

**FA5-MS01-P30**

**Structural Study of Negative Thermal Expansion in Yttrium and Rare Earth Molybdates.** Cristina González-Silgo<sup>a</sup>, Manuel E. Torres<sup>b</sup>, Javier González-Platas<sup>a,c</sup>, Javier Campo<sup>d</sup>, V. Sánchez Fajardo<sup>b</sup>, Diego Lozano-Gorrín<sup>c</sup>, Candelaria Guzmán-Afonso<sup>b</sup>, Nanci Sabalisk<sup>b</sup>. <sup>a</sup>*Departamento de Física Fundamental II. Universidad de La Laguna. España.* <sup>b</sup>*Departamento de Física Básica. Universidad de La Laguna, España.* <sup>c</sup>*Servicios Generales de Apoyo a la Investigación. Universidad de La Laguna. España.* <sup>d</sup>*Instituto de Materiales de Aragón. CSIC. España.*  
E-mail: [metorres@ull.es](mailto:metorres@ull.es)

Molybdates with formula  $A_2(\text{MoO}_4)_3$  show a very intense negative thermal expansion (NTE) above 450K, when A=Y, Ho-Lu with  $\text{Sc}_2(\text{WO}_4)_3$ -type structure (Pbcn) [1]. There is not a detailed structural investigation at lower temperatures because they are hygroscopic [2]. Three samples  $\text{Y}_2(\text{MoO}_4)_3$ ,  $\text{Er}_2(\text{MoO}_4)_3$  and  $\text{Lu}_2(\text{MoO}_4)_3$  have been prepared by the conventional solid-state synthesis with preheated oxides. We have analysed the diffraction data of dehydrated compounds (A= Y, Er, Yb and Lu) from an ILL experiment (5-24-360) at the D2B powder diffractometer. We have found that all compounds show negative thermal expansion (NTE) behaviour in the temperature range of 150-400K. All the structures have been well refined by multipattern procedure [3], through X-ray powder diffraction data too, obtained on the laboratory equipment.

Given an accurate and precise crystal structure we have measured the exact scope polyhedral distortion with the temperature and ionic radii and the role of the transverse vibration of binding A-O-Mo oxygen atoms in the structure, since several authors have related such vibrations with the NTE behavior [4]. Also, we have studied the structural changes depending on the temperature and the ionic radii using the symmetry mode amplitude formalism [5], by comparing the distortions of lower temperatures respect to those at the highest temperature.

[1] Imanaka, N. *et al. Chem. Mat.*, **2000**, 12, 1910. [2] Manrinkovic, B. A., Jardim, P. M. De Avillez, R. R., Rizzo, F. *Solid State Sci.*, **2005**, 7, 14. [3] FullProf Suite: <http://www.ill.eu/sites/fullprof/> [4] Ravidran, T.R., Arora, A. K., Mary, T. A. *Phys. Rev. Letter.* **2000**, 84, 3879. [5] Bilbao Crystallographic Server: <http://www.cryst.ehu.es/>

**Keywords:** molybdates; neutron and X-ray diffraction; thermal expansion

**FA5-MS01-P31**

**Crystal Structures and Properties of Novel Inorganic-Organic Materials.** Wiesław Łasocha<sup>a,b</sup>, Piotr Putaj<sup>a</sup>, Alicja Rafalska-Łasocha<sup>a</sup>, Bartłomiej Gawel<sup>a</sup>, Wojciech Nitek<sup>a</sup>. *Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland.* <sup>b</sup>*Institute of Catalysis and Surface Chemistry PAS, ul. Niezapominajek 8, 30-239 Kraków, Poland.*  
E-mail: [lasocha@chemia.uj.edu.pl](mailto:lasocha@chemia.uj.edu.pl)

The synthesis of new hybrid inorganic-organic materials is a growing field of research. The main purpose of designing such new structural types is to combine the functional properties of organic and inorganic structures to create materials with desired/tailored properties for new challenging applications. Such materials can be used interchangeably with zeolites, as molecular reactors or for the storage of various gases.

