

**MS16-P6** Structure, elasticity, thermodynamics and high pressure behavior of  $\text{ZnB}_4\text{O}_7$  and  $\text{CdB}_4\text{O}_7$ . Leonore Wiehl<sup>a</sup>, Björn Winkler<sup>a</sup>, A. Guillermo Castellanos Guzman<sup>b</sup>, Lkhamsuren Bayarjargal<sup>a</sup>, Victor Milman<sup>c</sup>, <sup>a</sup>Institut für Geowissenschaften, Universität Frankfurt am Main, Germany, <sup>b</sup>Centro de Investigación en Materiales, Universidad de Guadalajara, Mexico, <sup>c</sup>Accelrys Inc., Cambridge, United Kingdom  
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An accurate single crystal determination of the structure of  $\alpha$ - $\text{ZnB}_4\text{O}_7$  is reported, and an improved description, with respect to that of Martínez-Ripoll et al. [1], of the polyhedral network (Fig.1) is presented. The structure was solved in space group *Pbca* with unit cell parameters of  $a = 8.1093(2)$  Å,  $b = 8.6340(2)$  Å, and  $c = 13.7200(3)$  Å. The experimental data are used to evaluate density functional theory calculations. The agreement between the results of the experiments and the calculations was very satisfactory. The models were therefore used to predict the compression behavior ( $B_{\alpha\text{-ZnB}_4\text{O}_7} = 59.9(7)$  GPa), the elasticity tensor, bond populations, and a transition pressure of 3.7 GPa for the transition into the high pressure  $\beta$ -phase. The predicted bulk modulus of the high pressure polymorph is  $B_{\beta\text{-ZnB}_4\text{O}_7} = 210.4(4)$  GPa. The heat capacity of the  $\alpha$ -phase has been determined with quasi-adiabatic microcalorimetric measurements and at low temperatures a Debye temperature of  $\theta = 787$  K has been obtained. The results obtained for  $\alpha$ - and  $\beta$ - $\text{ZnB}_4\text{O}_7$  are compared to those of the isostructural  $\text{CdB}_4\text{O}_7$  compounds. The transition from the  $\alpha$ - to a high pressure  $\beta$ -phase of  $\text{CdB}_4\text{O}_7$  is predicted to occur at 1.9 GPa, but within the uncertainty of the model, the high pressure phase may also be isostructural to  $\beta$ - $\text{CaB}_4\text{O}_7$ .

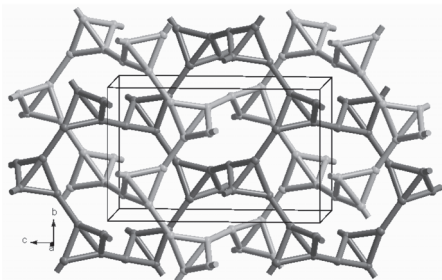


Fig.1. The crystal structure of  $\alpha$ - $\text{ZnB}_4\text{O}_7$  can be described in terms of two interpenetrating -B-O-B- networks. Small spheres represent the boron atoms. Sticks joining the spheres represent B-O-B bonds.

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- [1] Martínez-Ripoll, M., Martínez-Carrera, S. & García-Blanco, S. (1971). *Acta Cryst.* **B27**, 672-677.

