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Glowing synthetic chlorohectorite: The luminescent features of a trioctahedral clay mineral

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ABSTRACT

Clay minerals are versatile materials with numerous industrial applications. Their unique layered structure can act as a host for many optically active species. The synthesis and luminescence properties of chlorohectorite clays are now reported for the first time. The synthesized clays are composed of quasi-circular nanoparticles with diameters around 20–30 nm showing blue/green emission and persistent luminescence with a duration of ca. 5 s. The luminescence features are associated with titanium impurities in the chlorohectorite structure. It is shown that Ti can act as activator ion even at low concentrations: the XRF and ICP-MS measurements of the chlorohectorite materials indicate a Ti concentration around 60 ppm originating from the precursors. The XPS measurements of the clay materials showed the Ti $2p_{3/2}$ signals at 457.8 and 458.9 eV associated with Ti^{3+} and Ti^{IV}, respectively. The excitation spectra confirm Ti^{3+} as the luminescent center in the chlorohectorites through the bands at 287 and 370 nm, related to the $e^{-}(O^{2-}(2p)) \rightarrow Ti^{IV}$ charge transfer and the electronic transitions from the t_{2g} to e_g levels of Ti^{3+}, respectively. The persistent luminescence properties are due to structural defects common for layered silicates.

1. Introduction

Luminescence is a phenomenon where a material converts different radiation, particle, chemical, thermal or electric energy into electromagnetic radiation in the ultraviolet, visible or infrared regions [1]. The occurrence of luminescence requires the existence of a system composed of a host lattice and a luminescent center (activator). Both components are of equal importance [2] since even the best activators (*e.g.* Eu^{3+} or Tb^{3+}) cannot luminesce if the host's electronic structure and/or lattice vibration energies are not appropriate.

The clay minerals represent an attractive class of potential host matrices for optically active ions due to their capability of intercalating additional species (molecules or ions) into their interlayer space [3,4]. Previously, luminescent materials have been produced by intercalating synthetic clays with organic complexes of Eu^{3+} [5–7], Tb^{3+} [6] or with PbF_2:Yb^{3+},Er^{3+} [8]. These luminescent materials show different possibilities for applications in *e.g.* the production of highly photo- and thermo- stable nanocomposites [5,6], photon up-conversion [8], and enhanced latent fingerprint detection [7]. Moreover, the versatile structure of the clay minerals plays an important role in the research of solar converters [9–14]. In addition to the intercalated clays, also non-intercalated clay minerals belonging to the smectite class have been reported to show luminescence, for instance kaolinite ($Al_2Si_2O_5(OH)_4$) [15–21], or montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$) [22–24] have been explored in luminescence studies.

In the present work, the clay studied is hectorite, a smectite type clay mineral. Its synthesis has been well explored, known through the patented commercial brand laponite® [25,26]. The hectorite structure is the T:O:T type (also called 2:1 type), *i.e.* it is composed of one sheet of edge-sharing $M(O,OH)_6$ octahedra (O) sandwiched between two sheets

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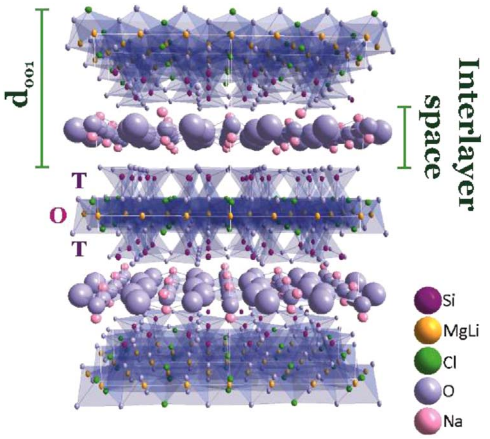

Fig. 1. A Diamond 3.2 (Crystal Impact, Bonn, Germany) view of the T:O:T clay structure (based on fluorohectorite structural data [31]).

of corner-sharing SiO_4 tetrahedra (T). These T:O:T units are connected by an interlayer space composed of hydrated Na^+ species (Fig. 1). The cation M may be either mono-, di- or trivalent [27], but the most common composition is $Na_{0.7}(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4$ [28]. Some variation in the composition may be found for example, when the OH^- groups are partially substituted by F^- generating the fluorohectorite [3,29]. The removal of the OH^- groups is important, when luminescence applications are intended, because the presence of the OH^- groups with high energy phonons (3500 cm^{-1}) may lead to quenching of luminescence by multiphonon de-excitation [2].

Synthetic chlorohectorite clays, hereafter referred to as Layered Silicates (Cl) (LS(Cl)), are presented here for the first time together with their luminescence properties. The LS(Cl) was obtained by replacing the OH^- ions with Cl^- in the octahedral units of hectorite while still retaining the T:O:T structure (Fig. 1). The materials introduced in the present work combine the advantages of the versatility of the clay minerals (*i.e.* inertness or reactivity, chemical and physical stability, selective catalytic activity and tailorable structure [30]) with luminescence. The effect of titanium doping was studied to confirm the role of Ti impurity as the emitter in the non-doped materials. It is also shown that the chlorohectorites yield short persistent luminescence demonstrating the capability of storing optical excitation energy, which should be a useful feature for solar cell applications.

