Solid solution of lamellar metal-metal hydroxi salts with varying interlayer anions borate, chloride and sulfate containing different water contents

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LDH-phases are forming lamellar layered crystal structures with positively charged main layers and negatively charged interlayers. These phases can generally be given as $[Me_{(1-x)}^{2+}\ Me_{(x)}^{3+}\ (OH)_2]^{x+}\ [A_{(x/y)}^{y-} \cdot mH_2O]^{x-}$. Additionally, Lithium (1+) can be incorporated in the structure instead of the metals (2+). The interlayer consists of different anions and varying amounts of water, depending on the anion and temperature. Additionally, the interlayer can contain uncharged amounts of alkali salts like sodium sulfate. Some of these phases form natural analogues and are summarized in the so called hydrotalcite group with magnesium as main element. Boron containing phases are of high interest because of the retarding admixture effect in cement hydration. Also Boron is important concerning the immobilization of radioactive waste using cementitious materials. In table 1 the components of the different anion containing systems are described.

Tab.1.: Lattice parameters of relevant components of LDH-phases

Composition of phases	Lattice parameter a_o in pm	Lattice parameter b_o in pm	Lattice parameter c_o in pm	Lattice parameter ß in ° (monoclinic) α,ß,γ in ° (triclinic)
$3CaO{\cdot}Al_2O_3{\cdot}CaHBO_3{\cdot}11.5H_2O$	1000.5	576.5	1684.0	101.30
α-$3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$	997.2	573.6	1627.4	104.35
ß-$3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$	573.8	------	4688.4	--------
$3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}14H_2O$	575.5	-------	2867.8	--------
$3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$	576.4	--------	2685.2	------
$3CaO{\cdot}\ Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$	578.3	573.8	785.5	92.64/101.96/120.1
α-$3CaO{\cdot}Al_2O_3{\cdot}Ca(OH)_2{\cdot}11H_2O$	575.5	------	9527.2	------
α-$3CaO{\cdot}Al_2O_3{\cdot}Ca(OH)_2{\cdot}18H_2O$	575.5	---------	6402.0	---------

The crystal structure of the relevant boron containing phase was determined by [1], whereas the boron containing LDH phases at various temperatures were investigated by [2]. In presence of other anions like carbonate, chloride or sulfate different solid solutions can be formed and some limited compositions exist :

$3CaO{\cdot}Al_2O_3{\cdot}(1-x)CaHBO_3{\cdot}(x)CaSO_4{\cdot}12H_2O$ with $0.83 < x < 1$

$3CaO{\cdot}Al_2O_3{\cdot}0.34CaHBO_3{\cdot}0.66\ CaCO_3{\cdot}13.6\ H_2O$ with $0 < x < 0.66$

$3CaO{\cdot}Al_2O_3{\cdot}(1-x)CaHBO_3{\cdot}(x)CaCl_2{\cdot}(11.5-1.5)H_2O$ with $0.17 < x < 1$

Also ternary solid solutions could be established: $[Ca_4(Al(OH)_6)_2]\ [(1-x)HBO_3{\cdot}(x-y)CO_3\ (2y)OH{\cdot}(m)H_2O]$ with $0 < x < 0.66$ and $y > 0$

[1] Champenois, J.-B., Abdel Mesbah, Céline Cau Dit Coumes, Renaudin, G., Leroux, F., Mercier,C., Revel, B., Damidot,D.: Crystal structures of Boro-AFm and Boro-AFt phases, CCR 42, (2012), 1362-1370

[2] Pöllmann, H. & Wenda, R.: Fixation of Borate-anions in lamellar AFm-phases in the system CaO - Al_2O_3 - B_2O_3 - H_2O at 20 ° C, 40 ° C and 50 ° C, Journal of solid state chemistry,286, (2020)