

P11.01.16*Acta Cryst.* (2008). A64, C512**Phase transition in Gd₃RuO₇ and Tb₃RuO₇ at elevated temperatures**Nobuo Ishizawa¹, Saki Kondo¹, Hisashi Hibino¹, Hiromi Nakano²¹Nagoya Institute of Technology, Asahigaoka, Tajimi, Gifu, 5070071, Japan, ²Ryukoku University, Seta, Otsu 520-2194, Japan, E-mail : ishizawa@nitech.ac.jp

The ordered oxygen-deficient fluorite-type compounds, Gd₃RuO₇ and Tb₃RuO₇, undergoes a structural phase transition between the P2₁nb and Cmc₂m 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 RuO₆ 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 [-RuO₅-] 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 Cmc₂m 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 (Ta₂O₅). 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 (MO₂), which in this instance include ZrO₂, HfO₂ and TiO₂ to Ta₂O₅ 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 MO₂ concentration results in the formation of solid solutions with

the Ta₂O₅ which exhibit increasingly positive thermal expansion with an increase in MO₂ concentration. This trend is evident up to the formation of a pure AM₂O₇ 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

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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 Thorogood¹, Brendan J Kennedy², Vanessa K Peterson³, Margaret M Elcombe³, Gordon J Kearley³, John V Hanna¹¹ANSTO, Institute of Materials Engineering, PMB1, Menai, NSW, 2234, Australia, ²School of Chemistry, The University of Sydney, NSW, Australia 2006, ³Bragg Institute, ANSTO, Lucas Heights, NSW, Australia 2234, E-mail : gjt@ansto.gov.au

Materials that form the A_{2-y}B₂O_{7-x} 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)₂(Zn,Nb)₂O₇. 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_{0.5}W_{1.5}O₆ 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_{1.33}W_{1.67}O₆ 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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Inflation rules are not only a way to characterize the self-similarity of aperiodic structures (that is, tilings or patterns), but they are also used as a tool to construct yet unknown structures. The latter, however, has applied mainly to low-dimensional cases, while the use has been scarcely explored for three-dimensional icosahedral quasilattices (IQL's). In this paper, we make use of point inflation rules (PIR's) [1] for generating various IQL's of all the three Bravais classes (P, F and I-types). A PIR operates on a point set as firstly expand it by a scaling ratio of the underlying Z-module and secondly replace every point by an icosahedral cluster which is the prototype of the IQL. The Bravais class of the IQL is determined by the prototype cluster and the scaling ratio. It is a natural consequence of the method that the IQL will have a dense packing of the prototype clusters, while the atomic surface tends to exhibit a fractal boundary. [1,2] Note that the arrangement of the clusters are not based on any of the tiling models (e.g., the Ammann rhombohedral tiling). An extension of the method is presented where several different prototype clusters are used. Such an extension corresponds to introducing several different atomic surfaces on different special points of the six-dimensional icosahedral lattice. The widened range of IQL's that can be generated contains possible candidates that may be used for modeling real quasicrystals. [1] K. Niizeki, *J. Phys. A: Math. Theor.* 41 (2008), in print. [2] N. Fujita and K. Niizeki, *Phil. Mag.* (2008), in print.

Keywords: quasicrystal crystallography, theoretical structure modelling, aperiodic structures

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Study of stoichiometric glass ceramics formation in the BaO-Bi₂O₃-B₂O₃ system

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Interest to BaO-Bi₂O₃-B₂O₃ system is connected to revealing new passive and active functional glasses and glass ceramics (GC). This system isn't investigated enough and its phase diagram is absent. The incongruent melted at 754°C ternary BaBiBO₄ compound was synthesized and characterized recently by the solid-state sintering. Three ternary compounds were revealed in this system: congruent melted BaBi₂B₄O₁₀ (730°C) and BaBiB₁₁O₁₉ (807°C) compounds and Ba₃BiB₃O₉ compound which has phase transition at 850°C and subsequent solid state decomposition at 885°C. In the present work our attention has been concentrated on the study of stoichiometric ternary borates glass forming ability and the GC availability on their basis and the formed crystals characterization. The batches of all testing compositions were prepared from chemically pure grade reagents and were melted in quartz crucibles at 900-1000°C in electrical furnace. Due to chemical analysis SiO₂ transition in glass melts at melting didn't exceed 2 wt. %. All compounds have good glass forming ability and form stable glasses. The temperature intervals and character of synthesized glasses crystallization and m.p. of formed crystals have been revealed from the DTA curves. Regimes of powder and bulk glass samples crystallization are studied and products of their crystallization are identified by X-ray analysis. The studies have shown that all stoichiometric glass basis are perspective for the GC with different functionality development: crystallized frits with high resistivity for packaging or covering on the ceramic or

metallic plates; transparent nonlinear-optical GC.

Keywords: barium bismuth borate compounds, glass ceramics, stoichiometric glass basis

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Transparent glass-ceramics containing lead fluoride crystals

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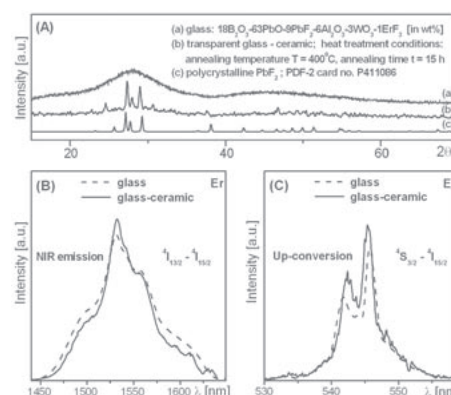
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Transparent glass-ceramics (TGC) as new host materials for rare earths have a great deal of interest due to their unique behavior like fluoride nanocrystals in oxide glass matrices. Heat treatment introduces transformation from glass to glass-ceramic, causing changes in spectroscopic properties like: narrowing of spectral lines and elongation in lifetimes of fluorescent states. Er-doped lead borate glasses before and after annealing were investigated using X-ray diffraction and luminescence spectroscopy. They present interesting spectroscopic properties in relation to NIR emission and up-conversion applications [1]. During heat treatment, TGC systems were obtained. Phase identification reveals, that crystalline peaks can be related to the orthorhombic lead fluoride phase, in contrast to other TGC systems containing cubic lead fluoride crystals [2].

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References

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Keywords: glass-ceramics, X-ray diffraction, luminescence spectroscopy

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Influence of starting materials on hydrothermal synthesis of six-pointed starlike anatase aggregates

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Six-pointed starlike anatase aggregates were hydrothermally synthesized from aqueous mixtures of titanium tetraisopropoxide and tetramethylammonium hydroxide (TMAOH). It is noteworthy that though anatase has a tetragonal lattice, the anatase aggregates