

**PS08.01.45**  $\text{Li}_x\text{B}$  - A LITHIUMBORIDE CONTAINING LINEAR BORON CHAINS. Michael Wörle, Reinhard Nesper, Laboratorium für anorganische Chemie, ETH Zürich, Universitätsstr. 6, CH-8092 Zürich.

The structure, magnetic and spectroscopic properties of  $\text{Li}_x\text{B}$  ( $0.67 < x < 1.22$ ) are reported. The composition of this compound has earlier been described as  $\text{Li}_5\text{B}_4$  [1] or  $\text{Li}_7\text{B}_6$  [2,3]. Hitherto published structural data are wrong.

The compound crystallizes in the space group  $\text{P}6_3/\text{mmc}$ . The lattice constants are with  $a = 402.86$  pm and  $c = 290.2$  pm (for  $x=1$ ) or  $a = 401.81$  pm and  $c = 279.4$  pm (for  $x=1.22$ ) dependent on the lithium content. The crystal structure was determined from X-ray powder diffraction data.

The structure consists of a distorted hexagonal closed packing of lithium atoms. The stacks of octahedra are centered by linear chains of boron atoms along the crystallographic c-axis.

This is the first compound known to contain isolated linear [B]-chains in the ideal case. However, crystal defects limit the average chain length to about 67 boron atoms and lead to variations of the stoichiometry. These chains are the first examples of carbinoid systems (boryne) of a really large size.

[1] F. E. Wang, M. A. Mitchell, R. A. Sutula; *J. Less Common Met.*, **57**, (1978), 161

[2] R. Szwark, R. D. Walton, S. Dallek, B. F. Larrick; *J. Electrochem. Soc.* **129**, (1982), 1168

[3] D. W. Emst; *J. Electrochem. Soc.*, **129**, (1982), 1513

**PS08.01.46** SPECIFIC FEATURES OF DEFECT STRUCTURE OF  $\text{Na}_{0.39}\text{Y}_{0.61}\text{F}_{2.22}$  CRYSTALS. Zhurova, E.A., Maximov, B.A., Hull S., Keen, D.A., Wilson, C.C., Sobolev B.P., Simonov, V.I. Inst. of Crystallography RAS, Moscow, Russia Rutherford Appleton Laboratory, England

The specific features of structure and electron density distribution have been studied in the temperature range 10-296 K in the  $\text{Na}_{0.39}\text{Y}_{0.61}\text{F}_{2.22}$  fluorite crystal.

The structure refinements of the crystal were realized to  $R \sim 0.5\%$  for the X-ray experiment and to  $R \sim 3-7\%$  for the neutron ones at different temperatures. It was found, that there are three different F atom sites, the main one (8c) F, relaxed (32f) FR with coordinates (0.29, 0.29, 0.29) and supplementary (48i) F' with coordinates (0.5, 0.13, 0.13). Cationic sites are splitted about 0.1 Å in the directions of the coordinate axes. If we take into account the multiplicity of the (32f) site, the occupancy of the FR atom per one formula unit is close to Na content, and we can suppose that there are two sublattices in the  $\text{Na}_{0.39}\text{Y}_{0.61}\text{F}_{2.22}$  crystal. One of them contains Y and F atoms, the other one contains Na and FR, and one of the sublattices is displaced relative to the other by a distance of  $\sim 0.1$  Å.

The temperature dependence of the lattice parameter indicates a possible change in the crystal structure model at  $\sim 110$  K. However, such a specific feature was not revealed in the course of structure refinement.

On the deformation electron density maps there are peaks  $\sim 0.1$  e/Å<sup>3</sup> in height, which are slightly displaced from Na(Y)-F line. They can be due to partial covalent character of the Y-F chemical bond.

**PS08.01.47**  $\text{Ca}_x\text{WO}_3$  BRONZE SYNTHESIZED UNDER HIGH PRESSURE. Zibrov I.P.<sup>1</sup>, Filonenko V.P.<sup>2</sup>,<sup>1</sup>Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Leninsky pr.59, Russia. <sup>2</sup>Institute for High Pressure Physics, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russia.

