P10.06.47

X-ray single-crystal study on partially guest-free melanophlogite
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Melanophlogite (MGP), 23SiO₄ · M¹²⁺ · M¹⁴⁺ (Z = 8 for low MGP and 2 for high MGP), is a silica clathrate mineral. MGP can accommodate small gas molecules (CO₂, CH₄, N₂, etc.) in two kinds of cage-like voids, M¹²⁺ and M¹⁴⁺. The single-crystals of guest-free MGP (GF-MGP) were obtained by heating natural guest-bearing MGP from Mt. Hamilton, California, USA at 950 or 1000°C for 6 hours. The crystal structure of GF-MGP at five different temperatures, -50, 23, 100, 200 and 400°C, was investigated by the X-ray single-crystal diffractions, which showed cubic symmetry at the five temperatures. Although Liu et al. (1997) suggested two phase transitions in NMR experiments, Pm-3n gave the most satisfactory results at all the temperatures in our study. Difference-Fourier maps, where Fc includes only framework atoms Si and O, showed that positive electron densities remained in the cages (Figure 1). It has been a common practice for the guest-molecule to substitute their form factor with those of dummy atoms having comparable numbers of electrons and sizes. The refinement using F and Mg as dummy resulted to 32.3% for M¹²⁺ and 84.8% for M¹⁴⁺ at 100°C as the occupancy factors.

Keywords: clathrate compounds, silica, single-crystal X-ray crystallography

P10.07.50

Ab initio calculation on the smallest perfect mineral: Nano-ball allophane
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Recent advancement in computer hardware and software has made it possible to perform quantum chemical calculations on large molecules. In the present study, the first principle density functional theory (DFT) method was applied to calculate the quantum chemistry properties of a small molecule, nano-ball allophane.

Keywords: ab initio DFT, quantum chemistry, nano-ball allophane
Nano-ball allophane is a naturally occurring aluminum silicate mineral with hollow spherical morphology. Diameter of the mineral is observed as 3.5 to 5.0 nm with TEM, and cation exchange experiments have proven the existence of some pores along the spherule wall. Chemical structure of the wall is similar to that of imogolite with nano-tube structure, where orthosilicates are bonded inside of gibbsite vacant site (imogolite sheet). However, whole chemical structure of the nano-ball has not been clarified. We succeeded to tentatively construct the whole chemical structure of the ball by assuming an expanded truncated octahedron composed of hexagonal imogolite sheets. By changing size of the imogolite sheets, diameters of the ball become 1.5 nm, 3.0 nm, 4.5 nm, and so on. Here we present full-structural optimization results for the nano-ball with diameter of 1.5 nm. Gaussian 03 for UNIX revision C.01 with HF/6-31G(d) method was used for calculations. The 6-coordinated Al and the 4-coordinated Si atom in the optimized structure were stable and no change in its ball shape structure. The calculated O···O atom distance in the vacant octahedral site that is substituted with orthosilicate has average value of 2.62 Å. Meanwhile, in the outer vacant octahedral sheet, the distance has average value of 4.25 Å. For Ca(B,C)₆ the smallest of nano-ball allophane is stable and possible exists in the soil natural environmental.

Keywords: nano-ball allophane, ab initio, perfect mineral

Crystal structures and diffuse scattering of compounds with graphite-like (B,C)-nets

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The crystal structures of the new compounds Ca(B,C)₆ (hexagonal, a = 4.563(1)Å, c = 4.396(1)Å) and Ca(B,C)₈ (hexagonal, a = 2.588(1)Å, c = 4.434(1)Å) were determined from powder diffraction data. The compounds consist of planar graphite-like (B,C)-nets, intercalated by calcium atoms. In Ca(B,C)₆, one third of the hexagonal prismatic voids formed by the (B,C)-layers is occupied by Ca. In Ca(B,C)₈, the Ca-atoms are disordered, which gives rise to honeycomb-like diffuse scattering visible in the electron diffraction pattern (Fig.1a). A model for the calcium distribution was developed and the diffuse scattering could be simulated successfully with the program DISCUS [1] (Fig. 1b).

Keywords: diffuse diffraction, powder diffraction, intercalation chemistry

Preparation of ferrites MFe₂O₄ (M=Co,Ni) nanoporous ribbons structure and their magnetic properties

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Spinel ferrites, MFe₂O₄ (M=Co,Ni), ribbons with nanoporous structure were prepared by electrospinning combined with sol-gel technology. The ribbons were formed through the agglomeration of magnetic nanoparticles with PVP as structure directing template. The length of the polycrystalline ribbons can reach several hundred micrometers and the width of the ribbons can be tuned from several micrometers to several hundred nanometers by changing the concentration of precursor. Nanoporous structure was formed during the decomposition of PVP and inorganic salts. The ribbons exhibited weak saturation magnetizations and low coercivities at room temperature, but at low temperature, saturation magnetizations and coercivities increased a lot, especially for CoFe₂O₄ ribbons, reaching to 72 emu/g and 1.45 T at 2 K respectively. These novel magnetic ribbons can potentially be used in micro/nano electronic devices, magnetic sensors and flexible magnets.

Keywords: synthesis inorganic, magnetic oxides, ferrites