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Basaluminite structure and its environmental implications

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Abstract

Basaluminite is a nanocrystalline aluminum oxyhydrosulfate of important environmental implications. It is present in areas affected by acid mine drainage and acid sulfate soils, where potential toxic elements present in solution, such as Cu and As, can be retained by co-precipitation or adsorption onto it. Basaluminite has been described as a nanomineral variety of felsöbányaite. In the present study, high-energy X-ray diffraction (HEXD) and extended X-ray adsorption fine structure (EXAFS) experiments were performed to determine the local order of basaluminite nanoparticles. Pair distribution function (PDF) analyses showed that both synthetic and natural basaluminite have identical short-range order, with 1 nm coherent domain size. PDFs also show strong similarities between the local order of basaluminite and felsobanyaite. On the other hand, S K-edge EXAFS showed different structural coordination between natural and synthetic basaluminite, where sulfate in the natural phase were coordinated in outer-sphere positions whereas inner-sphere sulfate was observed in the synthetic samples. Preliminary results indicated that basaluminite is a highly defective felsobanyaite mineral nanoparticle. This nanocrystalline character has therefore important implication in terms of stability in natural condition and contaminant mobility in stream affected by acid sulfate water.

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1. Introduction

Basaluminite is the name that receives the white precipitate formed in streams affected by acid mine drainage (AMD) and in acid solid soils (ASS), with high aluminum and sulfate concentrations in solution when pH values are around 4.5[1]. Basaluminite has important environmental implications since this mineral shows high affinity by

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potentially hazardous elements present in solution (e.g. Cu and As) in basins impacted by AMD and ASS[2,3]. As described by[4] basaluminite as the nanomineral variety of felsöbányaite ($Al_4(OH)_{10}(SO_4)\cdot 4H_2O$), a rare mineral (space group $P2_1$-C_2^2). However, previous researches have indicated that nanoparticles may contain high levels of structural disorder that can substantially modify material properties and thus cannot solely be considered as small piece of a bulk material.[5] On the other hand, while basaluminite has been disaccredited as a mineral by International Mineralogical Association (IMA), hydrobasaluminite, the hydrated variety of basaluminite, is still considered as a mineral. The main aims of the present study are: (1) to characterize the local structure of basaluminite and (2) to indicate its differences and similarities with felsöbányaite. To this end, high-energy X-ray diffraction (HEXD) and extended X-ray adsorption fine structure (EXAFS) experiments in the S K-edge were performed in natural and synthetic samples of felsöbányaite and basaluminite, in order to determine the local order and to establish the sulfate coordination in the structure.

2. Materials and methods

2.1. Solid samples

Three types of Al-phases were used in this study: natural felsöbányaite, and synthetic and natural basaluminite. A sample of natural felsöbányaite from the Felsöbányaite region (Romania) was obtained from a private collection. Natural basaluminite was obtained by slow titration under continuous stirring of an AMD solution, from the Perrunal abandoned mine (Iberian Pyrite Belt, SW Spain), with $Ca(OH)_2$ 0.01 M until pH 5, removing previously the iron precipitates, as described by [3]. Synthetic basaluminite was prepared by drop-by-drop addition of 214 mL of a 0.015 M $Ca(OH)_2$ solution to 30 mL of 0.05 M $Al_2(SO_4)_3\cdot 18H_2O$ in continuous stirring. These precipitates were washed several times with deionized and freeze-dried. After drying, the samples were digested in aqua regia for further chemical analysis.

2.2. Analytical techniques

HEXD experiments were performed at the beamline ID31 of the European Synchrotron Radiation Facility (ESRF; Grenoble, France). Powder samples were loaded into polyamide (Kapton) capillaries. Sample and background measurements were carried out at room temperature in a q-range of 0-25 $Å^{-1}$. Incident X-rays had an energy of 69.5 KeV (λ = 0.1784 Å). Structure factors and pair distribution functions (PDF) were obtained using the PDFGetX3 software[6]. EXAFS data was collected for natural and synthetic basaluminite at the XAFS (11.1) beamline of the ELETTRA Synchrotron Light Source (Trieste, Italy). Spectra were collected at the sulfur K-edge (2485 eV) in fluorescence scan mode at a temperature of 100º K. EXAFS data reduction was performed using the Athena and Artemis softwares of the IFFEFIT package[7]. Statistical F-tests were applied to determine the statistical significance of different tested hypothesis.

3. Results and discussion

3.1. HEXD results

PDFs of natural felsöbányaite and of natural and synthetic basaluminite are shown in Figure 1 together with calculated PDFs of felsöbányaite[4] along with its respective partial-PDFs (Al-Al, Al-O, Al-S, S-S, S-O and O-O atom pairs). PDFs of synthetic and natural basaluminite revealed that the synthesis process yields nanoparticles with similar local order than the natural samples. Particle size of both basaluminite types and of felsöbányaite were fitted with a size-function reproducing particles of spherical shape[8]. Basaluminite showed identical coherent domain sizes in both natural and synthetic samples, with a nanoparticle diameter of 1 nm, while the particle diameter obtained for the felsöbányaite sample was in the range of 4-5 nm. PDFs of both felsöbányaite and basaluminite exhibited similar structural features in the region between 1 and 6 Å, with significant variations in peak intensities and width. Both basaluminite and felsöbányaite PDFs were compared in order to identify similarities and to associate individual peaks to interatomic distances using the calculated pair PDFs of felsobanyaite. The position of the first peak at 1.45 Å corresponded to the S-O distance in the sulfate tetrahedron, whereas the second peak at 1.88 Å was attributed to