

STRUCTURAL RELATIONS IN THE ADELITE- AND DESCLOIZITE-STRUCTURE TYPEH. EffenbergerUniversitaet Wien Institut Fuer Mineralogie Und Kristallographie
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More than a dozen minerals and some synthetic compounds (arsenates, vanadates, silicates, and molybdates) are known to belong to the adelite-descloizite structure type. The double salts are formed by two cations featuring distinct environments. The cation A is in a [7]- or [8]-coordination (Na, Ca, Pb atoms) whereas the cation B is octahedrally [6] or tetragonal bipyramidally [4 plus 2] coordinated to O atoms (Mg, Mn, Fe, Co, Ni, Cu, Zn atoms). All compounds crystallize orthorhombic. The parental structure is centrosymmetric and exhibits a mono-capped trigonal prism for the coordination polyhedron around the A atoms (descloizite type). An acentric structure variant is known (adelite type); the main difference is the [8] coordination of the A atoms in form of a square antiprism. Further deviations from the centrosymmetric parental structure are moderate. A tendency is observed that the centrosymmetric symmetry goes along with lead-vanadates whereas calcium, arsenate and silicate favour the acentric symmetry. The system Cd(II)-Cu(II)-arsenate(V) system was investigated under hydrothermal conditions; as a result, a new Cd-member was synthesized. Single-crystal X-ray structure investigations proved that this compound is a centrosymmetric *Pnam* member of the adelite-descloizite group: $a = 7.415(1)$, $b = 9.016(2)$, $c = 5.890(1)$ Å; NONIUS four-circle diffractometer, CCD detector, capillary-optics collimator, Mo tube, graphite monochromator; $R1 = 0.020$, $wR2 = 0.046$, total 772 reflections (689 observed reflections); for non-hydrogen atoms anisotropic displacement parameters were refined; the H atom was found from a difference Fourier map and refined isotropically. The [4 plus 2] coordinated Cu atoms are located in an inversion centre; they are linked by O-O edges to chains parallel to [001]: Cu-O = 1.8967(14), $2x / 2.0533(16)$, $2x / 2.3083(16)$ Å, $2x$. Each of the arsenate tetrahedra link two such chains to a three-dimensional network, the average As-O bond distance is 1.6908 Å. Cavities house the A = Cd atoms: Cd-O is 2.224(2) to 2.542(3) Å. The hydrogen bond O-H...O is 2.622(4) Å. Despite similar ionic radii of Ca and Cd atoms, the Ca compound crystallizes acentric.

Keywords: ADELITE GROUP, DESCLOIZITE GROUP, CD(II)-CU(II)-ARSENATE(V)**THE DISPLACIVE PHASE TRANSFORMATION IN THE BINARY SYSTEM Sn-Sb**M. Ellner E. J. MittemeijerMax Planck Institute for Metals Research Heisenbergstraße 3 STUTTGART
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The significant berthollidic phase of the binary system Sn-Sb is stistaite (SnSb, β phase), stable in the composition range $0.43 < x_{Sb} < 0.61$ and at temperatures below 698 K [1]. The structure of SnSb is of the rhomboedrally deformed NaCl type: hR8, *R-3m*, 1Sn (a), 3 Sn (e), 1 Sb (b), 3 Sb (d), $a = 0.6123$ nm, $\alpha = 89.38^\circ$ [2]. For compositions $x_{Sb} < 0.5$, the atomic positions of antimony are substituted by tin and vice versa for the compositions $x_{Sb} > 0.5$. The rhomboedric angle of SnSb decreases and the unit cell volume increases with increasing valence electron concentration. In the temperature range $523 \text{ K} < T < 597 \text{ K}$, another intermediate phase - Sn_3Sb_2 - exists; this high-temperature phase of fixed stoichiometry can be retained neither by quenching of the heat-treated alloys nor by means of the liquid-quenching technique. *In situ* investigation of alloys in the composition range $0.39 < x_{Sb} < 0.41$ (at temperatures $530 \text{ K} < T < 580 \text{ K}$) in a modified Guinier-Simon high-temperature X-ray camera with $\text{CuK}\alpha$ radiation showed that the high-temperature phase Sn_3Sb_2 has a non-deformed NaCl structure: cF8, *Fm-3m*, $a = 0.6192(2)$ nm. The symmetry relationship for this displacive phase transformation can be characterized by the equation: Sn_3Sb_2 (cF8, *Fm-3m*) (R) SnSb (hR8, *R-3m*) (+ α -Sn(Sb), tI4, *I41/amd*). In the binary and ternary systems containing the 4d/5d elements of the B12 to B16 groups and showing the similar valence electron concentration ($4.50 < \text{VEC} < 4.75$), high-pressure phases isotypical with the NaCl structure also occur: $\text{Cd}_{0.25}\text{Sn}_{0.75}\text{Te}$, $\text{Cd}_{0.5}\text{Sn}_{0.5}\text{Te}$, $\text{Cd}_{0.25}\text{Pb}_{0.75}\text{Te}$, $\text{Cd}_{0.5}\text{Pb}_{0.5}\text{Te}$ [3].