2. Experimental

2.1. Synthesis and reference material

The LS(Cl) were synthesized in a reflux system at 100 °C using stoichiometric amounts of all reagents (except for a threefold excess of NaCl), in neutral or basic aqueous solutions. $LiClO_4$ (≥ 99.99%, Sigma-Aldrich, USA), NaCl (≥ 99.5%, J.T. Baker, USA), MgO (≥97%, Merck, DE) and SiO_2 (99.8%, Sigma-Aldrich, USA) were used as the precursors. Reflux was continued for 24 h in deionized water (neutral medium) or in a 0.01 $mmoldm^{-3}$ solution of NaOH (≥ 99%, Merck, DE) (basic medium, pH 12). Subsequently, all materials were vacuum filtered and washed with deionized water several times up to the total extinction of the Cl^- ions in the filtrate liquid (checked with the test with silver nitrate). Thereafter, the materials were dried at 200 °C for 12 h.

The LS(Cl) material in the neutral medium was doped with Ti in three steps. First, five homogeneous colloidal suspensions were generated by adding 0.1 g of neutral LS(Cl) into deionized water (10 cm^3), while continuously stirring and heating (30 min @ 50 °C). Then, stoichiometric amounts of 0.1 $moldm^{-3}$ solution of $TiCl_3$ were added to these suspensions to obtain 0.1, 0.5, 1.0, 1.5 and 2.0 mol-% of Ti^{3+} (relative to the Na^+ amount in the interlayer space). The suspensions were stirred and heated (3 h @ 200 °C) and then vacuum filtered and dried (12 h @ 200 °C).

The purified natural hectorite sample was obtained from Newberry Hectorite Mine (San Bernardino, California, USA).

2.2. Characterization

The crystal structure and purity of the products were verified with routine room temperature (RT) X-ray powder diffraction (XPD) measurements using a Huber G670 Guinier camera with an image plate detector and Cu $K_{\alpha 1}$ radiation. The crystallite size was calculated using the Scherrer formula (Eqs. 1 and 2):

$$D = 0.9\lambda/\beta cos\theta \tag{1}$$

$$\beta^2 = \beta_s^2 - \beta_r^2 \tag{2}$$

Where D (nm) is the average size of the crystallites, λ (Å) the X-ray wavelength, β (rad) the full width at half maximum (FWHM) of the (001) reflection and θ (°) half of the Bragg's angle (2θ) [32]. The reflection broadening (β_r) due to the diffractometer set-up was eliminated from the β_s–value by using a microcrystalline Si (NIST SRM 640d) reference.

The FTIR spectra of the materials were obtained at RT using two different equipment in the range of 400 to 4000 cm^{-1}: (i) a Nicolet Nexus 870 FTIR spectrometer, and (ii) a Bruker Vertex 70 spectrometer, equipped with a RT-DLaTGS detector, and a MVP Star Diamond ATR Accessory. In the former, the materials were mixed with KBr, pressed to transparent disks and measured in a transmission mode, while in the latter, the materials were studied as such in ATR mode.

The chemical composition and impurities were investigated with the X-ray fluorescence (XRF) measurements. The XRF spectra were obtained with a Panalytical Epsilon 1 apparatus using Ag K_α radiation (22.16 eV) and a high-resolution Si drift detector (with a typical energy resolution of 135 eV @ 5.9 keV / 1000 cps). The determination of the impurity Ti concentration was made for the neutral LS(Cl), with an ICP-MS instrument, PerkinElmer 6100 DRC Plus (Toronto, Canada), in quantitative mode.

The morphology of the chlorohectorites was analysed from the images obtained by a JEOL JSM-6701 F field emission scanning transmission electron microscope (STEM) operating at low voltage (30 kV). The samples were diluted in acetone for the analyses.

The photoluminescence emission and excitation spectra at RT were measured using a Varian Cary Eclipse Spectrophotometer. The excitation source was a 150 W Xe lamp. The luminescence decay curves were measured with the same spectrometer with the excitation and emission wavelengths equal to 255 and 490 nm, respectively. The valence of titanium was probed with X-ray photoelectron spectroscopy (XPS) measurements carried out using a Perkin-Elmer PHI 5400 spectrometer with a Mg Kα X-ray source (1253.6 eV) and a hemispherical electron energy analyser. The LS(Cl):Ti (2 mol-%) was analysed with a scanning step of 0.1 eV and pass-energy of 17.9 eV, by using 14.0 kV as the accelerating voltage in an Mg-anode. The curve fitting was carried out using Origin 2015 software (OriginLab, Northampton, USA).

The thermoluminescence (TL) measurements were made for all non-doped LS(Cl) with a MikroLab Thermoluminescent Materials Laboratory Reader RA'04 using a heating rate of 10 $°Cs^{-1}$. Before the measurements, the samples were irradiated for 5 min at RT with a 4 W UVGL-25 UV lamp at 255 nm. After turning off the irradiation, there was a delay of 5 s before the start of the measurement. The TL glow curves were measured in a range of 40 to 400 °C. Estimations of the trap energies were obtained with the initial rise method: $lnI = C - E_t/kT$, where I is the TL intensity, C is a constant including the frequency factor, E_t is the trap depth or activation energy, k Boltzmann constant and T temperature (in K) [33].