[2] Synthesis and Crystal Structure of the Pentahydrated Uranyl-Orthovanadate $(\text{UO}_2)_3(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$, M. SAADI, C. DION, F. ABRAHAM, *Journal of Solid State Chem.*, 150, 72-80, 2000.

[3] Synthesis, Crystal Structure and Comparison of two New Uranyl Vanadate Layered Compounds $\text{M}_6(\text{UO}_2)_5(\text{VO}_4)_2\text{O}_5$ with $\text{M} = \text{Na}, \text{K}$, C. DION, S. OBBADE, E. RARAEKELBOM, F. ABRAHAM, M. SAADI, *Journal of Solid State Chemistry* 155 (2), 342-353, 2000.

[4] Synthesis and Crystal Structure of α and β $\text{Rb}_6\text{U}_5\text{V}_2\text{O}_{23}$, a New Layered Compound, S. OBBADE, C. DION, L. DUVIEUBOURG, M. SAADI, F. ABRAHAM, *Journal of Solid State Chemistry*, 173, 1-12, 2003.

[5] Synthesis, Crystal Structure and Electrical Characterization of $\text{Cs}_4[(\text{UO}_2)_2(\text{V}_2\text{O}_7)\text{O}_2]$ a uranyl divanadate with chains of corner-sharing uranyl square bipyramids, S. Obbade, C. Dion, M. Saadi, F. Abraham, *Journal of Solid State Chemistry*, 177, 1567-1574, 2004.

[6] Synthesis and Crystal Structure of Two New Uranyl Oxychloro- Vanadate : Layered Compounds: $\text{M}_7(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}$ with $\text{M} = \text{Rb}, \text{Cs}$, I. Duribreux, M. Saadi, S. Obbade, C. Dion, F. Abraham, *Journal of Solid State Chemistry* 172, 351-363, 2003.

[7] A novel open-framework with no -crossing channels in the uranyl vanadates $\text{A}(\text{UO}_2)_4(\text{VO}_4)_3$ ($\text{A} = \text{Li}, \text{Na}$), S. Obbade, C. Dion, M Rivenet, M Saadi, F. Abraham, *Journal of Solid State Chemistry*, 177, 2058-2067, 2004.