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Luminescence properties of Pr^{3+} ion doped Mg-picromerite Tutton salt

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ABSTRACT

In the present work we focused on the elaboration of Mg-picromerite-type Tutton salt doped with Pr^{3+} by the slow evaporation method at room temperature. The obtained crystals, with prismatic morphology, were characterized by means of X-ray diffraction (XRD), luminescence, infrared (IR) spectroscopy and scanning electron microscopy (SEM), and the results showed a high purity phase of a monoclinic system with the space group $P2_1/a$. Dehydration and decomposition into langbeinite and potassium sulfate of this salts were done by means of thermal analysis measurements as well as XRD experiments at high temperature. Pr^{3+} exhibits a maximum of absorption in the blue region with the transition $^3H_4 \rightarrow ^3P_2$ (445 nm). Luminescence study showed that this material possesses numerous emission bands from the visible (VIS) to the near-infrared (NIR) region, which make it interesting to be used in a wide range of optical applications.

1. Introduction

Praseodymium rare earth with $4f^2$ configuration, and its trivalent oxidation number, presents an efficient luminescence when incorporated in some host matrices. This property is due to dipole electric transitions between the excited levels $^3P_0$and$^1D_2$ to the ground state ($^3H_4$) and to other excited levels [1].

The second predominant transition $^1D_2 \rightarrow ^3H_4$ of Pr^{3+} has a much longer decay time. It is well known that only magnetic dipole transitions occur and intra 4f electric dipole transitions are parity forbidden. The interactions of the crystal field, however, can break down this parity selection rule. At sites without inversion symmetry, forced electric dipole transitions become possible, leading to short decay times [2]. On another hand Pr^{3+} has been used as an activator in various host matrices to prepare phosphors that can be used in types of light emitting devices for emission efficiently from the VIS to the IR spectral regions depending on the host matrix and the ion concentration [3,4].

Research on scintillator materials with efficient Pr^{3+} d-f emission has attracted much attention in the recent years [5–10]. Due to its interesting luminescent properties, the f-d transitions, the photon cascade emission (PCE) and the persistent luminescence of Pr^{3+} have been extensively investigated for various potential applications including medicine, dosimetry and industry (TV lighting, markers, amplifiers, lasers or optical storage [11–13]). Inorganic scintillator materials with a short response time are widely investigated for applications based on the fast radiative decay rate of f-d transition [5–8].

These materials have a rigid structure and they are well-defined, such as phosphates, apatites, sulfates, etc., having interstitial sites of variable symmetries and being able to accept different types of cations or anions.

Tutton salts are a large family of double salts with the formula $A_2B(SO_4)_2(H_2O)_6$ where A^+ is a monovalent cation such as potassium, rubidium, cesium or ammonium, and B^{2+} a divalent cation such as magnesium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc or cadmium [14]. Tutton salts are sometimes called picromerites after the mineral with the same name $K_2Mg(SO_4)_2(H_2O)_6$. They crystallized in the simple monoclinic system with space group $P2_1/a$ $(Z=2)$. The B^{2+} ion is located in octahedral hexahydrate complexes $[M^{II}(H_2O)_6]^{2+}$ in the crystal at (0, 0, 0) and (1/2, 1/2, 0) positions, whereas all the other atoms are in general positions. These salts have various applications linked especially to the optical properties of the transition metal. Hence, they have been used in developments concerning domestic heating and hot-water supply because of their high melting temperatures and high enthalpies of fusion, as well in fertilizer industry as ionic conductors [15].

Tutton salts doped with transition metals have been elaborated and many studies have reported the chemical or physical properties for this family of salts such as EPR studies on Fe(III), Co(III), VO(II), Cu(II), and Mn(II) [16–20]. Spectroscopic and thermal behaviors of magnesium, cobalt and cupper picromerite were studied by means of thermogravimetric and differential thermal analyses (TG-DTA) and XRD at high

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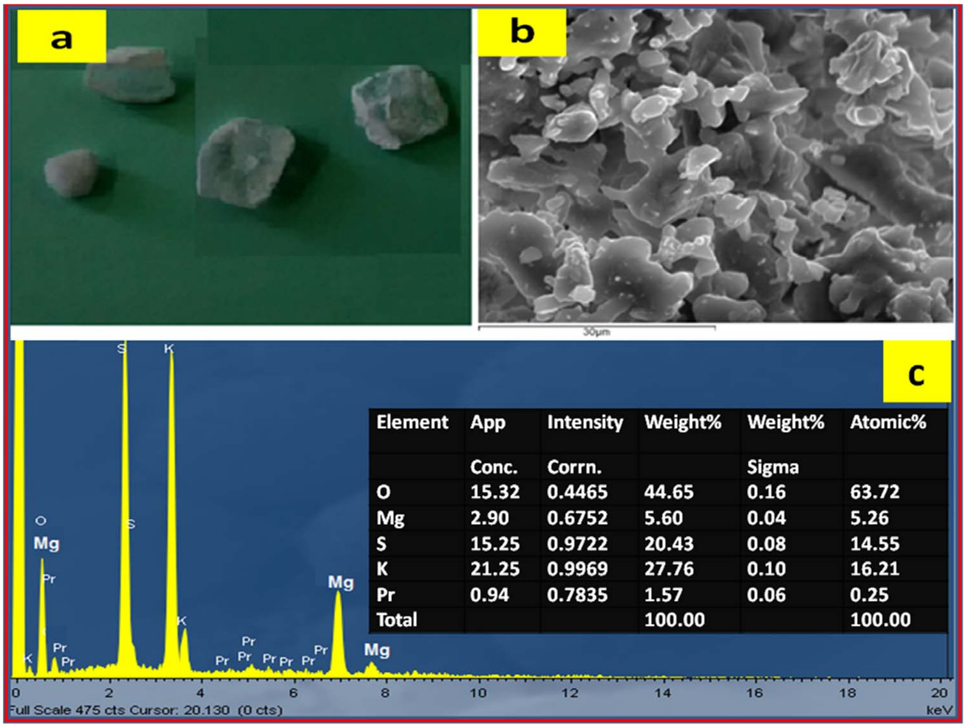

