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Up-conversion luminescence – A new property in tenebrescent and persistent luminescent hackmanites

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ABSTRACT

The aim of this work was to broaden the optical properties of the synthetic mineral hackmanite by adding ytterbium and erbium dopants inside the hackmanite structure. By this addition we were able to achieve a synthetic hackmanite material capable of showing green and red up-conversion luminescence, blue/white photoluminescence, blue/white persistent luminescence as well as purple tenebrescence in one material. These optical properties can be obtained by exciting with different wavelengths making hackmanite a perfect candidate for optical multiplexing.

1. Introduction

Hackmanite is a mineral that has the structure of sodalite [1]. The general formula of hackmanite is $Na_8Al_6Si_6O_{24}(Cl,S)_2$ and thus the Cl/S ratio in the structure can be slightly modified when preparing synthetic hackmanites [2]. Hackmanite crystallizes in the cubic space group $P\bar{4}3n$ and it has the unit cell axis length of 8.877 (2) Å [1]. SiO_4 and AlO_4 tetrahedra form the basic net-structure of hackmanite. Inside the network cavities Cl^- and Na^+ ions form $(Na_4Cl)^{3+}$ entities (Fig. 1). Cl^- ions can partly be replaced by sulfur-containing ions such as S^{2-}, S_2^{2-} and SO_4^{2-}. This aliovalent substitution creates anion vacancies in the structure [3].

Hackmanites found in nature exhibit tenebrescence [4], luminescence [5,6] and sometimes also persistent luminescence [7]. Synthetic hackmanites have been reported to exhibit the same properties [2].

Tenebrescence, also known as photochromism, is a reversible color change induced by exposure to radiation [3]. It is defined as a reversible phototransformation between two states that have a difference in absorption spectra [8]. In a previous article [9] we have described the detailed mechanism of tenebrescence in hackmanites: high enough energy will transfer electrons from the $[Na_4(\square,S)]$ units' excited levels to the conduction band from where the electrons will transfer to chloride vacancies. This will form color centers, which can then absorb visible light resulting in the purple color of hackmanite. Absorbed energy (visible light) lifts electrons back to conduction band from where they can transfer back to the excited levels of the S_2^{2-} ion resulting in the loss of the purple color over time.

Photoluminescence is a process where a material absorbs energy and then emits the energy as light. Persistent luminescence, on the other hand, means a prolonged emission after the removal of the excitation source. There is no official definition for how long this emission lifetime should be to be considered as persistent luminescence, but usually the time required is minutes or hours of length. The overall mechanism of persistent luminescence involves sustained release of visible light after absorbing energy from the excitation source. A more detailed mechanism has been described in the authors' previous article [9] for persistent luminescence in hackmanites. The persistent luminescence in hackmanites takes place in the SiO_4 and AlO_4 tetrahedra and the emitter is a Ti^{3+}-V_O pair. The absorbed energy transfers electrons from the Ti^{3+}-V_O pairs' excited levels to nearby oxygen vacancies that act as traps. The energy available at room temperature will then gradually raise the electrons back to the conduction band and to the excited levels of the Ti^{3+}-V_O pair from where the energy is released as persistent luminescence.

In up-conversion luminescence, the output photon is of higher energy than the input photon [10]. This is achieved by transferring the energies from two or more excited sensitizer ions to one activator ion that then emits the output photon. (Fig. 2a) In the case

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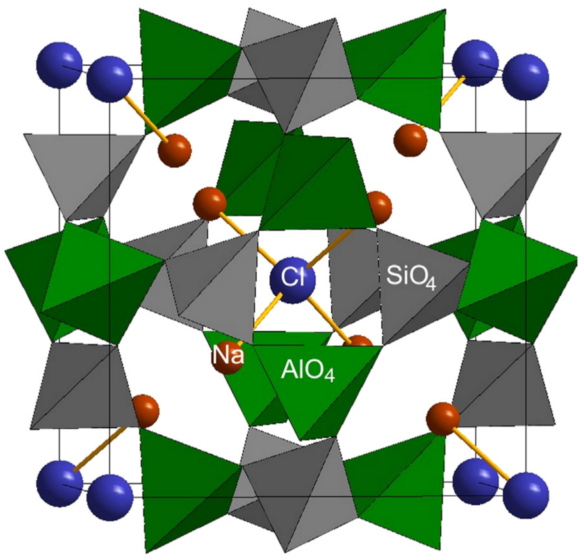

Fig. 1. Structure of a sodalite unit cell (drawn with structural data reported in Ref. [1]).

