

ing leads to two entirely different chalcogen coordinations for the two independent  $Rb^+$  ions; one of them occupies a split position and shows drastically enhanced thermal displacements.

[1] K.O. Klepp, D. Mayr & H. Boller, *IV<sup>th</sup> European Conference on Solid State Chemistry*, Dresden 1992, Book of Abstracts, p.363.

Compound	a (Å)	b (Å)	c (Å)	$\beta$ (°)	s.g.
$Tl_2Cu_4V_2S_8$	7.262(3)	17.63(1)	5.337(2)		Pna2 <sub>1</sub>
$Tl_2Cu_4Nb_2S_8$	7.351 (4)	18.045(8)	5.517(1)		Pna2 <sub>1</sub>
$Tl_2Cu_4Ta_2S_8$	7.395(2)	18.051(6)	5.525(1)		Pna2 <sub>1</sub>
$Tl_4Ag_2Ta_2S_8$	7.932(9)	10.395(6)	10.025(5)	90.61(0)	P2 <sub>1</sub> /n
$Tl_2Cu_2Hf_3Se_8$	14.392(3)	3.828(1)	14.387(3)	113.69(2)	C2/m
$Tl_2Cu_2Zr_3S_8$	14.328(2)	3.787(0)	14.250(2)	113.59(2)	C2/m
$Tl_2Cu_2Zr_3Se_8$	14.033(2)	3.7008(6)	13.874(3)	113.93(1)	C2/m
$Rb_2Cu_2Hf_3Se_8$	25.15(1)	3.783(3)	9.409(5)	105.37(5)	C2/m

**PS08.01.22 COMPOSITION, CRYSTAL STRUCTURES, THERMAL STABILITY OF NEW TERNARY POTASSIUM-CONTAINING MOLYBDATES.** R.F.Klevtsova, L.A. Glinskaya, Zh.G. Bazarova, P.V. Klevtsov, Institute of Inorganic Chemistry, Novosibirsk, Russia

The  $K_2MoO_4 - AMoO_4 - Zr(MoO_4)_2$  (A=Mg,Mn) systems were investigated by using quasibinary sections and new phases, ternary molybdates of different compositions (I -  $K(Mg_{0.5}Zr_{0.5})(MoO_4)_2$ ; II -  $K_{0.6}(Mn_{0.9}Zr_{0.9})(MoO_4)_3$  III -  $K_5(A_{0.5}Zr_{1.5})(MoO_4)_6$ ), were established to exist there. Single crystals were prepared by spontaneous flux crystallization and studied by an X-ray structure analysis (KUMA and CAD 4 diffractometers, Mo K radiation). Some crystallographic data are given in the table.

	Sp.gr	a	c	Z	dx	R
I	P3(-)m1	5.763	7.187	1	3.348	0.022
II	R3(-)c	9.474	24.371	6	3.336	0.046
III-Mg	R3c	10.576	37.511	6	3.576	0.026
III-Mn	R3c	10.584	37.576	6	3.606	0.027

The compounds were shown to fall into three different structure types: (a) glaserite (I); (b) NASICON (II); (c)  $-Ca_3(PO_4)_2$  (III). These are built up on the base of three-dimensional frameworks of  $MoO_4$  tetrahedra and  $MO_6$  octahedra with the potassium atoms in the voids. All structures investigated have the following characteristic: a statistic filling of M octahedral positions by the Mg( or Mn) and Zr atoms. Structural peculiarities (size, shape, site occupancy and modes of joint of the coordination polyhedra) were used to interpret physical properties. The comparative crystal chemical analysis of the investigated and related compounds has been carried out. The thermal analysis showed that all compounds melt incongruently at 550-700°C. Polymorphism has not been revealed in the crystals.

**PS08.01.23 X-RAY DIFFRACTION STUDY OF  $Nd_{2-x}Ce_xCuO_{4-y}$ .** I.P. Makarova<sup>1</sup>, A. Bram<sup>2</sup>, H. Burzlaß<sup>3</sup>. <sup>1</sup>Institute of Crystallography, Russian Academy of Sciences, 117333, Moscow, Russia; <sup>2</sup>ESRF, BP220, 38043 Grenoble, France, <sup>3</sup>Lehrstuhl für Kristallographie, Institut für Angewandte Physik der Universität Erlangen-Nürnberg, 91054 Erlangen, Germany.

