

**MS07.06.02 SOLID STATE CONVERSION IN SINGLE CRYSTALS OF A COORDINATION COMPOUND.** Ulli Englert, Beate Ganter, and Trixie Wagner, Institut f. Anorg. Chemie, RWTH Aachen, 52056 Aachen, Germany; Wolfgang Kläui, Institut f. Anorg. Chemie, Heinrich-Heine-Universität, 40225 Düsseldorf, Germany.

Topotactic elimination of an aqua ligand in  $[\text{Eu}(\text{LOE})_2(\text{H}_2\text{O})_2]\text{BF}_4$  (cation in fig 1,  $\langle\text{LOE}\rangle = [\text{CoCp}\{\text{P}(\text{OEt})_2\}_3]$ ) may be achieved in single crystals under very mild conditions, *i.e.* simply in a stream of dry dinitrogen for *ca.* 2 hrs at room temperature! Color and morphology of the crystals do not change, but the half-width of the reflections increases. The molecular and crystal structures of both the diaqua complex in fig 1 and the monoqua reaction product (showing shorter Co-Eu distances and a larger Co-Eu-Co angle) are closely related: The space group symmetry is retained, lattice constants are very similar, and the cell volume decreases only slightly during reaction. The reaction is reversible - a crystal of the monoqua complex takes up water and reverts to the starting complex under ambient conditions! Experiments on oriented single crystals reveal the close relation between the two unit cells, fig 2.

In contrast to our results, most solid state reactions of molecular crystals yield only microcrystalline or amorphous reaction products.

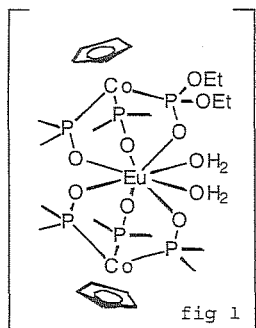


fig 1

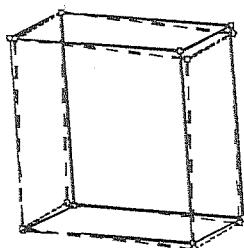


fig 2

**MS07.06.03 STRUCTURE CHANGE DUE TO THE CHARGE DISPROPORTIONATION IN  $\text{CaFeO}_3$  WITH  $\text{Fe}^{4+}$**  S. Morimoto, T. Yamanaka\* and M. Tanaka\*\*, Faculty of Engineering Science, Osaka Univ., Toyonaka 560, Japan., \*Faculty of Science, Osaka Univ., Toyonaka 560, Japan., \*\*Photon Factory, National Laboratory for High Energy Physics, Tsukuba 305, Japan.

$\text{Fe}^{4+}$  in  $\text{CaFeO}_3$  shows "charge disproportionation" into  $\text{Fe}^{3+}$  and  $\text{Fe}^{5+}$  at low temperature and the structure analysis is of great interest.

The crystal structures of  $\text{CaFeO}_3$  have been investigated at 293 K and 113 K which is low temperature enough to exhibit the charge disproportionation of  $\text{Fe}^{4+}$ . The cube-shaped crystalline samples with edge size of 0.06 mm were synthesized under 3 GPa and at around 1273 K. Data collections of diffraction intensity were carried out in the Photon Factory with the incident beam of *ca.* 0.7 Å in wavelength.

$\text{CaFeO}_3$  was revealed to have a same structure as  $\text{GdFeO}_3$  with Pbnm at 293 K [ $Z=4$ ,  $a=5.3480(3)$ ,  $b^*=a$ ,  $c=7.5730(5)$  Å]. At 113 K,  $\text{Fe}^{3+}$  and  $\text{Fe}^{5+}$  are suggested to arrange NaCl type sub-lattice of Fe. Thereby the space group at 113 K is resulted to be monoclinic  $\text{P}2_1/n$  [ $Z=4$ ,  $a=5.3409(3)$ ,  $b^*=a$ ,  $c=7.5585(13)$  Å,  $\beta^*=90$ ] which is one of sub-groups of Pbnm. The smaller bond angle (*ca.* 160 deg.) of Fe-O-Fe in  $\text{CaFeO}_3$  than that in  $\text{SrFeO}_3$  should suppress a itinerant nature of  $e_g(\text{Fe})$  electrons and causes the disproportionation. The  $\text{FeO}_6$  octahedron with negligibly small Jahn-Teller distortion can be regarded as an ideal  $\text{O}_h$  symmetry at both temperatures. This is explained by delocalization of  $e_g(\text{Fe})$  electrons at 293 K and charge disproportionation at 113 K.

