

BOOK OF ABSTRACTS



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Optimized time-resolved photoluminescence detection of rare earth elements in apatites and calcites

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Photoluminescence (PL) is effective and fast way to analyse the occurrence of luminescence activators in minerals. Especially interesting are the rare earth element (REE) activators, which are considered as critical raw materials for the EU and important for the modern society and technology. REEs show several narrow luminescence bands at relatively constant emission wavelengths. The host mineral, however, may contain other interfering activators, like Mn²⁺-ions, which can hinder the detection of luminescence of REEs.

In this research, we demonstrate that by selecting optimal PL measurement parameters, including excitation wavelength and detection wavelength range, and applying time-resolved detection in the analysis of natural calcite and apatite samples, the different REEs can be recognized and the spectral interference can be minimized. Comparison of REE luminescence in apatite and calcite in carbonatite samples is presented.

The effect of M(II)/M(III) molar ratio on the LDH structure derived from chemicals and minerals: a spectroscopic study using FTIR, Raman and XPS

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Layered double hydroxides (LDH) is a supergroup of crystalline non-silicate hydroxides with the following general formula: $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+} [A^{n-}]_{x/n} \cdot x y H_2O$. Due to similarities with clay minerals they are called 'anionic clays'. Their structure comprises positively-charged brucite-like layers balanced with the intercalated hydrated anions. LDH have perfect anion exchange properties, therefore they are promising materials for the wastewater treatment. Two most common LDH groups are hydrotalcites and pyroaurites with Mg/Al and Mg/Fe chemistry, respectively. They are rare in nature, however synthesis can be easily carried out in the laboratory conditions. However, the synthesis involving chemical reagents is expensive, therefore in this work, the synthesis was done by transformation of abundant minerals (magnesite [M] and dolomite [D]), which were a source of Mg. Mg/Al LDH and Mg/Fe LDH were synthesized via the co-precipitation method in different variants including three M(II)/M(III) molar ratios and two ageing times. The goal was to characterize these materials and to get insight into structural differences which may affect the sorption affinity towards aqueous anions.

For the synthesis, M and D were used as M(II) source, while $AlCl_3 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ were used as M(III) source. Reference materials were synthesized from chemical reagents with $MgCl_2 \cdot 6H_2O$ and appropriate Al and Fe chlorides. Firstly, M and D were dissolved in order to release M(II) in $AlCl_3$ via the hydrolysis process in the case of Mg/Al LDH, or in HCl in the case of Mg/Fe LDH. Then, solution of both M(II) and M(III) was added dropwise to the 2 M NaCl solution, with constantly controlled pH=10 with NaOH aqueous solution. The formed precipitates were aged for 2 or 24 h, washed and dried at 60°C overnight. The obtained phases were investigated with XRD, FTIR, Raman spectroscopy and XPS.

The XRD confirmed the presence of hydrotalcite, with admixtures of gibbsite and calcite for the Mg/Al LDH and pyroaurite for the Mg/Fe LDH in all samples. The FTIR spectra showed bands attributed to the water content and carbonates, as well as lattice vibrations. Differences were observed in positions of bands related to carbonates in the region of 1510-1360 cm^{-1} for the materials with different molar ratio. Two carbonate species were identified: monodentate carbonate and bicarbonate in the interlayer space of LDH. The results were confirmed by Raman spectroscopy, where different band positions were observed in the region of 1370-1320 cm^{-1} . Both FTIR and Raman spectroscopy showed differences in the region related to lattice vibrations. The C1s XPS spectra displayed the presence of monodentate carbonates and bicarbonates in the samples. Moreover, a chemical shift of Mg1s was observed as a result of increasing content of Mg-O-Mg bonds with increasing molar ratio.

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