Synthesis and characterization of a [Li$_{1+x}$Mg$_{2-2x}$Al$_{1-2x}$OH$_2$]Cl$_x$·mH$_2$O solid solution LDH

A. Nitsch, H. Pöllmann
University of Halle, Mineralogy/Geochemistry, 06120 Halle, Germany

Introduction

Layered double hydroxides (LDHs) consist of alternate positively charged mixed metal hydroxide layers and negative charged interlayer anions. The stoichiometry of these materials can be formulated as [M$^{2+}$, M$^{3+}$·(OH)$_2$]$_y$[(A$^-$, B$^{3+}$)x·H$^-$]·nH$_2$O with $z = 2$, M = bi- and trivalent metallic elements, A = organic or inorganic anion and m = amount of interlayer H$_2$O depending on the temperature, relative humidity and hydroxide concentration. The special case are phases with M$^{2+}$ to 100% (Li$^+$) and M$^{3+}$ to 100% (Al$^3+$). The ratio between M$^{2+}$ and M$^{3+}$ (z = 2) can vary strongly [1] depending which metal ion is used. The structure of Al(OH)$_2$ is built up of double layered sheets of hexagonally packed O atoms. Two thirds of the octahedral holes are occupied by Al atoms. Using LiX as the reaction partner leads to the formation of [LiAl$_2$(OH)$_6$]Cl with Li$^+$ cations entering the vacancies in the aluminium hydroxide layers and X entering the interlayer space. In the brucite-like structure of [MgAl(OH)$_2$]Cl·mH$_2$O, Mg$^{2+}$ is octahedrally coordinated to six OH$^-$ anions. The distance between Li$^+$ and O$^{2-}$ ions in a [LiAl(OH)$_2$]Cl·mH$_2$O LDH is 2.129 Å [2] and between Al$^{3+}$ and O$^{2-}$ is 1.926 Å [3]. In a Mg$_2$Al(OH)$_6$Cl·mH$_2$O LDH, Mg$^{2+}$ and Al$^{3+}$ ions occupy the same positions with the same distance of 2.013 Å between the cations and O$^{2-}$. Comparing both structures, it should be possible for Mg$^{2+}$ ions to occupy the Al$^{3+}$ and the Li$^+$ position in the solid solution.

Synthesis & Characterization

The synthesis were done in 35 ml autoclaves by mixing solutions of LiCl, MgCl$_2$, 6H$_2$O and AlCl$_3$, 6H$_2$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, 120 °C, 140 °C, 160 °C), pH (8.5 – 9.5). Stoichiometric ratios, synthesis time (10 – 48 h) 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 mole % steps until 100 mole % Li was reached. Following experiments were done in the area between 90 mole % Li and 100 mole % Li with 2 mole % reduction steps. The products were filtered, washed and dried (RH 30%).

The analysis of every solid solution LDH was done by X-Ray Diffraction (PANanalytical), Infrared Spectroscopy, Thermogravimetric Analysis and ICP-OES. The XRD results (Fig. 4) were used to calculate the lattice parameter of the different LDHs by least square refinement. TG and IR results show the amount of interlayer water and the possible carbonatization of the product. Furthermore Scanning Electron Microscope images were taken to characterize the shape of the synthesized LDHs (Fig. 8).

Results

To find a stable area for a [Li$_{1+x}$Mg$_{2-2x}$Al$_{1-2x}$OH$_2$]Cl·mH$_2$O solid solution, test series with different parameters (pH, temp., time, W/S) were done. The best result for pH was 9.5, for the synthesis time 10 h, for the temperature 120 °C and the W/S ratio 15/1. By investigating the XRD peaks, it is possible to see the separation in a Mg$^{2+}$ dominated and an Al$^{3+}$ dominated solid solution between 10 and 80 mole %. At 90 mole % Li no separation is visible (Fig. 1/2/3).

The XRD and XRD patterns measured at 100 °C, 120 °C and 140 °C show peak shifts and no separation. The optimal result was achieved at 120 °C. Temperatures higher than 140 °C resulting in the formation of a AIO(OH) phase next to the LDH phase. Investigations of the lattice parameter (a) of the products show a straight decrease from 5.10A (100 mole % Li) to 5.08A (90 mole % Li) as expected. The space group was determined as P6$_3$/m for all products. To calculate the chemical formula, the products were dissolved in nitric acid and investigated with ICP-OES. Examples for 120 °C are shown in Table 1. Based on the assumption that Mg$^{2+}$ ions can occupy the positions of Li$^+$ and Al$^{3+}$ because of the fitting bonding length and the determined hexagonal P6$_3$/m space group, the structure of the pure phased solid solution should be identical with the pure Li-LDH (Fig. 6). If Mg$^{2+}$ ions could only occupy the position of the Li$^+$ ions, a reduction of the Li$^+$ amount in the solid solution would be the case while the amount of Al$^{3+}$ would not change, or they would exchange only with Al$^{3+}$ ions with the opposite result. The results of this work show, that in fact Mg$^{2+}$ ions have to be statistically distributed with 5 mole % on the Li$^+$ and 5 mole % on the Al$^{3+}$ position to provide the measured chemical formula.

Conclusions

It is possible to synthesise a pure [Li$_{1+x}$Mg$_{2-2x}$Al$_{1-2x}$OH$_2$]Cl·mH$_2$O solid solution using autoclaves with temperatures of 100 °C, 120 °C and 140 °C with a maximum amount of 10 mole % Mg$^{2+}$. Using more Mg$^{2+}$ in the reactant leads to a parallel formation of an Mg$^{2+}$ dominated and an Li$^+$ dominated solid solution. Optimal results for a pure solid solution can be achieved at 120 °C, pH 9.5, S/W 1:1.5, 10 h synthesis time. Temperatures above 140 °C provide the formation of an Al(OH) phase. The solid solution with the highest Mg$^{2+}$ content has the chemical formula [Li$_{0.98}$Mg$_{0.04}$Al$_{1.98}$](OH)$_2$·Cl·0.50H$_2$O.

References