A new intergrowth tungsten bronze (ITB),  $\text{Ca}_x\text{WO}_3$   $x=0.04-0.06$  has been prepared by solid state reaction ( $\text{CaO}+\text{WO}_3+\text{W}$ ) at  $P=50-80$  kbar and  $T>1300$  C. The compounds were studied by X-ray powder diffraction and high resolution transmission electron microscopy. The samples with starting composition  $x=0.05-0.5$  were investigated.  $\text{Ca}_x\text{WO}_3(\text{ITB})+\text{CaWO}_4$  were revealed in the samples with  $x<0.15$ , the mixture of  $\text{CaWO}_4+\text{Ca}_x\text{WO}_3(\text{HTB}[1]+\text{PTB}[2])$  in the samples with  $x>0.15$ . The calculated unit cell parameters of the ITB phase are:  $a=10.152$ ,  $b=7.423$  and  $c=3.790$  Å.

According to the nomenclature of the ITB families of related phases introduced in [3], the structure of this compound is denoted (2)-ITB and belongs to the (*n*)-ITB family of related phases. The number *n* corresponds to the number of  $\text{WO}_6$ -octahedra across the  $\text{WO}_6$ -type slabs in the structure. The theoretical upper limit of *x* is 0.20. However, in the  $\text{Ca}_x\text{WO}_3(\text{ITB})$  phase the sixsided tunnels seems to be filled to about 25%. The (2)-ITB structure can be considered to consist of hexagonal tungsten bronze (HTB) slabs, one single hexagonal tunnel row wide, which are mutually linked by corner-sharing.

[1]. P.E.Bierstedt et. al., *Solid State Commun.* **4**, 25, 1966.

[2]. D.Vandeven et. al., *Mater. Res. Bull.*, **2**, 809, 1967.

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**PR08.01.48** SYNTHESIS OF SOME CRYSTALLOCHEMICAL ANALOGS STRONTIUM ANORTITE AND THEIR INTERRELATIONS. Arifov P.A. Inst. of Chemistry, Tashkent, Uzbekistan.

The results of synthesis and investigation of some strontium anortite varieties and their analogs interrelations are given.  $\text{SrAl}_2\text{Si}_2\text{O}_8$  and  $\text{SrAl}_2\text{Ge}_2\text{O}_8$  triclinic forms were obtained by solid phase reactions, differently from the former,  $\text{SrAl}_2\text{Ge}_2\text{O}_8$  was obtained close to the melting temperature. Anortite hexagonal and orthorhombic forms and their analogs were obtained by glass or melt crystallization.  $\text{SrAl}_2\text{Si}_2\text{O}_8$   $a=8.21$ ;  $b=12.84$ ;  $d=3120$  kg/m<sup>3</sup> tricl.  $\text{SrAl}_2\text{Ge}_2\text{O}_8$   $a=8.562$ ;  $b=13.27$ ;  $c=7.28$ ;  $d=3740$  kg/m<sup>3</sup> tricl. The synthesis temperature of  $\text{SrAl}_2\text{Si}_2\text{O}_8$  corresponds to 1500°C and for  $\text{SrAl}_2\text{Ge}_2\text{O}_8$  - 1450°C, the melting temperature is respectively 1710 and 1515°C. Also, studied the interrelations of hexagonal varieties of solid solution in the system  $\text{SrAl}_2\text{Si}_2\text{O}_8$  -  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (Table).

Compound	Dens kg/m <sup>3</sup>	Prms a	elem. cell, Å		Ind/refr.	
			c	V, Å <sup>3</sup>	Ng	Np
$\text{SrAl}_2\text{Si}_2\text{O}_8$	2980	5,25	7,56	180	1,573	1,571
$\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Al}_2\text{Si}_2\text{O}_8$	3010	5,25	7,58	181	1,573	1,571
$\text{Sr}_{0.7}\text{Ba}_{0.3}\text{Al}_2\text{Si}_2\text{O}_8$	3080	5,25	7,64	182	1,573	-
$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Al}_2\text{Si}_2\text{O}_8$	3150	5,25	7,68	183	1,573	-
$\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Al}_2\text{Si}_2\text{O}_8$	3220	5,25	7,74	184	1,573	-
$\text{Sr}_{0.1}\text{Ba}_{0.9}\text{Al}_2\text{Si}_2\text{O}_8$	3300	5,25	7,76	185	1,573	-
$\text{BaAl}_2\text{Si}_2\text{O}_8$	3320	5,25	7,82	186	1,573	-

The crystallochemical similarities in the homological series system of  $\text{SrGa}_2\text{Si}_2\text{O}_8$  -  $\text{SrGa}_2\text{Ge}_2\text{O}_8$  have also been studied.