## MS11 P06

**Reflux effect In the vanadium phosphate hydrates Structure** L. OUALAL[a,b], S. A. ENNACIRI[a], E. K. HLIL[b], A. LAAMYEM[c], [a]*Laboratory of Coordination Chemistry, Department of Chemistry, Cadi Ayyad University Faculty of Sciences-Semlalia, Marrakech, Morocco,* [b]*Institut Néel, Département MCMF, CNRS/UJF, Grenoble, France,*
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**Keywords: Vanadium phosphate dehydrates, X-ray diffraction, Sol-gel**

Vanadyl phosphate dehydrate $VOPO_4.2H_2O$ is one of the principal precursors to obtain all phases of the VPO [1] system. This phosphate is easily crystallised when vanadium oxide is refluxed in concentrated $H_3PO_4$ [2]. It can be also synthesised at room temperature via the acidification of an aqueous solution of sodium metavanadate $NaVO_3$ and sodium metaphosphate $Na_3PO_4$ [3] or via sol-gel method, by reacting phosphoric acid with vanadium oxo-alkoxides $VO(OR)_3$ [4] .
In this study, the structure of vanadyl phosphate hydrates undergoes different transformations when it was refluxed in different solvent depending in the nature of solvent. Indeed after 24 hours of $VOPO_4.2\ H_2O$ reflux in isopropanol the $VOHPO_4.0,\ 5\ H_2O$ [5] is formed. This phase was already, obtained in other conditions by Hutchings and all [6], and O'Mahony and all [7]. Another phase which has not been reported up to date is obtained when the n-propanol is used. The XRD pattern of this phase is completely different from that of $VOHPO_4.0,\ 5\ H_2O$ or any other phases in the VPO system. The identification of this new phase is under study. It evidences that we obtain the $VOPO_4.xH_2O$ when reflux is in tetrahydrofurane.
X-ray diffraction, I.R infrared microscopy, DTA/GTA differential thermographic analysis and scanning electron microscopy are used in this study.

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## MS11 P07

**Synthesis and crystal structure of the new lead thiophosphates $APbPS_4$ (A = K, Rb, Cs).** I. Belkyal[I], M. El Azhari[I], Y. Wu[II], C. Näther[II], W. Bensch[II] and W. Depmeier[III] [I] *Laboratoire Matière Condensée et nanostructures, Faculté des Sciences et Techniques, Département des Sciences Chimiques, Université Cadi Ayyad, Marrakech Morocco.* [II]*Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel Germany.* [III]*Institut für Geowissenschaften / Kristallographie, Christian-Albrechts-Universität zu Kiel Germany.*

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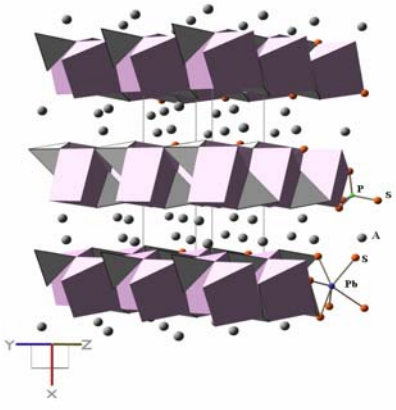
**Keywords : Layered compounds, Crystal structure, Inorganic synthesis.**

The new lead potassium thiophosphates $APbPS_4$ (A = K, Rb, Cs) were synthesized by reacting Pb with an in situ formed melt of $A_2S_3$, $P_2S_5$ and S. The structures were determined by single crystal X-ray diffraction. $APbPS_4$ (A = K, Rb, Cs) crystallizes in the orthorhombic system, space group Pnma [1,2]. The structure is isotypic with that of $KEuPS_4$ [3] and consists of two-dimensional $[PbPS_4]_n^{n-}$ anionic layers extending in the *yz* plane, separated by alkali cations. The layers are comprised of alternating zigzag parallel chains of $PbS_6$ trigonal prisms running along [010] connected by $PS_4$ tetrahedral units.
The bond valence analysis method (BVM) is used to study the Pb $6s^2$ lone pair effect in the crystal structure of these compounds. The data collected at 153K by Yao et al [4] show that the $RbPbPS_4$ crystallizes in the orthorhombic space group $P2_12_12_1$. For this compound, our DSC measurements confirmed the existence of a phase transition $P2_12_12_1 \longrightarrow$ Pnma at 182K




Extended structure of $KPbPS_4$ projected along [001]

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