Applied Clay Science 118 (2015) 295–300

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

A new luminescent montmorillonite/borane nanocomposite

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ARTICLE INFO

Article history:
Received 27 March 2015
Received in revised form 7 October 2015
Accepted 8 October 2015
Available online 21 October 2015

Keywords:
Luminophore
Montmorillonite/borane nanocomposite
X-ray photoelectron spectroscopy
X-ray diffraction
UV–Vis spectra
Electrokinetic analysis

ABSTRACT

Herein we present the first luminescent montmorillonite/borane nanocomposite materials, formed by the modification of montmorillonite phyllosilicate matrices with cysteamine and the highly fluorescent boron hydride (borane) compound *anti*-$B_{18}H_{22}$. Immobilization of *anti*-$B_{18}H_{22}$ in small quantities into the montmorillonite matrix leads to materials with a luminescence that is dependent on the borane concentration. At the lower concentration exceeds even the fluorescence intensity of the original highly fluorescent borane compound. The use of layer silicate – a cheap and naturally-available mineral – as a carrier of the borane, which, on the contrary, does not occur naturally, reduces the amount of expensive borane required for useful luminescence in the solid-state and thus provides a less expensive luminophore. Is the first usage of a blue borane laser compound for nanocomposite with montmorillonite. For purposes of comparison we have also studied a bentonite/borane composite.

1. Introduction

Due to their unique structure and crystallochemical properties, phyllosilicates are very useful matrices for the preparation of various functional nanostructures via their intercalation and/or surface modification (for a detailed review see, e.g.: Čapková et al., 2003; Lagaly, 1986; Ogawa and Kuroda (1995); Schoonheydt, 2003). Such structural modifications of phyllosilicates by organic and/or inorganic species are usually affected either by thermal and/or chemical treatment (Matoušek et al., 2015). Intercalation and surface-anchoring of organic dyes into and/or onto phyllosilicates are a good means to tune the optical properties of these dyes, especially their photoluminescence, by the selection of a suitable phyllosilicate with appropriate silicate layer charge (Čapková et al., 2004; Čeklovský et al., 2009; Martynková et al., 2007; Klika et al., 2011). Such studies have revealed that the magnitude of the layer charge, and its distribution, are important parameters for determination of the structure and properties of phyllosilicate/organic dye nanocomposite materials. For example, (Klika et al., 2011), achieved a dramatic increase in the fluorescence intensity of methylene blue (MB) saturated montmorillonite (Mt) nanocomposites by reducing the Mt layer charge through the intercalation of lithium ions that subsequently limited the MB load in the matrix (Klika et al., 2009). Of these layered silicates, montmorillonites are especially convenient matrices for the preparation of nanocomposites that have a wide range of applications such as, for example, adsorbents, catalysts, photocatalysts, drug carriers, luminophores, antibacterial nanocomposites, etc. (Ray and Okamoto, 2003; Liu and Zhang, 2007). The particular suitability of Mt as a guest matrix for the intercalation of organic dyes is due to the facile isomorphous replacement of cations (Al → Mg) that occurs predominantly in the octahedral sheet. Consequently the intercalation of Mt is easily compared to other phyllosilicates, for example, vermiculite, that have mainly tetrahedral substitutions (Si → Al) (Tokarský et al., 2013).

One of the advantages of clay mineral based nanocomposites is the low cost of the clay mineral matrix that can accommodate various guest molecules, which keep their functions even at lower concentration then in their original state. In case of clay minerals the guest concentrations and their arrangement is ruled by the magnitude and distribution of the silicate layer charge (Klika et al., 2007; Klika et al., 2009). For intercalation and guest arrangement it is then very important to know whether the isomorphous substitution is in the octahedral or in the tetrahedral sheet.

We have recently become interested in the luminescence and photophysical properties of the boron hydride (borane), *anti*-$B_{18}H_{22}$ (Londesborough et al., 2012) and its derivatives (Sauri et al., 2013). *Anti*-$B_{18}H_{22}$ is a highly fluorescent material; its solutions emitting blue light on excitation with UV irradiation with a quantum yield close to unity (Londesborough et al., 2012). This fluorescence has been shown to withstand the stringent excitation pumping conditions required to achieve laser light emission, making *anti*-$B_{18}H_{22}$ the first boron hydride laser and, indeed, the first molecular inorganic laser material (Cerdán et al., 2015). The quasi-aromatic polyhedral structures that the boron

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http://dx.doi.org/10.1016/j.clay.2015.10.009
0169-1317/

hydrides form give compounds such as *anti*-$B_{18}H_{22}$ large potential for novel properties. In the case of the laser emission from *anti*-$B_{18}H_{22}$, this is manifested in its exceptionally high photostability compared to commercially available blue-emitting laser materials (Cerdán et al., 2015).

In this study we combined montmorillonite and *anti*-$B_{18}H_{22}$ to develop a new fluorescent composite. According to the previous experience and to the generally known fact the layer charge of silicates located in tetrahedral sheet of silicate layer very complicates the intercalation of large guest molecules. That is the reason why we have chosen the montmorillonite (Mt) with octahedral replacements as host matrix (Klika et al., 2007; Klika et al., 2009; Klika et al., 2011) which plays the most important role for the intercalation behavior and guest arrangement.

In addition the composition of silicates affects a charge and the charge subsequently influences the concentration of guest molecules. The higher concentration of guest molecules leads to and aggregation and subsequent quenching of fluorescence (Klika et al., 2007; Klika et al., 2009). Therefore we have also studied the dependence of borane concentration and we confirmed the above mentioned relation between concentration and luminescence intensity.

