MS07.06.02 SOLID STATE CONVERSION IN SINGLE CRYSTALS OF A COORDINATION COMPOUND. Ulli Englert, Beate Ganter, and Trixe 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 [Eu<LoEt>:2(H2O)]BF4 (cation in fig.1, <LoEt> = {Co(OEt)2}+) may be achieved in single crystals under very mild conditions, i.e. simply in a stream of dry nitrogen for ca. 1.2 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 diqua 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 and the monoaqua reaction product (showing shorter Co-Eu distances and a larger Co-Eu-Co angle) are closely related: The space group at 113 K is resulted to be monoclinic P21/n [Z = 4, a = 5.730(5) Å, b = a, c = 7.5730(5) Å, b/a = c]. At 113 K, Fe3+ and Fe5+ are suggested to arrange NaCl type sub-lattice of Fe. Thereby the structure at 113 K is resulted to be monoclinic P21/n [Z = 4, a = 5.349(3), b = a, c = 7.5730(5) Å]. At 113 K, Fe3+ and Fe5+ are suggested to arrange NaCl type sub-lattice of Fe. Thereby the structure at 113 K is resulted to be monoclinic P21/n [Z = 4, a = 5.349(3), b = a, c = 7.5730(5) Å]. At 113 K, Fe3+ and Fe5+ are suggested to arrange NaCl type sub-lattice of Fe. Thereby the structure at 113 K is resulted to be monoclinic P21/n [Z = 4, a = 5.349(3), b = a, c = 7.5730(5) Å]. At 113 K, Fe3+ and Fe5+ are suggested to arrange NaCl type sub-lattice of Fe. Thereby the structure at 113 K is resulted to be monoclinic P21/n [Z = 4, a = 5.349(3), b = a, c = 7.5730(5) Å].

Residual charge densities were revealed by difference Fourier synthesis at both temperatures. A residual peak with 1.2 eÅ2 as a maxima is confirmed clearly at the center of Fe-O bond. This suggests that strong covalency due to overlapping of eg(Fe) orbitals and 2p(0) ones.

MS07.06.04 CRYSTAL STRUCTURE OF 4H BaRuO3: HIGH PRESSURE PHASE PREPARED AT AMBIENT PRESSURE. Seung-Tae Hong, Arthur W. Sleight, Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003.

Single crystals of four-layer hexagonal (4H) BaRuO3 were grown at ambient pressure, and the crystal structure was determined (space group P63/mmc: a = 5.7289(6) Å and c = 9.5003(9) Å; Z=4). It is known that BaRuO3 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 BaRuO3 were grown by using BaCl2 as a flux with a nominal composition of BaRu2O4Cl2. The mixture was heated to 1200°C and cooled slowly. Black BaRuO3 crystals formed together with unidentified orange crystals. Most of the BaRuO3 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 F0) and wR2 (based on F2) are 2.01 and 4.07%, respectively. The structure of 4H BaRuO3 may be described as a perovskite-related compound with a four-layer stacking of BaO2 layers in the sequence of hccc. 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 [Ru2O6], the Ru-Ru distance is 2.537(1) Å which is close to that in 9R BaRuO3 (2.55 Å), and comparable with the value in La2RuO4 (~2.488 18L), 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.

MS07.06.03 STRUCTURE CHANGE DUE TO THE CHARGE DISPROPORTIONATION IN CaFeO3 WITH Fe3+ and Fe5+. Morimoto, T. Yamanaka* and M. Tanaka**, Faculty of Engineering Science, Osaka Univ., Toyonaka 560, Japan, *Faculty of Science, Osaka Univ., Toyonaka 560, Japan.

The structure of CaFeO3 has been investigated at 293 K and 113 K which is low temperature enough to exhibit the charge disproportionation of Fe3+. The structures differ essentially from each other. CaFeO3 is 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 1050 K. The low temperature structure consists of an open framework of corner sharing ZrO6 octahedra and WO4 tetrahedra. Around 430 K the structure undergoes a phase transition from acentric P21/a to the centric spacegroup Pa. Above the phase transition the structure can be described in terms of the same ZrO6 units as at low temperature, but with a disordered arrangement of WO4 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.

MS07.06.05 NEGATIVE THERMAL EXPANSION FROM 0.3 TO 1050 K IN ZIRCONIUM TUNGSTATE, ZrWO4. 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 at 1050 Kelvin. The low temperature 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 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.