Recently, we have synthesised and investigated the complexes of  $\text{MeX}_2$  (Me=Cd or Zn, X=Cl or Br) with different amines.

Coordination polymers (1-3) were obtained when ethylenediamine or triethylenamine were used in the synthesis. These compounds are built of straight, inorganic chains of  $-\text{Cd}-\text{X}_2-\text{Cd}-$  and organic groups. In the case of ethylenediamine inorganic chains were joined by diamine molecules forming two-dimensional layers (1,2), whereas in the case of triethylenamine (a bigger molecule, one nitrogen atom) double inorganic chains with the formula  $\text{Cd}_2\text{Cl}_5(\text{H}_2\text{O})$  were formed (3). The chains in this compound are isolated from each other by organic groups which are connected to the chains by H-bonds only. The same type of structures has been recently described in the literature [1].

Isolated, butterfly-like moieties (4) were obtained when  $\text{ZnCl}_2$  reacted with 3,5-dimethylaniline (a big monovalent ligand).

Crystallographic data for the investigated compounds (space group, lattice parameters [ $\text{\AA}$ ], V [ $\text{\AA}^3$ ], Z)

(1)  $[\text{Cd}(\text{C}_2\text{H}_8\text{N}_2)\text{Cl}_2]$ , Pbam (55), 9.9032(3), 7.819(4), 4.0692(5), 315.09(17), 2.

(2)  $[\text{Cd}(\text{C}_2\text{H}_8\text{N}_2)\text{Br}_2]$ , Pbam (57), 10.415(2), 7.8653(5), 4.2085(8), 344.75(10), 2.

(3)  $[\text{Cd}_2\text{Cl}_5(\text{H}_2\text{O})]$  ( $(\text{C}_2\text{H}_5)_3\text{NH}$ )  $\text{P}2_1/\text{n}$  (14), 11.271(1), 19.089(3), 7.648(2), 96.93(3), 1633.9(4), 4.

(4)  $[\text{ZnCl}_2 \cdot \{(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NH}_2\}_2]$  C2/c (15), 30.029(5), 4.8990(8), 12.067(2), 103.52(2), 1726.0(5), 4.

The crystal structures of compounds 1 and 2 were solved by powder diffraction methods, whereas the structures of 3 and 4 were solved by single crystal methods.

[1] Thom A, Willett R.D, Twamley B, *Cryst. Growth and Design*, **2006**, 6(5),1134.

**Keywords:** crystal engineering; inorganic-organic coordination polymers; powder diffraction

**FA5-MS01-P32**

**Ba<sub>2</sub>Ni<sub>3</sub> - A New Phase in the Binary System Ba-Ni.** Peter Höhn<sup>a</sup>, Stefan Hoffmann<sup>a</sup>, Rüdiger Kniep<sup>a</sup>. <sup>a</sup>*MPI-CPFS, Dresden, Germany.*  
E-mail: [hoehn@cpfs.mpg.de](mailto:hoehn@cpfs.mpg.de)

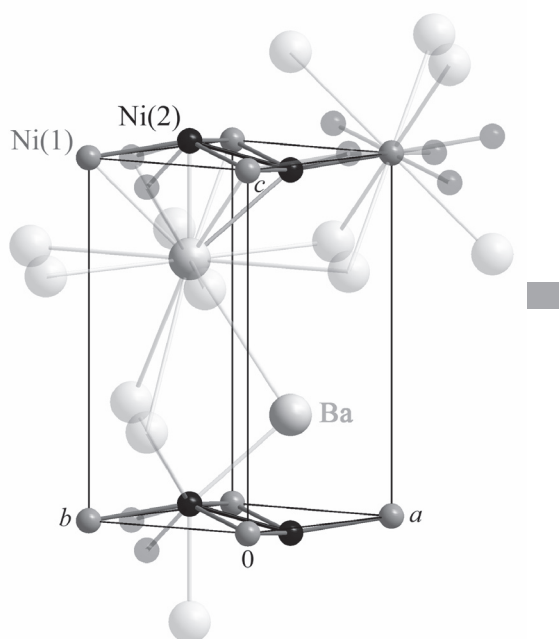
For investigation of the formation of intermediate phases in the ternary (and quaternary) system Ba-Ni-N(-C) pelletized mixtures of the elements and binary alkaline-earth nitrides were preferentially used [1]. In order to prevent impurities of elemental Ni in the samples, alternate routes of preparation via intermetallic precursors were evaluated.

