

X-ray diffraction

**P10.02.07***Acta Cryst.* (2008). A64, C492**Crystal chemistry of some garnet solid-solutions viewed from neighboring cation-cation repulsion**Akihiko Nakatsuka<sup>1</sup>, Akira Yoshiasa<sup>2</sup>, Eiji Ito<sup>3</sup><sup>1</sup>Yamaguchi University, Science and Engineering, Tokiwadai 2-16-1, Ube, Yamaguchi, 755-8611, Japan, <sup>2</sup>Kumamoto University, 2-39-1 Kurokami, Kumamoto, 860-8555, Japan, <sup>3</sup>Okayama University, 827 Yamada, Misasa, Tottori, 682-0193, Japan, E-mail: tuka@yamaguchi-u.ac.jp

In crystal structures with shared edges between coordination polyhedra such as garnets, spinels and rutiles, the cation-cation repulsions across the shared edges play an important role in their structural stabilities. In the present study, we discuss the effect of the cation-cation repulsion on garnet structure, from single crystal X-ray diffraction studies of the garnet solid solutions in the systems  $Y_3Fe_5O_{12}$ - $Y_3Ga_5O_{12}$  ( $Y_3Fe_{5-x}Ga_xO_{12}$ ) synthesized using a  $PbF_2$  flux and  $Mg_3Al_2Si_3O_{12}$ - $MgSiO_3$  [ $Mg_3(Mg_xSi_xAl_{2-2x})Si_3O_{12}$ ] synthesized at 20 GPa and 2273 K using a Kawai-type high-pressure apparatus. In the system  $Y_3Fe_{5-x}Ga_xO_{12}$ , we found that the tendency of cation distribution changes around  $x = 1.6$  and  $3.8$ . In the system  $Mg_3(Mg_xSi_xAl_{2-2x})Si_3O_{12}$ , which had been considered to have a cubic symmetry ( $Ia\bar{3}d$ ) in the range of  $x = 0-0.8$  and a tetragonal symmetry ( $I4_1/a$ ) in the range of  $x = 0.8-1.0$ , we found the presence of a new tetragonal phase ( $I4_1/acd$ ) in the range of  $x = 0.38-0.64$ . Such change in the tendency of cation distribution and symmetry change from  $Ia\bar{3}d$  to  $I4_1/acd$  occur when the structural geometric restriction brought by the substitution of the cations with different sizes forcibly stretches the shared edges compared with the unshared ones and thereby the cation-cation repulsion increases because of the decrease in the shielding effect. Thus, these changes observed in both garnet solid-solution systems are the good examples exhibiting the structural destabilization of garnets due to the cation-cation repulsions across the shared edges of polyhedra. From thermal vibration behaviors of atoms, the effect of cation-cation repulsion on such structural destabilization is expected to be the most prominent between tetrahedral and dodecahedral cations.

Keywords: crystal chemistry, structural stability, single-crystal X-ray diffraction

**P10.02.08***Acta Cryst.* (2008). A64, C492**Single-crystal structures of the FeOOH, FeOOD and GaOOH high-pressure phases**Nadezhda Bolotina<sup>1</sup>, Vladimir Molchanov<sup>1</sup>, Tat'yana Dyuzheva<sup>2</sup>, Ludmila Lityagina<sup>2</sup>, Nikolay Bendeliani<sup>2</sup><sup>1</sup>Institute of Crystallography R.A.S., Leninsky prospekt 59, Moscow, Moscow region, 119333, Russia, <sup>2</sup>Institute of High Pressure Physics R. A.S., Troitsk, Moscow region, 142190, Russia, E-mail: bolotina@ns.crys.ras.ru

Crystal structures of the e-FeOOH, e-FeOOD and a new b-GaOOH high-pressure phases have been determined using single-crystal X-ray diffraction techniques (1). The structures belong to the InOOH structure type (distorted TiO<sub>2</sub>). Measurements were performed with CCD-Xcalibur and CAD-4F diffractometers, and calculations were made using JANA2000 program in the P2<sub>1</sub>nm symmetry group. Some crystals grow together being combined by a close to 62 degree

turn around the b-axis. The twinning by the b-axis rides on a pseudo-hexagonal close packing of the oxygen atoms distorted by the entering of the metal cations into the half of the packing spaces. The same crystals reveal another law of the merohedral twinning, namely, a 180-degree turn around the c-axis. An interchange of these twin domains in the crystal volume gives rise to the corresponding long-order disorder of the hydrogen sites. There is a reason to believe that this kind of proton disordering described in terms of twinning is very typical for the high-pressure phases of MOOH oxihydroxides (M = V, Cr, Mn, Fe, Co, Ni, Al, Ga, In) related to the InOOH structure type. (1) N.B. Bolotina et. al. // Kristallografiya, 2008 (in press)

