

the Mahabaleshwar area of Maharashtra state, India. The feldspar phenocrysts contain different types of melt inclusions. These melt inclusions significantly show variation in melting temperature. Presence of different types of melt inclusions along crystal boundaries indicated the change in composition and this may be the function of temperature. Different types of melt inclusions found in plagioclase phenocrysts are amorphous and crystalline (monophase, biphasic and multiphase). Variation in the composition of these melt inclusions, itself reveals the immiscibility as well as the degassing phenomena of magma. An attempt has been made to correlate the melt inclusion geothermometry with the evolution pattern of magma/melt that of calcic-plagioclase phenocrysts present in a deccan basalts. Petrographic results were confirmed by the XRD and Cathodoluminescence studies. Heating stage experiment was carried out to find out the formation temperatures/melting temperatures of melt inclusions.

Keywords: geothermometry, melt inclusion, crystallography

### P10.02.04

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#### Calculation of graphs representing crystal structures

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Some crystal structures can be described by certain graphs (Chung & Hahn, *Acta Cryst.* A31 (1975) S.J. Chung, Hahn & Klee, *Acta Cryst.* A40 (1984) 42-50). In this method, each periodic infinite net can be expressed by a labelled directed finite graph which is called also labelled quotient graph. Each point and each line in the quotient graph corresponds to a set of equivalent vertices and edges in the three periodic net. Quotient graphs and spanning trees can be obtained with given numbers of vertices and edges in this calculation. We use the determinant and trace of the matrix representing the quotient graph for the criteria of isomorphism of quotient graph. Special algorithm is applied to this program because the isomorphism of quotient graphs seriously delays the computation time with increase of the number of vertices and edges. The labelling to the quotient graphs can be applied. The structure of the network also can be obtained from the labelled graphs with least square fitting. A computation method for the enumeration of three periodic regular nets with a given number of vertices and edges will be discussed in detail.

Keywords: graph, network, crystal structure

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#### Hybrid twins in minerals

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Twins in which the lattice nodes (quasi) restored by the twin operation belong to more than one sublattice are termed *hybrid twins* [1]. The fraction of (quasi) restored nodes takes into account all these sublattices and an *effective twin index*  $n_E$  is defined. In Friedelian

twins (twin index not higher than 6), the hybrid character shows that the choice of the sublattice is not unique. In non-Friedelian twins,  $n_E$  allows a rationalization of these twins within the framework of the classical reticular theory [2]. A survey of twins in minerals has shown that a number of them should be reinterpreted as hybrid twins. For high-symmetry twins (cubic and uniaxial minerals), this is normally the case for twin elements of relatively high indices. E.g., (031) twin in cassiterite (four sublattices,  $n_E = 3.8$ ), (311) twin in nickeline (three sublattices,  $n_E = 6.3$ ), (203) twin in maucherite (three sublattices,  $n_E = 5.83$ ), (241) twin in diaphorite (two sublattices,  $n_E = 4.0$ ), and [313] twin in staurolite (two sublattices,  $n_E = 6.0$ ). For lower symmetry minerals, even low-index twin elements may correspond to a non-Friedelian twin that is better interpreted as hybrid twins. E.g., (110) twin in becquerelite (three sublattices,  $n_E = 3.0$ ), (110) twin in geocronite (three sublattices,  $n_E = 3.0$ ), and (211) twin in cryolite (three sublattices,  $n_E = 3.7$ ). Examples of Friedelian twin that can be interpreted as hybrid twins have also been found; e.g., (011) twin in anhydrite: here one sublattice corresponds to index 4 and obliquity  $0.7^\circ$ , another sublattice to index 3 and obliquity  $3.1^\circ$ . If both sublattices are taken into account, one obtains  $n_E = 2.0$ . [1] Nespolo M, Ferraris G (2006). *Acta Cryst.* **A62**, 336. [2] Friedel G (1926) *Leçons de cristallographie*. Berger-Levrault.

Keywords: twinning, hybrid twins, effective twin index

### P10.02.06

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#### Atomic displacements of tetrahedral cations in garnets

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We had reported that in most of reported garnets, the root mean-square displacements (RMSD) of tetrahedral ( $Z$ ) cations are the smallest in the directions of adjacent dodecahedral ( $X$ ) cations (direction 1), parallel to a crystal axis, because of strong  $X$ - $Z$  repulsions and the largest in the directions of the remaining two crystal axes (direction 2). However, we recently found that RMSD of  $Z$  cation in Pb vanadate garnets ( $\text{NaPb}_2\text{M}_2\text{V}_3\text{O}_{12}$ ;  $M$  is divalent cations) is the largest in the direction 1, in which adjacent  $X$  cations exist, and the smallest in the direction 2, in which no adjacent atoms exist, in contradiction to the above general tendency. In the present study, to examine whether this peculiar feature in Pb vanadate garnets is due to the positional disorder of  $Z$  cation toward the direction 1 caused by lone pair electrons of  $\text{Pb}^{2+}$  in  $X$  site, we perform the structure refinements of  $\text{NaSr}_2\text{Mg}_2\text{V}_3\text{O}_{12}$ , having  $X$  cation ( $\text{Sr}^{2+}$ ) without lone pair electrons and expected to possess  $X$ - $Z$  repulsion comparable to those in Pb vanadate garnets, at 298 K and  $\text{NaPb}_2\text{Mg}_2\text{V}_3\text{O}_{12}$  in the range of 83-298 K. Moreover, the crystal structures of uninvestigated Ca vanadate garnets ( $\text{NaCa}_2\text{Co}_2\text{V}_3\text{O}_{12}$ ,  $\text{NaCa}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ ) are refined at 298 K.  $\text{RMSD}_1/\text{RMSD}_2$  ratios of  $Z$  cations ( $\text{V}^{5+}$ ) in  $\text{NaCa}_2\text{Co}_2\text{V}_3\text{O}_{12}$  and  $\text{NaCa}_2\text{Ni}_2\text{V}_3\text{O}_{12}$  are below 1.0 according to the general tendency, whereas that in  $\text{NaSr}_2\text{Mg}_2\text{V}_3\text{O}_{12}$  is much larger than 1.0 as in Pb vanadate garnets, where  $\text{RMSD}_1$  and  $\text{RMSD}_2$  are RMSD's in the directions 1 and 2, respectively. The  $U_{eq}$  value in  $Z$  cation of  $\text{NaPb}_2\text{Mg}_2\text{V}_3\text{O}_{12}$  can be extrapolated to 0 at 0 K, and no separation of electron density peak on  $Z$  site can be observed on Fourier map. These show that the peculiar atomic displacement behavior of  $Z$  cation in Pb vanadate garnets cannot be due to its positional disorder.

Keywords: crystal chemistry, thermal vibration, single-crystal

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. 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