

**[o.m13.p1] Crystal structure and thermal expansion of LuB<sub>12</sub> single crystals.** A. Pietraszko, A. Czopnik, *Institute of Low Temperature and Structure Research of PASci, 50950 Wroclaw, Poland*, N. Shitsevalova, Yu. Paderno, V. Pluzhnikov *I.Frantsevich Institute for Problems of Materials Science of NASU, Kiev, Ukraine*  
 Keywords: phase transitions, negative thermal expansion, dodecaborides.

LuB<sub>12</sub> crystals belong to the family of MeB<sub>12</sub> structures (Me= Y, Yb-Lu) with *fcc* lattice of UB<sub>12</sub>-type at room temperature.

The temperature dependence of thermal expansion of single crystal LuB<sub>12</sub> measured by both a three-terminal capacitor method and an X-ray Bond method was non-monotonous and becoming negative in temperature range from 50K to 120K. The lattice parameters versus temperature exhibited a small tetragonal deformation below 160-150K.

We have collected the diffraction data using single crystal KM4-CCD diffractometer at 90K, 125K, 145K, 165K, 295K and 410K. The crystal structures were refined in the cubic system and below 160K in the tetragonal system. The LuB<sub>12</sub> structure consists of rigid nets based on the space framework units B<sub>12</sub> (cubooctahedron). The metal atoms are located in cavities of cubic lattice formed by B<sub>12</sub> cages. The Lu atoms are shifted from central position and occupy statistically few non-equivalent positions. We have found a correlation between the distortion of crystal structure and the negative thermal expansion. The anisotropy of dilatation confirmed non-equivalence of bonds in different directions.

This research was supported by a grant No 2 P03B 136 17 from the Polish State Committee for Scientific Research.

**[o.m13.p2] Phase Transitions in the Ba(OD)<sub>2</sub>-System: A new low-T polymorph.** A. Friedrich\*, M. Kunz\*, E. Suard\*\*, \*Laboratory of Crystallography, ETH Zentrum, Sonneggstr. 5, CH-8092 Zurich, Switzerland. \*\*ILL, 38042 Grenoble Cedex 9, France.  
 Keywords: phase transitions, powder diffraction.

The temperature-dependent structural behavior of Ba(OD)<sub>2</sub> was investigated by neutron powder diffractometry using the high-resolution two-axis diffractometer at the D2B beamline at the ILL, Grenoble.

Pure powder of β-Ba(OD)<sub>2</sub> was synthesized using BaO and D<sub>2</sub>O as starting material. Crystals of barium deuterioxide octadeuterate were grown under nitrogen atmosphere by cooling of a hot solution and were dehydrated at 100°C under vacuum. The powdered sample was loaded into vanadium cans under helium atmosphere.

Powder diffraction patterns were collected up to 2θ=160° (λ=1.594 Å). The refinement of the crystal structures was carried out with the GSAS Rietveld program, revealing accurate D sites at each temperature.

Monoclinic β-Ba(OD)<sub>2</sub> is known to undergo a phase transition at 526(±1) K [1]. The orthorhombic high-T α-phase is quenchable and remains stable at ambient T. The crystal structures were previously reported [2,3] and used as starting parameters for the refinements. We investigated both, the β- and the α-phase at the phase transition and at low T down to 10 K. While the β-phase remains stable to the lowest T investigated, the α-phase shows a reversible orthorhombic-to-monoclinic phase transition between 100 and 150 K.

Unit cells of the β-phase at ambient T (*P2<sub>1</sub>/n*) and the α-phase at 200 K (*Pnma*) are: a=9.4098(3) Å, b=7.9101(3) Å, c=6.7759(2) Å, β=95.765(2)°; a=10.9789(3) Å, b=16.4317(4) Å, c=7.0784(2) Å, respectively. The space group of the new α' phase was determined to be *P2<sub>1</sub>/n* with a unit cell (100 K) of a=7.0832(2) Å, b=10.8967(3) Å, c=16.4306(5) Å, β=91.060(2)°.

The *Pnma* ↔ *P2<sub>1</sub>/n* low-T phase transition is driven by an order-disorder mechanism, mainly caused by one of the D atoms, which occupies a special position on the *m* plane in the orthorhombic phase. Refinements of the α-phase above to the phase transition already indicate a dynamic disorder across the *m* plane through a conspicuously high isotropic displacement parameter if compared to the other D atoms. At low temperature the energy of the vibration is lowered and the D atom is frozen at a general position in a correlated way, thus violating the *m* plane and reducing the space-group symmetry.

[1] Cordfunke E.H.P. *et al.* "A study of the phase transitions in Ba(OH)<sub>2</sub> and a comment on the fusion of Sr(OH)<sub>2</sub>.", *Thermochimica Acta*, (1996), 273: 1 - 9.

[2] Lüke H. "Die Kristallstruktur von α-Bariumhydroxid α-Ba(OH)<sub>2</sub>", Dissertation, (1973), Universität Karlsruhe.

[3] Bärnighausen H. and Denzinger W. "Die Bestimmung der Kristallstruktur von β-Ba(OH)<sub>2</sub> bzw. β-Ba(OD)<sub>2</sub> mittels Röntgen- und Neutronenpulverdiffraktometrie.", *Z. Krist.*, (1997), Suppl. 12: 212.