References

- [1]. T. B. Massalski, H. Okamoto, P. R. Subramanian & L. Kacprzak (1990). Binary alloy phase Diagrams, Second Edition, Vol. 3, ASM International, The Materials Information Society, 3304.
- [2]. G. Hägg & A. G. Hybinette (1935). Phil. Mag., 20, 913.
- [3]. R. Marx & J. Range (1989). J. Less-Common Metals, 155, 49.

Keywords: DISPLACIVE PHASE TRANSFORMATIONS, NaCl HOMEOTYPES, X-RAY HIGH-TEMPERATURE POWDER DIFFRACTION**STRUCTURAL STUDY OF A GRAPHITE-LITHIUM-CALCIUM INTERCALATION COMPOUND**P. Lagrange S. Pruvost C. Herold J.F. Mareche A. Herold

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Lithium is able to intercalate by itself into graphite. This vapour solid reaction leads to a first stage compound, for which the formula is LiC_6 . All the graphitic intervals are spread apart and are occupied by a monoatomic metal layer. This latter is commensurate with respect to the graphene layers. Calcium leads to a similar intercalation reaction, and the synthesized compound is CaC_6 . The 2D structure of the intercalated metal layers are exactly the same for both MC_6 compounds. But, the graphene interplanar distance is weak for LiC_6 (370 pm) and larger for CaC_6 (455 pm), according to the size of the corresponding cations. Some lithium-calcium liquid alloys are also able to intercalate into graphite. But the first stage ternary compound, that is obtained, is strongly different from LiC_6 (or CaC_6). Indeed, this compound exhibits five-layered intercalated sheets, according to the Li-Ca-Ca-Ca-Li c-axis sequence, and its graphene interplanar distance is strongly larger than the former (776 pm). These crystallographic data were obtained of course by X-ray diffraction, but also by neutron diffraction, because lithium is a very light element, so that it is quasi-invisible for the X-rays. The chemical formula of the ternary compound is LiCa_3C_8 ; consequently, its metal content is particularly high, since the carbon/metal ratio comes down to 2. Intercalated lithium graphite is very interesting, due to its largely expanded use as negative electrode material in the Li-ion batteries.

Keywords: GRAPHITE INTERCALATION LITHIUM**AB INITIO INVESTIGATIONS OF β -Ba(OH)₂ AND ITS HIGH PRESSURE PHASE β -II-Ba(OH)₂**U. Hantsch¹ M. Hytha¹ A. Friedrich² B. Winkler¹ V. Milman³¹CAU Kiel Institut Fuer Geowissenschaften / Kristallographie
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The pressure dependence of the structural parameters and bonding characteristics of β -Ba(OH)₂ and its high pressure modification β -II-Ba(OH)₂ have been investigated up to 20 GPa by density functional theory (DFT) calculations using the generalized gradient approximation and a plane wave basis set in conjunction with ultrasoft pseudopotentials [1]. The agreement between the structural parameters obtained from theory ($a = 9.459$ Å, $b = 7.939$ Å, $c = 6.811$ Å, $\beta = 95.6^\circ$, $\text{SG} = P2_1/n$) and experiment [2] for the ground state structure is well within the usual limits of DFT-based calculations. Within the calculated pressure range no additional hydrogen bonding is induced whereas the coordination numbers of the atoms Ba1 and Ba2 change from 8 to 9 and 7 to 8, respectively. For β -II-Ba(OH)₂, the positions of the hydrogen atoms have been predicted. For β -Ba(OH)₂, the elastic stiffness coefficients have been determined by finite strain calculations. From these data and from the calculated compression behaviour, the bulk modulus of β -Ba(OH)₂ has been obtained. The finite strain calculation yields $B = 48.1(4)$ GPa, while the equation of state gives $B = 40.7(1.5)$ GPa and a pressure derivative of B, $B' = 4.9$. The agreement with the experimental value ($B = 39.5(1.3)$) [2] obtained by fixing B to a value of 6 and fitting only data points below the expected phase transition is satisfactory.

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- [1] Milman et al. (2000) Int. J. Quantum Chem. 77, 895-910 [2] Friedrich (2001) Acta Cryst. B 57, 747-758

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