Anion incorporation into layered solids

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Experiment Overview

Many inorganic solids have spaces or voids in their structure. Where these voids are of the appropriate size and geometry molecules (guests) can be captured by the inorganic lattice (host). In a layered structure guests can be incorporated as guests in the gaps between layers. These 2-dimensional voids are flexible, and the gap between layers or interlamellar spacing depends on the size of the guest molecule that is incorporated.

The layered compounds of interest here are those termed layered double hydroxides. As the name suggests, these compounds are hydroxides, have a layered structure, and include two different metal cations. The most widely studied class of these materials is the hydrotalcite group of minerals: these have the general formula [Mg1-xAlx(OH)2]•[An-x/n•zH2O], where the ratio of Mg:Al varies from 4:1 to 2:1 (0.20<=x<=0.33), and An- can be a range of different anionic species. The anions in these structures can be readily exchanged with alternative anions, to give new intercalation compounds. Hydrotalcite type materials are typically poorly crystalline, as well as having a variable stoichiometry, which can complicate investigation of their properties.

In contrast, layered double hydroxide materials with well defined structures and highly crystalline structures can be synthesised from gibbsite, one of the structural modifications of Al(OH)3. Gibbsite itself is a layered compound, and reaction with LiCl yields the layered double hydroxide [LiAl2(OH)6]Cl.H2O. This material is a well defined crystalline solid, and the structure of the dehydrated compound has been determined using X-ray diffraction methods (Fig 1).

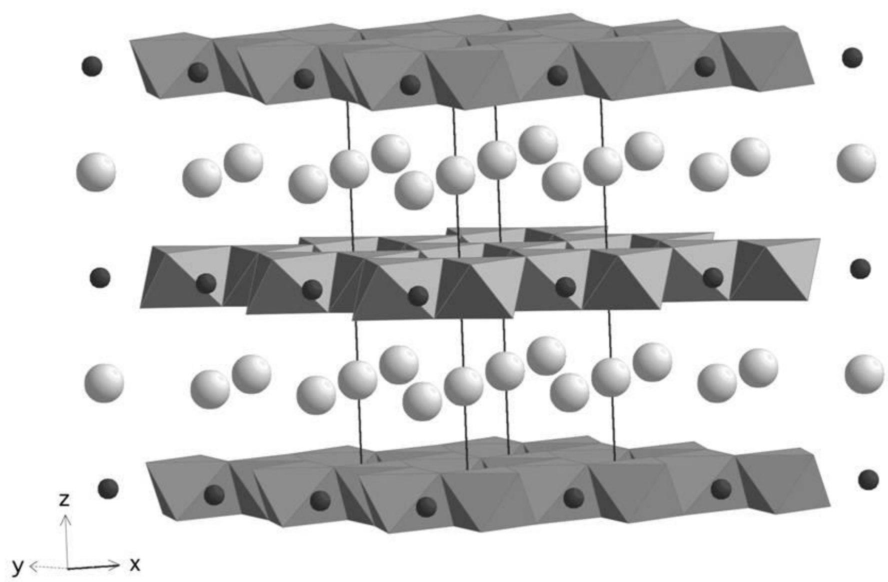

Fig 1 Structure of [LiAl2(OH)6]Cl, showing chloride anions between the layers; dark spheres are lithium, aluminium cations shown as octahedral polyhedra.

Learning Experience

This experiment was developed from industry-focussed research conducted at the home institution. It provides an introduction to layered solids and the phenomenon of intercalation with coupled interpretation of analytical data. It also utilises materials (gibbsite) produced in a regionally significant industry.

Aims and Objectives

- Determine the uptake of ferricyanide from the mother liquor by anion exchange for chloride within the layered double hydroxide by UV-Vis spectrophotometry and Atomic Absorption Spectrophotometry.
- Calculate the interlamellar spacing in the starting material and product by interpretation of powder X-ray diffraction patterns.
- Relate these results to the phenomenon of intercalation and the inherent crystalline structures of the starting material and product.

Level of Experiment

Third year inorganic or materials chemistry.

Keyword Descriptions of the Experiment

Domain
Inorganic Chemistry, Analytical Chemistry

Specific Descriptors
intercalation, layered solids, materials characterisation, alumina industry

Course Context and Prerequisite Knowledge and Skills

The students undertake in this unit (Inorganic Chemistry 301) a series of modules (4 x 6 lectures) on modern concepts in inorganic chemistry. Two of these lecture series currently taken (techniques in solid state characterisation and crystallisation) directly relate to this experiment. Students are expected to be able to visualise three-dimensional crystal structures and relate these structures through Bragg equation to the powder X-ray diffraction pattern.

Time Required to Complete

Prior to Lab: 2 hours of reading (references supplied)
In Laboratory: 2 hours

Comments

This experiment is undertaken concurrently with another solid-state materials experiment on formation of a clathrate with sulfur dioxide and quinol.

References

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