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**X-ray Diffraction Study of Order-Disorder Phase Transition and Thermal Properties in CuMPt6 (M=3d Elements) Alloys.** Ken-ichi Ohshima<sup>a</sup>, Miwako Takahashi<sup>a</sup>. <sup>a</sup>*Institute of Materials Science, University of Tsukuba, Tsukuba, Japan.*  
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The ordering behavior of ternary CuMPt6 alloys with M=Ti, V, Cr, Mn, Fe, Co, and Ni was investigated by high-temperature X-ray diffraction. The alloys undergo a phase transition from fcc disordered state to the Cu3Au-type ordered state, except for the alloy with Ni, in which only short-range order forms. The transition temperature is highest (1593 K) for M=Ti and decreases almost monotonically with increasing atomic number to 1153 K for M=Co. The observed dependence of ordering tendency on the atomic number of M is discussed in the light of ordering in transition-metal alloys and its significance for the study of ordering in ternary alloys. The effect of ternary addition of the 3d elements to CuPt3 to form CuMPt6 alloys on the thermal properties was also investigated using the same method. It was found that the addition increases the lattice spacing and the degree of thermal properties, and lowers Debye temperature. The results are discussed within the classical theory.

**Keywords:** phase transition; ternary alloys; high temperature X-ray diffraction

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**Structural Filiations in  $M^{II}(M^{IV}O)_2(PO_4)_2$  Oxyphosphates with  $M^{IV} = Ti, V$ .** Pierre Graveriau<sup>a</sup>, Saïda Kaoua<sup>b</sup>, Jean-Pierre Chaminade<sup>a</sup>, Saïda Krimi<sup>b</sup>, Saïd Benmokhtar<sup>c</sup>, Abdelaziz El Jazouli<sup>c</sup>. <sup>a</sup>*ICMCB-CNRS, Université Bordeaux, Pessac, France.* <sup>b</sup>*LPCMI, Faculté des Sciences Aïn Chock, Casablanca, Maroc.* <sup>c</sup>*LCMS, Faculté des Sciences Ben M'Sik, Casablanca, Maroc.*  
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The research on oxyphosphates materials is currently in progress due to their properties in several domains : optics, catalysis, electrochemistry... We have extended our research interest on titanium oxyphosphates ( $M^{II}(Ti^{IV}O)_2(PO_4)_2$ ) to vanadium analogs  $M^{II}(V^{IV}O)_2(PO_4)_2$  ( $M^{II} = Co, Ni$ ). Two phases,  $\alpha$  and  $\beta$ , have been characterized in these new compounds.

$\alpha$ -phase is a  $P2_1/c$  monoclinic deformation of the  $Pnma$  orthorhombic  $Li(TiO)(PO_4)$  type with a splitting of the Li site in (2a) and (2b)  $P2_1/c$ -sites. When  $M^{IV}=V$ , single crystals studies indicate that  $M^{II}$  cations (Co, Ni) are in the 2a-site [1]. When  $M^{IV}=Ti$  this structural type has been found for  $LiM_{0.50}^{II}(TiO)_2(PO_4)_2$  (powders) with Li in 2a-site and  $M^{II}$  cations (Co, Ni, Zn) in 2b-site (50%).

$\beta$ -phase is derived from the  $Ni(TiO)_2(PO_4)_2$ -type (monoclinic  $P2_1/c$ ) [2]. This type has been found for several titanium oxyphosphates  $M^{II}(TiO)_2(PO_4)_2$  ( $M^{II} = Mg, Fe, Co, Ni, Cu, Zn$ ).

For  $M^{II} = Cu$  a thermostructural study shows a phase transition  $\beta_1 \rightarrow \beta_2$  ( $\sim 800^\circ C$  during heating,  $\sim 400^\circ C$  during cooling) [3]. The  $\beta_1$  phase presents a Jahn Teller deformation with Cu-O elongation in the (a,c) plane. The  $\beta_2$  phase corresponds to a "rocking" of the Jahn Teller elongation from the (a,c) plane to the b direction.

$\alpha$  and  $\beta$ -structures consist of a three dimensional (3D) framework built up of infinite chains of tilted corner-sharing  $[M^{IV}O_6]$  octahedra, cross linked by corner-sharing  $[PO_4]$  tetrahedra. The  $M^{II}$  atom is located in a triangular based antiprism which shares faces with two  $[M^{IV}O_6]$  octahedra. Here we discuss a structural filiation based on a common double-sheet unit, parallel to (b,c) plane, where divalent cations  $M^{II}$  are inserted.

For the vanadium oxyphosphates the thermal study, by DTA and by X-ray diffraction, shows that the  $\alpha$  phase obtained from the mixture of starting reagents at  $\sim 700^\circ C$ , is stable until melting. Whatever the starting phase is ( $\alpha$  or  $\beta$ ), after melting the  $\beta$  phase is always obtained.

[1] Kaoua S., Graveriau P., Chaminade J.P., Pechev S., Krimi S., El Jazouli A., *Solid State Sci.*, **2009**, 9, 258. [2] Graveriau P., Chaminade J.P., Manoun B., Krimi S., El Jazouli A., *Powder Diffr.*, **1999**, 14(N°1), 10. [3] Graveriau P., Benmokhtar S., Chaminade J.P., El Jazouli A., Lebraud E. and Denux D., *Solid State Sci.*, **2007**, 9, 258.

**Keywords:** titanyl-oxyphosphates; vanadyl-oxyphosphates; structural filiations

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**NPD Study of Doped  $ZrO_2$  up to  $1500^\circ C$ : Implications for Glass Furnace Refractory Walls.** J. Haines<sup>a</sup>, A. Gioia<sup>a</sup>, P. Papet<sup>a</sup>, O. Isnard<sup>b</sup>, M. Gaubil<sup>c</sup>, I. Cabodi<sup>c</sup>. <sup>a</sup>*ICGM, PMOF, UMR 5253 CNRS/Université Montpellier 2, Montpellier, France.* <sup>b</sup>*Institut Néel, CNRS/ Université J. Fourier, Grenoble, France.* <sup>c</sup>*Saint-Gobain CREE, Cavaillon, France.*  
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Zirconia-based refractory materials are currently used in hostile environments in glass furnaces functioning at temperatures of close to  $1500^\circ C$ . Pure tetragonal zirconia exhibits a high electrical conductivity under these conditions, which leads to problems in furnace operation and corrosion. The resistivity of these materials can be improved via doping with pentavalent cations ( $Nb^{5+}$ ,  $Ta^{5+}$ ), which induces an excess stoichiometry in the oxygen sublattice. This contrasts with the use of trivalent cations to improve conductivity for applications as ionic conductors. In the present case, detailed structural information is lacking on the role of pentavalent cations on the monoclinic-tetragonal phase transition and the modifications of the electrical properties of the tetragonal phase, in particular with respect to the oxygen sublattice.

Nb- and Ta-doped zirconia were studied by neutron powder diffraction ( $\lambda = 1.28 \text{ \AA}$ ) up to  $1500^\circ C$  in a mirror furnace on D1B (ILL, Grenoble). Careful Rietveld refinements were performed using the neutron diffraction data. Doping was found to significantly displace the monoclinic to tetragonal