

Single crystals of samples 1-3 have been grown from complex boron-containing hydrothermal solutions at range of temperatures of 400-750°C and pressures of up to 150 MPa in the IEM RAS [1]. Cu-bearing tourmaline (sample 4) has been synthesised in the Institute of Mineralogy and Petrography SB RAS [2]. X-ray experiment was carried out on four-circle single-crystal diffractometer Nicolett R3.

The content of 3d-elements in multicolor synthetic tourmalines can rise up to 24 wt. % (in oxide form) and in the case of Ni, Co, Cu-tourmalines it is significantly higher than that found in natural specimens. The total content of 3d-elements and the ratio of its' ionic radii are the reason for the unit cell parameters and octahedral dimensions variations. In all cases chromophore elements occupied Y (mainly) and Z octahedra (table 2).

Table 2. Characteristic of Y and Z octahedral.

Smp	Y octahedron		Z-octahedron	
	Occupation, apfu	<Y-O>, Å	Occupation, apfu	<Z-O>, Å
1	Al <sub>1.69</sub> Ni <sub>0.81</sub> Fe <sub>0.50</sub>	1.991	Al <sub>5.40</sub> Fe <sub>0.60</sub>	1.922
2	Ni <sub>1.20</sub> Cr <sub>0.96</sub> Al <sub>0.63</sub> × Fe <sub>0.18</sub> Mg <sub>0.03</sub>	2.008	Al <sub>4.26</sub> Ni <sub>1.20</sub> × Cr <sub>0.48</sub> Ti <sub>0.06</sub>	1.937
3	Al <sub>1.80</sub> Co <sub>1.20</sub>	1.949	Al <sub>5.28</sub> Co <sub>0.66</sub> × Ti <sub>0.06</sub>	1.907
4	Al <sub>1.86</sub> Cu <sub>1.14</sub>	1.978	Al <sub>5.88</sub> Cu <sub>0.12</sub>	1.907

In the structure of samples 1, 3, 4 the main element in Y and Z sites is aluminium. The samples 3 and 4 (sodium in X site) are analogues of olenite mineral. The sample 1 (X site is mainly vacant) is an analogue of hypothetical oxyfoitite. Incorporation of bivalent 3d-elements (R<sup>2+</sup>) in these tourmalines is described by equation: Al<sup>3+</sup>+O<sup>2-</sup>=R<sup>2+</sup>+OH<sup>-</sup>. There are no close analogues of sample 2 in nature.

This work was supported by the RFBR (grant no. 09-05-00769-a).

[1] T.V. Setkova et al., *Journal of Crystal Growth*, **2010** (in print) [2] A.S. Lebedev et al., *Materials on Genetic and Experimental Mineralogy. Crystal Growth and Properties* [in Russian], Nauka, Novosibirsk **1988**.

**Keywords: crystallochemistry, silicate, X-ray.**

## MS54.P02

*Acta Cryst.* (2011) A67, C572

### First Silicate Mineral with Triple Tetrahedral Layer

Sergey M. Aksenov,<sup>a</sup> Ramiza K. Rastsvetaeva,<sup>a</sup> Nikita V. Chukanov,<sup>a</sup> *Shubnikov Institute of Crystallography, RAS, Moscow (Russia).*  
<sup>b</sup>*Institute of Problems of Chemical Physics, RAS, Chernogolovka (Russia).* E-mail: rast@ns.crys.ras.ru

The crystal structure of a new silicate mineral from the Eifel paleovolcanic area, Rhineland-Palatinate, Germany was studied by X-ray single crystal diffraction (diffractometer Xcalibur Oxford Diffraction, CCD-detector). The orthorhombic unit-cell parameters are:  $a=6.528(1)$  Å,  $b=6.970(1)$  Å,  $c=37.216(5)$  Å,  $V=1693.33(4)$  Å<sup>3</sup>, space group  $Pnm2_1$ . The structure was solved by direct methods and refined to  $R=4.9\%$ ,  $2706 |F| > 3\sigma(F)$ . Idealized crystal-chemical formula is: (K,Ca,Ba)<sub>2</sub>(Fe,Ca,Mg,Na)[(Si,Al)<sub>13</sub>O<sub>25</sub>(OH)<sub>4</sub>]·7H<sub>2</sub>O.