Consequently, it became our intention to combine the advantageous properties of Mt and *anti*-$B_{18}H_{22}$ (see Fig. 1 for graphical depictions) and prepare a novel thermally and mechanically stable Mt/borane luminescent nanocomposite material. Here the primary objective is to investigate whether the luminescent properties of *anti*-$B_{18}H_{22}$ are retained after introduction to the Mt matrix (and, for comparison, into bentonite as well), a goal that would provide a low-cost solid-state medium for the attractive photophysical properties of the borane. Hence, this work describes the preparation of such materials and their characterization by UV–Vis spectra, X-ray photoelectron microscopy (XPS), X-ray diffraction (XRD) and electrokinetic analysis.

2. Materials and methods

2.1. Material

Natural Na-montmorillonite (Mt) with the basal spacing $d = 12.5$ Å and crystallochemical formula: $Na_{0.25}$ $K_{0.07}$ $Ca_{0.10}$ $(Si_{4.0})$ $(Al_{1.45}$ $Fe^{3+}{}_{0.21}$ $Mg_{0.24}$ $Ti_{0.01})$ O_{10} $(OH)_2$ was used for the present experiments. Fig. 1 (right) presents the fragment of Mt structure, where Si – tetrahedra share oxygens with Al(Mg) – octahedra and Al → Mg isomorphous replacements cause the negative layer charge, compensated with interlayer cations. Also bentonite, the basal spacing also $d = 12.5$ Å (composition: SiO_2, 55–57%, Al_2O_3, 15.7–17.3%, Fe_2O_3, 0.1–1%, TiO_2, 3.8–6.3%, MnO, 0.1–0.3%, Na_2O, 0.1–0.4%, K_2O, 0.3–1.2%, Li_2O, 0.1%, P_2O_5, 0.1% and H_2O, 5.3–6.3%) was used for comparison. The chemical composition of Mt was determined by XRF (X-ray fluorescence analysis) and crystallochemical formula was calculated using method of Köster (1977).

2.2. Borane compounds preparation

Octadecaborane(22), *anti*-$B_{18}H_{22}$ (see Fig. 1, left) was synthesized by the hydrolysis of the hydronium ion salt of $[B_{20}H_{18}]_2$ according to the method described in the literature (Pitochelli and Hawthorne, 1962). Pure samples were obtained by repeated crystallizations from hot saturated *n*-hexane solutions and had ^1H and ^{11}B NMR and mass spectroscopic characteristics in agreement with the published data (Pitochelli and Hawthorne, 1962; Li and Sneddon, 2005; Plešek et al., 1967), experimental solution was characterized previously (Londesborough et al., 2010).

2.3. Montmorillonite and bentonite modification

2-Aminoethanethiol, (Cysteamine, $NH_2(CH_2)_2SH$, Sigma Aldrich, purity > 98%, CYS) was used for the first step of Mt intercalation and surface modification to obtain the amino-groups into/onto Mt, which facilitated the effective anchorage of borane compounds to the Mt (the second step of Mt modification). 500 mg of CYS was dissolved in 10 ml of distilled water and added to the vigorously stirred Mt (1.0 g, pH = 6.5). This mixture was subsequently stirred for 5 h, after which the mixture was filtered, washed three times with 10 ml of distilled water and the solid portion dried in air at 50 °C to a constant weight. To this powder 15 ml of freshly distilled dichloroethane was added and stirred. The dependence of borane compound as the guest molecule was tested. Solid borane, *anti*-$B_{18}H_{22}$, of three different amount, (i) 0.2, (ii) 0.6 and (iii) 1.1 mmol, was added into this mixture and the reaction mixture was stirred for 2 h, after which the mixture was filtered and washed three times with 10 ml of dichloromethane. Samples were dried to the constant weight under vacuum evaporation at 35 °C.

The bentonite was modified in the same way using only 0.3 mmol of *anti*-$B_{18}H_{22}$.

2.4. Characterization methods

The relative atoms concentration of all samples was determined by X-ray photoelectron spectroscopy (XPS). Omicron Nanotechnology

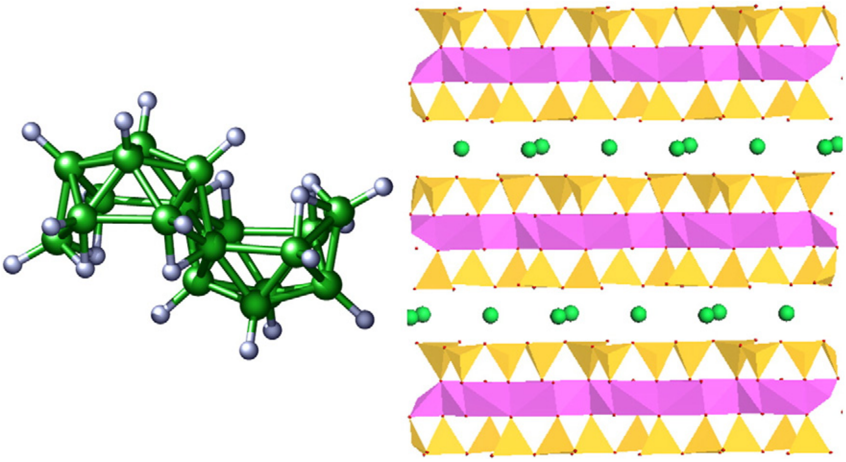

Fig. 1. The molecular structure of *anti*-$B_{18}H_{22}$ (left) as determined by single-crystal X-ray analysis (Simpson and Lipscomb, 1963), and a schematic of the layered structure of montmorillonite (right).