

**P11.01.16***Acta Cryst.* (2008). **A64**, C512**Phase transition in Gd<sub>3</sub>RuO<sub>7</sub> and Tb<sub>3</sub>RuO<sub>7</sub> at elevated temperatures**Nobuo Ishizawa<sup>1</sup>, Saki Kondo<sup>1</sup>, Hisashi Hibino<sup>1</sup>, Hiromi Nakano<sup>2</sup><sup>1</sup>Nagoya Institute of Technology, Asahigaoka, Tajimi, Gifu, 5070071, Japan, <sup>2</sup>Ryukoku University, Seta, Otsu 520-2194, Japan, E-mail : ishizawa@nitech.ac.jp

The ordered oxygen-deficient fluorite-type compounds, Gd<sub>3</sub>RuO<sub>7</sub> and Tb<sub>3</sub>RuO<sub>7</sub>, undergoes a structural phase transition between the P2<sub>1</sub>nb and Cmc<sub>2</sub>m modifications at elevated temperatures. This paper describes the phase transition from a structural point of view, based on the high-temperature single-crystal X-ray and electron diffraction studies. The transition is characterized by an additional tilt about the c axis that occurs in the low-temperature modification for half of the RuO<sub>6</sub> octahedra in association with a reduction of apparent coordination number from 6+2 to 7 for one-third of Gd atoms. Dimerization of the Ru array along the [-RuO<sub>5</sub>-] zigzagging chain occurs below the transition temperature, which provides a folding effect on the chain. The folding tendency of the chain explains geometrically an expansion of the b-length and a compression of the c-length near 382 K on cooling and vice versa on heating. One of the crystallographically independent Gd atoms in the high-temperature Cmc<sub>2</sub>m modification is statically or dynamically distributed between two positions located very close with each other. The disordered distribution of the Gd atom in the high-temperature modification is presumably correlated with the octahedral tilts about the c axis, resulting in the experimental observation of the extremely prolate atomic displacement ellipsoid for the O1 atom in the cis position along the chain. The in situ electron diffraction experiments and changes of cell dimensions suggested a possible existence of an incommensurately modulated intermediate phase between the high- and low-temperature modifications.

Keywords: defect fluorite, phase transition, single-crystal study

**P11.06.17***Acta Cryst.* (2008). **A64**, C512**The thermal expansion and phase behaviour of Tantalum (V) pentoxide based materials**

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A diverse group of materials have been found to possess negative and low positive coefficients of thermal expansion and their discovery has aided our understanding of the mechanisms and processes that lead to this kind of thermal behaviour and ultimately their application [1]. Our focus has been on the ceramics and solid solutions, including those of Tantalum(V)pentoxide (Ta<sub>2</sub>O<sub>5</sub>). Tantalum (V) pentoxide itself has been found to exhibit anisotropic negative thermal expansion behaviour [2]. In the present study we are investigating the addition of a divalent metal oxides (MO<sub>2</sub>), which in this instance include ZrO<sub>2</sub>, HfO<sub>2</sub> and TiO<sub>2</sub> to Ta<sub>2</sub>O<sub>5</sub> ranging from stoichiometric to non-stoichiometric mixtures. Samples were prepared via traditional solid state techniques from their constituent oxides. Sample characterization was performed using variable temperature Powder X-ray Diffraction (VT-PXRD) in conjunction with the Rietveld method. Thus far we have found that increasing the MO<sub>2</sub> concentration results in the formation of solid solutions with

the Ta<sub>2</sub>O<sub>5</sub> which exhibit increasingly positive thermal expansion with an increase in MO<sub>2</sub> concentration. This trend is evident up to the formation of a pure AM<sub>2</sub>O<sub>7</sub> phase which was found to exhibit low positive thermal expansion. Work towards producing phase diagrams of the various Tantalate oxide mixtures is ongoing with a view to further understand their thermal expansion behaviour. Selected results will be presented.

References

[1] R. Rustum, *et al.*, *Ann. Rev. Mat. Sci.*, **19** (1989) 59 - 81.[2] A. A. Frolov *et al.*, *Refract. & Ind. Cer.*, **48** (2007) 106 - 110.

Keywords: VT-XRD, negative thermal expansion, Rietveld

**P11.06.18***Acta Cryst.* (2008). **A64**, C512**Cation order/disorder and local structures in alkaline earth pyrochlores**Gordon J Thorogood<sup>1</sup>, Brendan J Kennedy<sup>2</sup>, Vanessa K Peterson<sup>3</sup>, Margaret M Elcombe<sup>3</sup>, Gordon J Kearley<sup>3</sup>, John V Hanna<sup>1</sup><sup>1</sup>ANSTO, Institute of Materials Engineering, PMB1, Menai, NSW, 2234, Australia, <sup>2</sup>School of Chemistry, The University of Sydney, NSW, Australia 2006, <sup>3</sup>Bragg Institute, ANSTO, Lucas Heights, NSW, Australia 2234, E-mail : gjt@ansto.gov.au

Materials that form the A<sub>2-y</sub>B<sub>2</sub>O<sub>7-x</sub> pyrochlore structure have various applications including use as catalysts, fuel cells, piezoelectrics, ferroelectric devices and ferro-magnets; have a wide range of electrical and ionic conductivities, including metallic, semi and super; can be used in nuclear-waste immobilisation due to radiation toughness, and have ion exchange properties. The degree of disorder of the A-cation is important and may play the major role in the effectiveness of these materials ion exchange properties; and contribute to the high relative permittivities displayed by (Bi,Zn)<sub>2</sub>(Zn,Nb)<sub>2</sub>O<sub>7</sub>. Previous Neutron and X-ray diffraction studies suggest that the disorder involves displacement of the A-cation along the six <112> or <110> directions. Our observation of diffuse scattering in electron diffraction patterns of CsTi<sub>0.5</sub>W<sub>1.5</sub>O<sub>6</sub> pyrochlores suggests there are strong local correlations among the disordered ions. Movement of O at 48f away from 0.375 reduces the interaction between the two networks and so may increase the amount of disorder of the A-cation. The structures of the defect pyrochlores AA<sub>1.33</sub>W<sub>1.67</sub>O<sub>6</sub> where A= K, Rb or Cs have been investigated using an array of advanced structural probes; X-ray and neutron diffraction methods, NMR spectroscopy as well as the ab-initio modeling using VASP. The structures do not show a simple correlation between the radius of the A-type cation and the cubic lattice parameter. Our structural studies suggest that this may reflect the degree of local disorder of the A-cation. The results of these studies will be presented in this presentation.

Keywords: oxides, neutron powder diffractometry, X-ray diffraction crystallography

**P11.07.19***Acta Cryst.* (2008). **A64**, C512-513**Icosahedral quasilattices generated by inflation rules**

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