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**MS16-P7** HT behaviour of orthorhombic amphiboles: ferroholmquistite. Michele Zema,<sup>a,c</sup> Massimo Boiocchi,<sup>b</sup> Roberta Oberti,<sup>c</sup> <sup>a</sup>Univ. Pavia, Italy, <sup>b</sup>CGS Pavia, Italy, <sup>c</sup>CNR-IGG Pavia, Italy  
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Amphiboles are a supergroup of rock-forming minerals with a really intricate crystal-chemistry, which however is able to record a number of markers of petrogenetic relevance. Hence, HT studies of amphiboles both allow experimental control on our present knowledge of cation ordering and provide precious information on phase stability, molar volumes and on the condition of water release and thus on the water budget in the Earth mantle. Diffraction data measured up to 750 °C on holotype ferro-holmquistite  $^A(\text{K}_{0.01}\text{Na}_{0.01})$   $^B(\text{Li}_{1.88}\text{Mg}_{0.08}\text{Na}_{0.03}\text{Fe}^{2+}_{0.01})$   $^C(\text{Al}_{1.89}\text{Fe}^{2+}_{1.70}\text{Mg}_{1.39}\text{Mn}^{2+}_{0.02})$   $^T\text{Si}_{8.00}$   $^W(\text{O}_{22}\text{OH}_{1.97}\text{F}_{0.03})$  [1] (FeHOL) and on its partially dehydrogenated (about 1 H pfu) counterpart (OXO), where part of the  $\text{Fe}^{2+}$  content oxidized to  $\text{Fe}^{3+}$  thus allowing for H loss, are presented and compared with those previously obtained for the other end-members of orthorhombic amphiboles, anthophyllite [1] and gedrite [2]. In this way, the effects of compositional variations such as  $^A_{0.5}$   $^A\text{Na}_{0.5}$ ,  $^B(\text{Mg,Fe})^{2+}_{-2}$   $^B\text{Li}_2$ ,  $^C(\text{Mg,Fe})^{2+}_{-2}$   $^C\text{Al}_2$  and  $^T\text{Si}_{-2}$   $^T\text{Al}_2$  are taken into account. Contrary to the almost linear behaviour observed for changes in unit-cell parameters in anthophyllite and gedrite, ferro-holmquistite shows a non-linear thermal expansion of the *c* edge, and a significant discontinuity around 500 °C for both the *b* and *c* edges of the partially dehydrogenated phase (measured on reversal). Best fits on our data (in the range RT-650 °C for FeHOL and RT-500 °C for OXO) give:  $\alpha_{\text{FeHOL}}: 1.36(2)\cdot 10^{-5}$ ,  $\alpha_{\text{OXO}}: 1.324(9)\cdot 10^{-5}$ ,  $\alpha_{\text{bFeHOL}}: 0.56(1)\cdot 10^{-5}$ ,  $\alpha_{\text{bOXO}}: 0.60(1)\cdot 10^{-5}$ ,  $\alpha_{\text{cFeHOL}}: 1.27(6)\cdot 10^{-5}$ - $8.9(7)\cdot 10^{-9}$ ,  $\alpha_{\text{cOXO}}: 0.68(2)\cdot 10^{-5}$ ,  $\alpha_{\text{VFeHOL}}: 3.5(1)\cdot 10^{-5}$ - $1.3(2)\cdot 10^{-8}$  or  $2.57(6)\cdot 10^{-5}$  (linear fit),  $\alpha_{\text{VOXO}}: 2.59(2)\cdot 10^{-5}$ .

Structure refinements done at different *T* values during heating and at room *T* on the partially dehydrogenated phase provide information on the mechanism and the structural consequences of the differential thermal expansion of the structural units, as well as on cation exchange and structural changes related to dehydrogenation. Differences in thermoelastic behaviour and in the starting *T* of the dehydrogenation processes as a function of the overall composition and cation order in the distinct orthorhombic end-members will be discussed. These data allow construction of a reliable model for orthorhombic amphiboles, that will be compared to that still in preparation for monoclinic amphiboles, the terms of the amphibole supergroup that are more relevant to petrogenetic studies but that have a far more complex compositional variability.

- [1] Cámara, F. & Oberti, R. (2005) *Am. Mineral.* **90**, 1167-1176.  
[2] Welch, M. D., Cámara, F. & Oberti, R. (2011) *Phys. Chem. Minerals* **38**, 321-334.  
[3] Zema, M., Welch, M. D. & Oberti, R. (2012) *Contrib. Mineral. Petrol.* **163**, 923-937.

**Keywords:** amphiboles; high-temperature diffraction; holmquistite