Residual charge densities were revealed by difference Fourier synthesis at both temperatures. A residual peak with 1.2 e/Å<sup>3</sup> as a maxima is confirmed clearly at the center of Fe-O bond. This suggests that strong covalency due to overlapping of  $e_g(\text{Fe})$  orbitals and 2p(O) ones.

\*coincidence within experimental error

**MS07.06.04 CRYSTAL STRUCTURE OF 4H  $\text{BaRuO}_3$ : HIGH PRESSURE PHASE PREPARED AT AMBIENT PRESSURE.** Seung-Tae Hong, Arthur W. Sleight, Department of Chemistry, Oregon State University, Corvallis, OR 973314003

Single crystals of four-layer hexagonal (4H)  $\text{BaRuO}_3$  were grown at ambient pressure, and the crystal structure was determined (space group  $\text{P}6_3/\text{mmc}$ ;  $a=5.7289(6)$  Å and  $c=9.5003(9)$  Å;  $Z=4$ ). It is known that  $\text{BaRuO}_3$  has the 9R polytype structure at atmospheric pressure, which transforms at 15 kbar to the 4H structure and further transforms to the 6H structure at 30 kbar. Single crystals of 4H  $\text{BaRuO}_3$  were grown by using  $\text{BaCl}_2$  as a flux with a nominal composition of  $\text{Ba}_6\text{Ru}_2\text{W}_2\text{O}_{17-y}$ . The mixture was heated to 1200°C and cooled slowly. Black  $\text{BaRuO}_3$  crystals formed together with unidentified orange crystals. Most of the  $\text{BaRuO}_3$  crystals have a 9R structure, while some of them turned out to have a 4H structure. The stoichiometry and possible W impurities were checked by microprobe analysis. The structure was determined by the interpretation of the Patterson map, which resulted in the positions of the metal atoms, and the subsequent difference Fourier maps located the positions of the oxygens. The final conventional R1 (based on  $F_0$ ) and wR2 (based on  $F_0^2$ ) are 2.01 and 4.07%, respectively. The structure of 4H  $\text{BaRuO}_3$  may be described as a perovskite-related compound with a four-layer stacking of  $\text{BaO}_3$  layers in the sequence of *hchc*. This leads to two face-sharing octahedra; the strings are held together by corner sharing. All of the octahedral sites are occupied by ruthenium ions. Concerning the dimer units  $[\text{Ru}_2\text{O}_9]$ , the Ru-Ru distance is 2.537(1) Å which is close to that in 9R  $\text{BaRuO}_3$  (2.55 Å), and comparable with the value in  $\text{La}_4\text{Ru}_6\text{O}_{18}$  (2.488 Å), suggesting a possible metal-metal bonding. This result shows that a phase which has been regarded as a high pressure phase can in fact be prepared at one atmosphere when using appropriate synthesis conditions.

**MS07.06.05 NEGATIVE THERMAL EXPANSION FROM 0.3 TO 1050 K IN ZIRCONIUM TUNGSTATE,  $\text{ZrW}_2\text{O}_8$ .** John S.O. Evans, T.A. Mary, A.W. Sleight, Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA.

It is well known that the vast majority of materials expand on heating. Zirconium tungstate, however, shows a negative and essentially linear thermal expansion from 0.3 Kelvin to its decomposition temperature of 1050 Kelvin. The structure remains cubic over the entire temperature range and the contraction is therefore isotropic in nature. Negative thermal expansion in other oxide materials is generally restricted to much narrower temperature ranges and is anisotropic. This material therefore has potential applications in the electronics and ceramic industries as a constituent of composites with overall zero expansion.

The structure has been solved using powder X-ray and neutron diffraction data and refined at 14 temperatures from 0.3 to 693 K. The low temperature structure consists of an open framework of corner sharing  $\text{ZrO}_6$  octahedra and  $\text{WO}_4$  tetrahedra. Around 430 K the structure undergoes a phase transition from acentric  $\text{P}2_13$  to the centric spacegroup Pa. Above the phase transition the structure can be described in terms of the same  $\text{ZrO}_6$  units as at low temperature, but with a disordered arrangement of  $\text{WO}_4$  tetrahedra. The nature of this phase transition suggests a high oxygen ion mobility in the structure. The mechanism for negative thermal expansion in this material will be discussed in light of the structural results.