The binary system Ba-Ni was first investigated in 1966 [2]. According to this study, no intermediate phases exist [3]. Our recent investigations [4] in the system Sr-Ni did

not confirm the literature data [2], instead we obtained the new phase  $\text{Sr}_2\text{Ni}_3$  ( $P\bar{3}1m$  (Nr. 164),  $a = 412.617(1)$  pm,  $c = 868.567(1)$  pm) which represents a new structure type. These results focussed our interest on the neighboring system Ba-Ni.

For the preparation of  $\text{Ba}_2\text{Ni}_3$  elemental barium and nickel are mixed in the molar ration 2:3, pelletized, sealed in niobium ampoules under argon and heated in a high frequency furnace at 1000°C for 10 minutes. Subsequent annealing at 580°C for 48 h results in single phase samples with a metallic luster. DTA investigations yield 610 °C for the eutectic temperature and 801 °C for the peritectic decomposition of  $\text{Ba}_2\text{Ni}_3$ . According to these investigations, the Ni-rich part of the system contains further binary phases, which are not yet completely characterized.

$\text{Ba}_2\text{Ni}_3$  ( $P\bar{3}1m$  (Nr. 164),  $a = 419.97(2)$  pm,  $c = 913.32(3)$  pm) is isotypic to  $\text{Sr}_2\text{Ni}_3$ . The dominant structural motif consists of corrugated Ni layers which are separated along [001] by planar double layers of barium. The complete coordination sphere around Ni(1) is built up by 6 Ba and 6 Ni(2), Ni(2) is surrounded by 3 Ni(1), 3 Ni(2) and 4 Ba, whereas Ba features 3 Ni(1), 4 Ni(2) and 9 Ba as nearest neighbors. Distances Ni-Ni (245-254 pm) and Ba-Ba (420 pm within the layers, 464 pm between the layers) correspond well with values from the elements (Ni: 244 pm [5], Ba: 434 pm [6]); distances Ba-Ni range between 294 pm and 354 pm.



[1] Mehta A., Höhn P., Schnelle W., Petzold V., Rosner H., Burkhardt U., Kniep R., *Chem. Eur. J.*, **2006**, 12, 1667. [2] Takeuchi Y. *et al.*, *Metall.*, **1966**, 20, 2. [3] Okamoto H., *Binary Alloy Phase Diagrams*, Second Edition, Ed. Massalski T.B., ASM International, Materials Park, Ohio, **1990**, 1, 598. [4] Höhn P., Nitsche F., Kniep R., *Z. Anorg. Allg. Chem.* **2008**, 634, 2046. [5] Hull A. W., *Phys. Rev.* **1917**, 10, 661. [6] Barrett C.S., *J. Chem. Phys.* **1956**, 25, 1123.

**Keywords:** intermetallic phases; crystal structures; nickel

#### FA5-MS01-P33

**Crystal Structures of the Rare Earth (RE) Thioborates  $\text{RE}_6\text{B}_{3.33}\text{S}_{14}$  ( $\text{RE} = \text{Lu}, \text{Ho}$ ).** Marija Borna<sup>a</sup>, Jens Hunger<sup>a</sup>, Dirk Zahn<sup>a</sup>, Alim Ormeci<sup>a</sup>, Rüdiger Kniep<sup>a</sup>. <sup>a</sup>Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany.