Changes in the atomic structure and the electron density distribution in single crystals of  $Nd_{2-x}Ce_xCuO_{4-y}$  caused by Ce-doping have been studied using X-ray diffraction data. Four samples of  $Nd_{2-x}Ce_xCuO_{4-y}$  have been investigated:  
 $Nd_2CuO_4$ , 293 K, 20 K [1];  
 $Nd_{2-x}Ce_xCuO_{4-y}$  (I), x=16%, 293 K [2];  
 $Nd_{2-x}Ce_xCuO_{4-y}$  (II), x=13%, 293 K [2], 296 K, 150 K, 25 K;  
 $Nd_{2-x}Ce_xCuO_{4-y}$  (III), x=15%, HTSC, 293 K.

The main change on the electron density maps is the rearrangement of the charge density at the Cu position with Ce-doping, that indicates the change of the valence state of the Cu atom. At room temperature the formation of a density maximum at the

Nd/Ce position was observed. As the temperature and the displacement parameters decrease, the maximum is split into six separated maxima, that may indicate the disordering at the Nd/Ce position. In contrast to the Ce-doped sample, no anomalous changes were observed in the undoped sample with temperature going down.

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1. I.P. Makarova, V.I. Simonov, M. Blomberg, M. Merisalo, accepted for publication in Acta Cryst.
2. I.P. Makarova, A. Bram, et al. (1994). Physica C, 223, 1.

**PS08.01.24 CRYSTAL STRUCTURE OF A NEW Li-Ge-S COMPOUND,  $Li_4GeS_4$ .** Yoshitaka Matsushita, Mercuri G. Kanatzidis, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322 USA

The new Li-Ge-S compound,  $Li_4GeS_4$ , has been successfully grown as the main product in the  $Li_2S-La_2S_3-Ge-S$  system at temperature under 973K. The clear white to light yellow moisture-sensitive crystals are grown by heating the above reagents in 2:1:2:6 proportions at 973K for 200hrs and slowly cooling to 773K. The reagents were mixed and put in a carbon tube which was sealed inside an evacuated quartz tube ( $\sim 10^{-5}$  Torr). The well-developed single crystals had pillar-shaped habits.

An X-ray single crystal intensity data collection has been carried out for  $Li_4GeS_4$  using a four-circle RIGAKU AFC6S diffractometer with  $MoK\alpha$  radiation at room temperature. The crystal was mounted inside of a capillary with mineral oil. The space group was found to be Pnma, and the cell dimensions are  $a=14.107(6)$ ,  $b=7.770(3)$  and  $c=6.162(2)$  Å estimated from 18 well-centered reflections in the range of  $55^\circ < 2\theta < 60^\circ$  using  $MoK\alpha 1$ . The intensity data were collected up to  $60^\circ$  in  $2\theta$ . The crystal structure including the lithium-sites has been solved by direct-methods using SHELXS-86 and successive Difference-Fourier synthesis. The final R and wR-values are 1.85 and 1.65% for 866 observed reflections, respectively.

The  $Li_4GeS_4$  structure has three lithium-sites and one germanium-site. The lithium sites have two different coordination types. The Li1-site is coordinated to five sulfurs in a square pyramidal geometry and can be viewed as a remarkably distorted NaCl-like framework. The other lithium sites, the Li2 and Li3 have distorted tetrahedral coordination types connected in a three dimensional framework. The Germanium atom is also tetrahedrally coordinated by four sulfur atoms and is found as an isolated  $GeS_4^{4-}$  unit. The crystal structure of  $Li_4GeS_4$  is similar to the  $K_4SnSe_4$  [1] structure type, but has slight differences caused by the differences in ionic radii of the alkali metals and the chalcogenides. The  $Li_4GeS_4$  structure exhibits disorder at the Li1-site which is not found for K1 in  $K_4SnSe_4$ .

- [1] K. O. Klepp; Z. Naturforsch. 47b (1992) 411