Layered double hydroxides (LDHs) consist of alternate positively charged mixed metal hydroxide layers and negative charged interlayer anions. Usually these materials can be formulated as [M\text{II}_{x}M\text{III}_{y}(OH)_{z}][A_{m}\text{Cl}_{n}]m\text{H}_{2}\text{O} with z = 2*, M = bi- and trivalent metallic elements, A = organic or inorganic anion and m = amount of interlayer H\text{2}O depending on the temperature, relative humidity and hydration level. Two well known and described LDHs are [M\text{g}_2\text{Al}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O} [1] and [L\text{i}_2\text{Al}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O} [2], which are the end members in this mixed crystal series. Due to the diagonal relationship in the periodic system between Li and Mg and the chemical similarities of Li / Mg containing salts, there is a possibility to produce a LDH containing Li. Using a stoichiometric ratio of Li / Mg / Al resulted in 100% of Mg were used to form a LDH phase but only 10% of Mg Li containing LDH phases but a peak shift of the h0l peaks (Fig. 4/5).

The synthesis were done in 35ml autoclaves by mixing solutions of LiCl, MgCl\text{2}, 6\text{H}_2\text{O and AlCl}_3, 6\text{H}_2\text{O}, adding NaOH until a basic pH was reached and heating it up for a specific amount of time. A series of experiments with different temperatures (100°C – 160°C), pH (8,5 – 9,5), stoichiometric ratios, synthesis time (10 – 48h) and W/S ratio were performed. Starting with the Mg end member, the amount of Li was raised and the amount of Mg was reduced in 10 mol% steps until 100 mol% Mg was reached. Following experiments were in the area between 90 mol% Li and 100 mol% Li with 2 mol% reduction steps. The products were filtered, washed and dried (RH 30%).

The analysis of every solid solution LDH was done by X-Ray Diffraction (PANalytical) , Infrared Spectroscopy, Thermogravimetric Analysis and ICP-OES. The XRD results (Fig. 4) were used to investigate and calculate the lattice parameter of the different LDHs. TG and IR results show the amount of interlayer water and the possible carbonatization of the product.

Investigations of the lattice parameter (a) of the products using an exact stoichiometric ratio of Li / Mg / Al resulted in the solid solutions of MgO LDH has been reached. Two well known and described LDHs are [Mg\text{II}_2\text{Al}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O solid solution, test series with different temperatures (100°C – 160°C), pH (8,5 – 9,5), stoichiometric ratios, synthesis time (10 – 48h) and W/S ratio 1:5].

By investigating the h0l peaks, it is possible to distinguish a separation in the two different phases [Mg\text{II}_2\text{Al}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O (K3m) and [L\text{i}_2\text{Al}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O (P6/m) from one solid solution phase. From 10 to 80 mol% Li is a separation in two phases, at 90 mol% Li no separation is visible (Fig. 1/2). The angular area for the 710 (Mg containing LDH) and 300 (Li containing LDH) peaks of the separated phases (10 – 80 mol% Li) are at the same area like the end members. Test series from 90 to 100 mol% (at 120°C synthesis time) Li show that there is no separation in two different LDH phases but a peak shift of the h0l peaks (Fig. 4/5). This peak shift follows nearly the ideal line of a theoretical solid solution. All test series with synthesis temperatures from 100°C to 170°C show peak shifts and no separation of two phases (Fig 6). The optimum result is 120°C. Temperatures higher than 140°C result in the formation of a LDH phase with higher Mg amounts next to the Al(OH) phase. Investigations of the lattice parameter (a) of the products (Fig. 7) and the shift of the 010, 002 and 012 peaks (at 100°C synthesis temperature) are shown in Table 1. The amount of interlayer water was determined by TGA and lies between 1,8 and 1,9mol.

Conclusions

It is possible to synthesise a [Li\text{II}_2\text{Mg\text{II}_2\text{Al}_2}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O solid solution LDH from 90 to 100 mol% Li. Using more than 10 mol% Mg in the reactant leads to the parallel creation of [Mg\text{II}_2\text{Al}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O and [L\text{i}_2\text{Al}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O. Optimal results for solid solution are at 120°C, pH 9,5, W/F 15:1, 20h synthesis time. The pure solid solution without AlO(OH) phases and with the highest Mg content is [Li\text{II}_2\text{Mg\text{II}_2\text{Al}_2}(\text{OH})_4\text{Cl}]m\text{H}_2\text{O at 120°C.}}

References