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O	15.32	0.4465	44.65	0.16	63.72
Mg	2.90	0.6752	5.60	0.04	5.26
S	15.25	0.9722	20.43	0.08	14.55
K	21.25	0.9969	27.76	0.10	16.21
Pr	0.94	0.7835	1.57	0.06	0.25
Total			100.00		100.00

Fig. 1. (a) Photograph of synthesized crystals KMgS6:Pr; (b) Powder micrographs of particles of Pr^{3+}-doped Mg-picromerite; (c) EDS spectrum and percentage of each element for the picromerite sample.

temperature. The results confirm a decomposition into langbeinite ($K_2Mg_2(SO_4)_3$) and β-K_2SO_4 at around 300 °C and, at high temperatures, a phase transition β-K_2SO_4↔α-K_2SO_4 was detected at 570 °C [21]. The crystal chemistry, metal–water interaction and the system of hydrogen bonds in different series of Tutton salts (Rb and Cs sulfates single crystals and powder diffraction) have been done [22–24].

In a previous publication, we successfully synthesized the Co-picromerite Tutton salt doped with Nd^{3+} and we concluded quite interesting optical properties for this material [25].

Starting from the idea of synthesizing a new material having botha host lattice for the lanthanide ion and interesting optical properties, we selected the picromerite since it has a rigid sulfate matrix on one hand and it is stable in a very wide range of temperature on the other hand.

2. Synthesis and experimental measurements

2.1. Crystal growth

The slow evaporation method was used for the synthesis of $K_2Mg(SO_4)_2·6H_2O$:Pr (noted as KMgS6: Pr) single crystals. This method can be described as follows: an aqueous solution containing equimolar amounts of K_2SO_4 (99%Fluka) and $MgSO_4·7H_2O$ (99% Fluka) firstly undergoes a magnetic stirring. Then, dissolved praseodymium sulfate ($Pr_2(SO_4)_3$)was added to aqueous solution with 1% amount of magnesium sulfate. The obtained mixture was left to evaporation at room temperature. After two weeks some transparent colorless crystals were obtained, taken out of the solution, washed with acetone and dried in open air. $K_2Mg(SO_4)_2·6H_2O$ (noted as KMgS6) was also synthesized in order to carry out comparisons by means of XRD experiments. It is fair to note that during our study we used the sample as finely ground powder.

2.2. Experimental techniques

XRD patterns for KMgS6:Pr powder were obtained in a diffractometer PANalyticalX'Pert Pro equipped with a primary monochromator and an X′Celerator detector, and using the $CuK_{\alpha1}$ radiation in steps of 0.02° in the 2θ angular range from 10° to 50°.

The crystalline phases detected in the patterns have been identified using the International Centre for Diffraction Data (ICDD) powder diffraction files. The cell parameters have been refined with the "Affma" program.

TG-DTA were recorded in a $STAR^e$ system: Mettler Toledo instrument in nitrogen atmosphere at a heating and cooling rates of 5 °C min^{-1} in the temperature range from 25 to 610 °C and a flux of 100 mL min^{-1}. $A1_2O_3$ was used as reference sample.

The surface morphologies were observed on a JEOL JSM 6300 LV SEM with the resolution of 3.0 nm, an accelerating voltage of 20 kV and maximum magnification of 5000–20,000x. Luminescence spectra at room temperature were obtained exciting at 457 nm and recorded with a system of two convex lenses which collimated and focalized the Pr^{3+}emission in an optical fiber coupled to a 0.3 m single grating spectrometer AndorSR-3031-B, and finally measured with a cooled CCD detector Newton DU920 N with a resolution of 0.7 nm and using an integration time of 1 s. All spectra were corrected for the instrument response. The time-resolved fluorescence was obtained by exciting the samples with a 10 ns pulsed Optical Parametric Oscillator (OPO) laser (Ekspla) and recording the luminescence with a photomultiplier using a digital storage oscilloscope controlled by a personal computer.

The absorption spectrum recorded from the ultraviolet (UV)to the NIR region was obtained by a "Cary 5000 spectrophotometer." The initial parameters were: acquisition time = 2 s; measuring interval = 0.5 nm; scan rate = 15 nm min^{-1}.

IR spectroscopic measurement data were obtained with a Fourier Transform Infrared spectrometer with an attenuated total reflectance accessory (FTIR-ATR). The Perkin Elmer Spectra 100 spectrometer system was equipped with a diamond ATR universal system and the spectral range spanned from 400 to 4000 cm^{-1} with a 2 cm^{-1} spectral resolution. The spectra data were analyzed by the Bruker OPUS 4.0 program taking into account the following steps: a baseline correction by spline method, a normalization of the spectra obtained and a transformation from IR-absorption spectra (AB) to IR-transmission