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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

**FA2-MS04-P02**

**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

**FA2-MS04-P03**

**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

phase transition to lower temperatures and modify the hysteresis loop. The tetragonal form is thus strongly stabilized via the addition of dopants. The tetragonal  $c/a$  ratio also increases with doping at 3% mol. An analysis of the isotropic atomic displacement parameters for the tetragonal phase indicates that in the case of oxygen the values are greater for doped samples. These higher values are most probably linked to additional static disorder resulting from modifications to the oxygen sublattice as a consequence of doping. It can be noted that doping had already resulted in an increase in  $B_{\text{iso}}$  for oxygen of 0.2-0.3 Å<sup>2</sup> at ambient temperature in the monoclinic phase. There are no significant effects of doping on the  $B_{\text{iso}}$  of Zr. The results, in particular the possible increase in static disorder, are linked to changes in electrical conductivity measured under the same conditions by complex impedance spectroscopy. Thus, structure-property relationships can be developed in order to optimize these materials for high-temperature refractory applications.

**Keywords:** zirconia; neutron powder diffraction; high-temperature crystallography

#### FA2-MS04-P04

**Magnetic and Magnetocaloric Result of Magnetic Field-induced Transitions in  $\text{La}_{1-x}\text{Ce}_x\text{Mn}_2\text{Si}_2$ .** Baris Emre<sup>a</sup>, Ilker Dincer<sup>a</sup>, Yalcin Elerman<sup>a</sup>. <sup>a</sup>Department of Engineering Physics, Ankara University, Ankara Turkey.

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Rare earth-based intermetallic compounds are having great attention due to their potential for various applications. Among ternary intermetallic compounds, the  $\text{RMn}_2\text{X}_2$  compounds (R=rare-earth, X=Si or Ge) have been extensively studied because of their interesting physical properties ranging from superconductivity to heavy fermion behavior [1]. Ternary  $\text{RMn}_2\text{X}_2$  compounds crystallize in the body-centered tetragonal  $\text{ThCr}_2\text{Si}_2$ -type structure (space group:  $I4/mmm$ ), which is characterized by stacked R–X–Mn–X–R layers along the  $c$  axis. Magnetic structure of these compounds contains two interacting magnetic subsystems: One of them is composed of rare-earth atoms and the other one is manganese atoms. The magnetic ordering of the Mn sublattice can take up various configurations, as a result the nature of the magnetic ordering is closely related to the Mn–Mn separation. Since, the magnetic ordering of Mn sublattice is very much dependent on the lattice parameters, the overall magnetic state of these compounds is quite sensitive to temperature, due to the thermal variation of lattice parameters. In this study we investigate the  $\text{La}_{1-x}\text{Ce}_x\text{Mn}_2\text{Si}_2$  ( $x=0.35$  and  $0.45$ ) where we expect a variety of magnetic structures to appear in these compounds since they may exhibit quite interesting magnetic and magnetocaloric properties. Among this series  $\text{LaMn}_2\text{Si}_2$  is ferromagnetic with  $T_C=310$  K and  $\text{CeMn}_2\text{Si}_2$  is a mixed valent compound with  $T_N=376$  K [2]. All compounds investigated crystallize in the  $\text{ThCr}_2\text{Si}_2$ -type structure with the space group  $I4/mmm$ . Substitution of Ce instead of La leads to a linear decrease in the lattice constants and the unit cell volume.

Magnetic properties have been examined between 5 and 350 K in 50 Oe. In both samples shows multiple AF-FM state transitions and field-induced transition from the AF to the FM state. The isothermal magnetic entropy change is found and both samples show inverse and conventional magnetocaloric effect around transition temperature. Finally we have used Landau theory on magnetic entropy changes around magnetic transitions.

[1] E. Duman, M. Acet, I. Dincer, A. Elmali, and Y. Elerman, *J. Magn. Magn. Mat.* **309**, 40, 2007. [2] G. Liang, H. Xi, E. Roberts, T. Binford, K. Mochizuki, J. T. Markert and M. Croft, *J. Appl. Phys.* **81**, 4924, 1997.

**Keywords:** field-induced magnetic transitions; magnetocaloric effect

#### FA2-MS04-P05

**Synthesis, Crystal Structure and Vibrational and Optical Spectra of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .** Abdelaziz El Jazouli<sup>a</sup>, Abderrahim Jirifi<sup>a</sup>, Jean Pierre Chaminade<sup>b</sup>, Michel Couzi<sup>c</sup>. <sup>a</sup>LCMS, Université Hassan II-Mohammedia, Faculté des Sciences Men M'Sik, Avenue Idriss El Harti, Casablanca, Maroc. <sup>b</sup>CNRS, Université Bordeaux, Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), 87 avenue Albert Schweitzer, 33608 Pessac, France. <sup>c</sup>Institut des Sciences Moléculaires, Université Bordeaux I, CNRS UMR 5255, Batiment A12, 351 cours de la libération, 33405 Talence cedex, France.

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Nasicon-type materials have been extensively studied as solid electrolytes, ionic conductors, electrode materials, low thermal expansion ceramics, sensors, etc. In contrast to the extensive studies of the Nasicon-type phosphates and silicates, only few investigations have been reported for the arsenates analogues [1-8]. We described in a previous work the structure of  $\text{NaZr}_2(\text{AsO}_4)_3$  [9]. Substitution of  $\text{Na}^+$  by divalent ions in  $\text{NaZr}_2(\text{AsO}_4)_3$  led to the synthesis of new arsenates  $\text{M}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  ( $\text{M} = \text{Ca}, \text{Cd}, \text{Sr}, \dots$ ). The present paper reports on the synthesis, crystal structure and vibrational and optical spectra of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ . Crystalline powder of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  was prepared from solutions of  $\text{SrCO}_3$  (or  $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ ),  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{H}_2\text{AsO}_4$ . Stoichiometric proportions of these reagents were dissolved in dilute nitric acid solution (6M) for the carbonate and in distilled water for the other reagents. The mixture of these solutions was heated at 60°C until complete evaporation. The white solid obtained was successively sintered at 100, 300, 500 and 700°C, for 24 hours with intermediate grinding, to obtain microcrystalline powder of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ . Its structure, which belongs to the Nasicon-type family, was refined by the Rietveld method in the R-3 space group, from X-ray powder diffraction data. The hexagonal unit-cell parameters were determined to be  $a_h = 8.965(2)$  Å,  $c_h = 23.955(6)$  Å,  $V = 1667.43(6)$  Å<sup>3</sup>, and  $Z = 6$ . The structure is formed by an ionic three-dimensional network of  $\text{AsO}_4$  tetrahedra and  $\text{ZrO}_6$  octahedra linked by corners with  $\text{Sr}^{2+}$  ions occupying half of the M1 sites in an