Keywords: oxihydroxides, high-pressure phases, twinning

**P10.02.09***Acta Cryst.* (2008). A64, C492**Structural investigation of synthetic CaTh(PO<sub>4</sub>)<sub>2</sub> and CaNp(PO<sub>4</sub>)<sub>2</sub> by X-ray diffraction**Philippe E Raison<sup>1</sup>, Karin Popa<sup>2</sup>, Regis Jardin<sup>1</sup>, Daniel Bouexiere<sup>1</sup>, Rudy J.M Konings<sup>1</sup>, Thorsten Geisler<sup>3</sup>, Claudiu C Pavel<sup>1</sup>, Jean Rebizant<sup>1</sup><sup>1</sup>European Commission, JRC-ITU Materials research Unit, PO Box 2340, KARLSRUHE, Baden Württemberg, 76125, Germany, <sup>2</sup>A.I.I. Cuza University, Department of Chemistry, 11 - Carol I Blvd., 700506 Iasi, Romania, <sup>3</sup>Institute für Mineralogie, University of Münster, Corrensstrasse 24, 48149 Münster, Germany, E-mail: philippe.raison@ec.europa.eu

The safe disposal of nuclear waste is a pressing issue in modern society. To date, a number of materials have been proposed as potential host phases to immobilise nuclear waste. In this regard, we have investigated the crystallographic structures of synthetic Cheralite, CaTh(PO<sub>4</sub>)<sub>2</sub>, and its homologue compound CaNp(PO<sub>4</sub>)<sub>2</sub>, by X-ray diffraction at room temperature with a diffractometer equipped with a position sensitive detector and dedicated to study highly radioactive samples. Rietveld analyses showed that both compounds crystallize in the monoclinic system and are isostructural to monazite, Ce(PO<sub>4</sub>). The space group is  $P2_1/n$  (I.T= 14) with two formula per unit cell ( $Z=2$ ). The refined lattice parameters are  $a = 6.7085 \text{ \AA}$ ,  $b = 6.9160 \text{ \AA}$ ,  $c = 6.4152 \text{ \AA}$ , and  $\beta = 103.71^\circ$ , for CaTh(PO<sub>4</sub>)<sub>2</sub> and  $a = 6.6509 \text{ \AA}$ ,  $b = 6.839 \text{ \AA}$ ,  $c = 6.3537 \text{ \AA}$ , and  $\beta = 104.12^\circ$  for CaNp(PO<sub>4</sub>)<sub>2</sub>. The best fit R values were  $R_{wp} = 4.87\%$ ,  $R_p = 3.69\%$ , and  $R_B = 3.99\%$  for CaTh(PO<sub>4</sub>)<sub>2</sub> and  $R_{wp} = 6.74\%$ ,  $R_p = 5.23\%$ , and  $R_B = 6.05\%$  for CaNp(PO<sub>4</sub>)<sub>2</sub>. The analysis of the diffraction data showed that significant distortions of the PO<sub>4</sub> tetrahedra occur in the CaTh(PO<sub>4</sub>)<sub>2</sub> compound, both in terms of P-O bond-lengths and O-P-O angles, which was also confirmed by Raman spectroscopy. Comparison with the isostructural compounds Ce(PO<sub>4</sub>) and Sm(PO<sub>4</sub>) confirmed that the substitution of a large rare-earth trivalent cation by Ca and Th introduces a distortion of the PO<sub>4</sub> tetrahedra. Bond-lengths and O-P-O angle distortions were also observed on CaNp(PO<sub>4</sub>)<sub>2</sub>, though to a lesser extent. Our presentation will report the experimental results and discuss structural aspects of both materials with respect to their long-term chemical durability and their suitability as host phase for actinide waste disposal.

Keywords: X-ray diffraction, structural crystallography, mineral synthesis