The mineral is representative of a new structure type. The most important specific feature of its structure is a block [Si<sub>13</sub>O<sub>29</sub>] consisting of three connected single layers formed by four- and eight-membered rings of tetrahedra (T) centered by Si and Al. Two outer layers [Si<sub>4</sub>O<sub>10</sub>]

are topologically identical to that in some single-layer phyllosilicates (mountainite, shlykovite, cryptophyllite) and in double-layer silicates rhodesite, delhayelite, hydrodelhayelite, macdonaldite, monteregianite-(Y) and fivegite. The third (inner) layer [Si<sub>5</sub>O<sub>11</sub>] is unique and contains an additional tetrahedron.

The triple tetrahedral blocks [Si<sub>13</sub>O<sub>29</sub>] are connected to each other via the discrete polyhedra (Fe,Ca)O<sub>7</sub> to form 3D framework with channels filled by large cations (mainly K, as well as subordinate Ba, Ca) and H<sub>2</sub>O molecules. Thus the new mineral is an intermediate between phyllosilicates and zeolites. One can outline polysomatic structures from single-layer via double-layer to triple-layer ones.

**Keywords: X-ray analysis, mineral, silicate**

## MS54.P03

*Acta Cryst.* (2011) A67, C572-C573

### New members in sodium cadmium bisulfate: structure, property and thermal studies

Dipankar Saha,<sup>a</sup> Giridhar Madras,<sup>b</sup> Tayur N. Guru Row,<sup>a</sup> *Solid State and Structural Chemistry Unit.* <sup>b</sup>*Department of Chemical Engineering, Indian Institute of Science, Bangalore 560 012 (India).* E-mail: s.dipankar@sscu.iisc.ernet.in

Bimetallic sulfates form an important constituent of the earth's crust and are recognized to provide essential link to mineral evolution. Depending on the level of hydration they form different class of minerals. The omnipresent water plays a decisive role in the formation of hydrates of complex inorganic materials generating complicated structural frameworks. These compounds exhibit properties like ionic conductivity, phase transitions in the context of electric, magnetic and elastic properties [1, 2] and believed to have played an important role in the formation of earth's atmosphere oxygen [3]. We have synthesized polymorphs of sodium cadmium bisulfate which differ in the extent of hydration and have studied their thermal properties and phase transition. Na<sub>2</sub>Cd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O, Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, were crystallized by slow evaporation method from water. Na<sub>2</sub>Cd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O crystallizes in a trigonal system with the space group  $P3c$ . It loses water completely after 250 °C and transforms to a dehydrated phase whose structure has been established using *abinitio* powder diffraction. The dehydrated form crystallizes in the space group  $I\bar{4}3d$ . The phase transitions have been investigated using DSC, TGA and ionic conductivity studies.  $\beta$ -Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>, a polymorphic form of  $\alpha$ -Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>, has been isolated by quenching the parent compound  $\alpha$ -Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub> and characterised to belong to a monoclinic system, space group  $P2_1/c$ .  $\beta$ -Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub> takes up water from the atmosphere and gets converted to a Kröhnkite type mineral Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O. Upon heating, mineral loses water and gets converted to  $\alpha$ -Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>. The phase transition analysis provides inputs for exploring the origin of Kröhnkite mineral. Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O crystallizes in a monoclinic system with a space group  $P2_1/c$ . It is isostructural with the mineral Astrakhanite which is also known as Blöditte [4]. This work describes a structure based analysis of phase transitions involved in these complexes, thus providing insights into their evolutionary aspects.

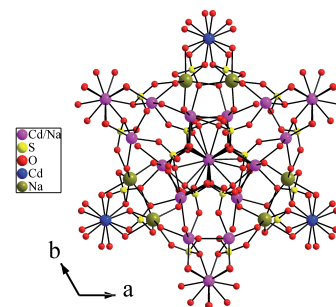


Figure 1. Repetitive unit of Na<sub>2</sub>Cd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O