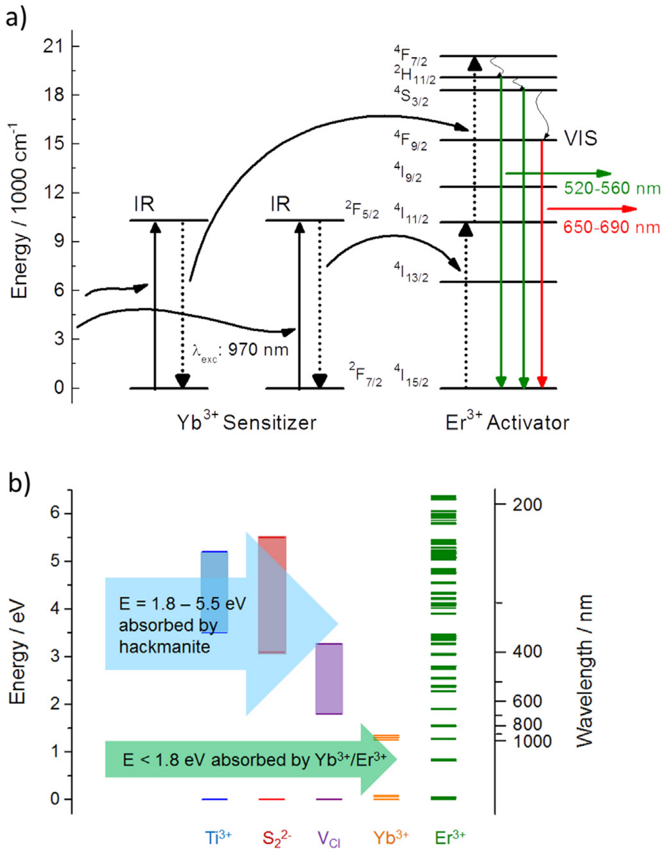

Fig. 2. a) Simplified mechanism of up-conversion luminescence in hackmanites doped with ytterbium and erbium. b) The absorption bands of the absorbing species of hackmanite [9] and the energy levels of Yb^{3+} and Er^{3+}.

of hackmanites the aim was to induce up-conversion luminescence using ytterbium as the sensitizer ion and erbium as the activator ion.

Optical multiplexing is used for example in medical diagnostics [11] and security markings [12]. Optical multiplexing allows one to get multiple information from one optical signal. Hackmanite seems to be a good candidate for optical multiplexing since it has many optical properties [9]. The aim of this work was to dope hackmanites with ytterbium and erbium making hackmanite also capable of producing up-conversion luminescence.

2. Materials and methods

2.1. Materials preparation

The composition used in these materials was chosen based on our previous results [2] which show that the material with n(S):n(Cl) $= 0.06$ has by far the best tenebrescence as well as luminescence of the tested n(S):n(Cl) compositions. The persistent luminescence of this material is also above average among the tested materials. Thus we choose this as the composition to be used in the non-doped material used as a reference as well as a base composition for the new materials to be prepared. When adding dopants into hackmanites, the molar amount of added dopants was reduced from the amount of NaCl used in the preparation to avoid excess of ions in the structure. With high dopant concentrations this might affect the n(S):n(Cl) ratio slightly but not enough to make a difference in the optical properties of the material. When hackmanites are doped with ytterbium and erbium, the rare earth elements are expected to replace some of the Na$^+$ in the caves, because the trivalent Al^{3+} site is too small for them. Occupying the Na$^+$ site requires charge compensation, which limits the amount of Yb^{3+} and Er^{3+} that can enter the structure. The doping is discussed in more detail in chapter 3.1.

To study the possibility of up-conversion luminescence in hackmanites we chose a fixed Yb/Er ratio that has been used previously in different host materials [13]. According to this, we prepared samples with the following ytterbium and erbium concentrations: 3 mol-% Yb and 1 mol-% Er, 6 mol-% Yb and 2 mol-% Er, 9 mol-% Yb and 3 mol-% Er and 20 mol-% Yb and 6 mol-% Er.

The materials were prepared using a solid state synthesis described previously [2]. Stoichiometric amounts of dried (500 °C, 1 h) Zeolite A (Sigma Aldrich), Na$_2$SO$_4$ (E.Merck, 99 %), NaCl (J.T. Baker, 99.5 %), Yb$_2$O$_3$ (Earth ltd, 99.99 %) and Er$_2$O$_3$ (Aldrich, 99.99+ %) were ground together for 20 min. After this they were heated in air atmosphere at 850 °C for 48 h. After freely cooling down samples were ground again and heated in flowing H$_2$/N$_2$ (12 %/88 %) atmosphere for 2 h. When preparing samples from rare earth chlorides, Yb$_2$O$_3$ and Er$_2$O$_3$ were replaced with YbCl$_3$ · 6 H$_2$O (International laboratory USA, 99.99 %) and ErCl$_3$ · 6 H$_2$O (Aldrich, 99.995 %).

2.2. Experimental methods

X-ray powder diffraction (XPD) measurements were carried out using a Huber G670 detector and Cu K$_{\alpha 1}$ radiation (λ=1.54060 Å). The exposure time was set to 20 min and the number of scans to 10. The unit cell parameters were obtained from the XPD patterns with whole pattern refinements using the FullProf program [14]. X-ray fluorescence (XRF) measurements were conducted with a PANalytical Epsilon 1 apparatus using a 1 h detection program and internal Omnian calibration.

Up-conversion luminescence spectra were measured with an Avantes AvaSpec HS-TEC detector at room temperature using an integration time of 1000 ms and 10 averaging measurements. Fiber-coupled NIR laser diode IFC-975-008-F was used as an excitation source (972 nm). Emission was measured at a 90° angle to the excitation source.

Photoluminescence and persistent luminescence spectra were measured with Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a Hamamatsu R928 photomultiplier tube (PMT) and a 15 W xenon lamp. The photoluminescence spectra were measured in Phosphorescence mode using the