E-mail: [marija.borna@cpfs.mpg.de](mailto:marija.borna@cpfs.mpg.de)

Our recent experiments have shown that the formation of RE chalcogenoborates from elements and/or binaries under autogenous pressure takes place only above the melting point of the RE metal. Therefore, the synthesis of these compounds with the high-melting RE metals is rather a difficult task. However, two new isomorphous compounds,  $\text{Lu}_6\text{B}_3.33\text{S}_{14}$  (yellow) and  $\text{Ho}_6\text{B}_3.33\text{S}_{14}$  (red), were obtained by a high-temperature high-pressure route from the elements [1] at 3 GPa (5 h, 1400 °C). The crystal structures were solved and refined using the Rietveld method. Both compounds adopt the  $\text{Ce}_6\text{Al}_3.33\text{S}_{14}$  structure type [2] (hexagonal,  $P6_3$ , No. 173,  $Z = 1$ ), with the lattice parameters  $a = 9.2104(2)$  Å,  $c = 5.8880(2)$  Å for  $\text{RE} = \text{Lu}$  and  $a = 9.3703(1)$  Å,  $c = 5.8826(1)$  Å for  $\text{RE} = \text{Ho}$ . In the crystal structure of  $\text{RE}_6\text{B}_3.33\text{S}_{14}$  the boron atoms occupy two different sites (2b and 2a) with tetrahedral and trigonal planar coordination by sulfur, respectively. Isolated  $[\text{BS}_4]^{5-}$  tetrahedra, all pointing in the [001] direction, are stacked along the three-fold axis. The  $[\text{BS}_3]^{3-}$  triangles, in which boron atoms are slightly shifted out of the trigonal plane, propagate along the 6c axis. The  $\text{RE}^{3+}$  ions are surrounded by two  $[\text{BS}_3]^{3-}$  and three  $[\text{BS}_4]^{5-}$  units resulting in an overall 6+1 coordination by sulfur atoms which form a mono-capped trigonal prism. All sulfur atoms coordinate to three  $\text{RE}^{3+}$  ions. Vacancies in the isotypic  $\text{Ce}_6\text{Al}_3.33\text{S}_{14}$  structure occur at the octahedral Al site (2a site, on 6<sub>c</sub> axis). Reflecting this fact on  $\text{RE}_6\text{B}_3.33\text{S}_{14}$  crystal structure, the vacancies are also expected to be at the 2a site. This is in agreement with the results of density-functional-theory based electronic structure calculations [3], carried out on 1x1x3 super cells to model vacancies either at the B1 (2b) or the B2 (2a) positions. The total energies of the models containing vacancies on the B2 site are found to be significantly lower (60 - 70 meV/atom) than those of the models with vacancies on the B1 site. Therefore, the chemical formula can be given as  $\text{RE}_3[\text{B}_2/3\text{S}_3][\text{BS}_4]$ .

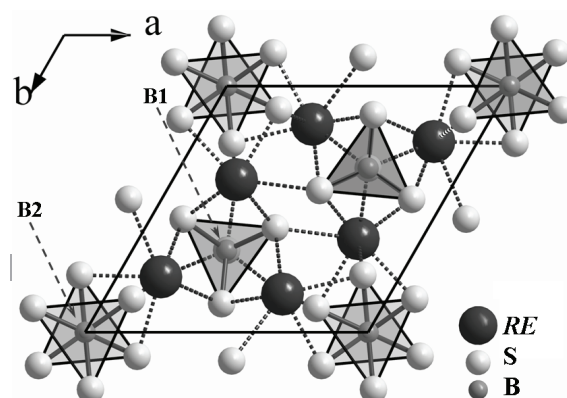


Figure 1. Crystal structure of  $\text{RE}_6\text{B}_3.33\text{S}_{14}$  viewed along [001].