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Towards the development of new phosphors with reduced content of rare earth elements: Structural and optical characterization of Ce:Tb:Al_2SiO_5

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A new promising inert matrix as host of luminescent ions is proposed. Al2SiO5 samples, doped with rare earths (Ce, Tb single doped and co-doped) are proposed as good prospect for the development of new UV–vis converter with reduced content of rare earths elements. Structural characterization by Raman, XRD spectroscopy and TEM imaging reveals the sillimanite phase and nano sized dimension of the investigated powders. Optical characterization by steady time and time resolved emission spectroscopy for the single doped and co-doped samples allows to identify an efficient energy transfer from Ce to Tb ions under near UV excitation wavelength. The intense green emission observed in the Ce:Tb co-doped Al2SiO5 system suggests its potential application as efficient blue pumped green emitter phosphor to be exploited for white LED: to this purpose we tested the compound in combination with a red emitting doping ion recording for Ce:Tb:Cr:ASO system a correlated color temperature of 6720 K.

1. Introduction

In the past decade the technological progress in solid-state lighting (SSL) was remarkable and strictly connected to the requirement of reducing the global electric energy consumption and developing new environmental friendly lighting devices. Each year, about 4500 GW/h are exploited for lighting in commercial, home and industrial application accounting for more than 2000 Mt CO_2 emission worldwide [1]. In this scenario, the role of solid state lighting devices is quickly increasing, passing from 1.5% of the total lighting market in 2009 to 25% in 2014, and the estimations foresee a percentage close to 90% in 2020.

The generation of a “white emission” for SSL purposes relies on the phosphor conversion approach, where multiple emissions of colors from different phosphors and/or LEDs are adequately mixed. For White LEDs (WLEDs), phosphor down-conversion is most commonly applied, exploiting the emission of a blue or near-ultraviolet LED combined with a yellow-emitting phosphor, or a combination of different phosphors, to produce a broad energy distribution that, through “metamerism”, generates a white emission. The evaluation criteria of a SSL device, that is a joint system of phosphor(s) and pumping LED, account for the global emission spectrum, the color properties (CRI or CQS, CCT, duv), and the luminous efficiency (in lumen per watt of electrical input power), but also the efficiency as a function of LED driving current and junction temperature. At the moment the commercial WLEDs utilize Cerium doped Yttrium aluminum Garnet $Y_2Al_5O_{12}$ (Ce:YAG) as down-conversion phosphors, pumped by InGaN/GaN based LED. The ubiquity of Ce:YAG phosphors in commercial devices is related to their very simple and cost-effective fabrication, as well as their long term stability, which is related to the high melting point and stable thermal and chemical properties of the system. However, the supply of Rare Earths (RE) to industry, such as Ce and Y in Ce:YAG phosphors, is relying on a global potentially disruptive supply chain, because of the high geographic localization of RE mines and refineries: for these reasons RE elements were recently inserted in the list of critical raw materials by the European Commission [2]. Indeed, the overcome of the use of RE in most technologies, not only in lightning but also, for example, as magnetic or superconducting materials, represents a great and ambitious scientific and technologic challenge. Concerning SSL devices, the actual attempts to substitute Ce:YAG still consider RE based compounds, where RE elements are still present both in the host matrix and as emitting phosphor, such as green-emitting $SrGa_2S_4:Eu^{2+}$ mixed with red-emitting $Ca_{1-x}Sr_xS:Eu^{2+}$ or red-emitting $Sr_2Si_5N_8:Eu^{2+}$ phosphors [3,4]. On the other hand, alternative nitride phosphors

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require extreme and expensive preparation conditions, including high temperature and high nitrogen pressures [4].

Other hosts for rare earths recently proposed as alternative to REE garnets are: Ba2SiO4 and Ba3SiO5 [5], Sr2SiO4 and Sr3SiO5 [6], Ba3MgSi3O8 and Sr3MgSi3O8 [7]. Besides promising results, their use in the commercial devices was not already achieved due to low efficiency or production problems connected to the toxicity of the starting compounds.

Among the different RE compounds, promising candidates are RE oxyorthosilicates (RE_2SiO_5, RE generally being Y, Gd and or Lu) doped with RE ions, due to the chemical–physical characteristics of the matrix and the efficient emission properties of the RE doping element (typically Ce, Tb and/or Eu) [8–11]. In particular, Y_2SiO_5 (YSO) crystals present a high chemical and thermal stability, and it is already known as an excellent host material for cathodoluminescent phosphors or in compact fluorescence lamps [11].

In the present paper the alternative approach we propose is to substitute the host matrix with a totally RE free crystal based on aluminum silicates compounds, reducing the exploitation of RE exclusively to the emitting doping elements. Among aluminum silicates, Al_2SiO_5 (ASO) is known to be present in nature in three different polymorphs, andalusite, sillimanite and kyanite, where aluminum occurs in three different types of coordination [12]. Several studies were already performed on these materials, mainly for the stability of the polymorphs as a function of pressure and temperature, pointing out that Sillimanite is the stable phase at room pressure condition and high temperature [13]. It also presents interesting optical properties, in particular an indirect band gap structural feature, with a band gap value of 5.18 eV and a refractive index almost constant (1.67) in the whole UV–vis range [14]. As far as we know, it was never considered in the past as a matrix for luminescent ions, although its optical features combined with its crystal stability make it potentially suitable for the development of new phosphors with strongly reduced amount of RE elements. In this paper we report the optical and structural characterization of ASO matrix doped with RE luminescent ions as possible phosphors with reduced amount of critical raw elements as compared to commercially available Ce:YAG compounds for WLEDs applications.

2. Experimental

2.1. Materials and preparation

Samples containing different amounts of terbium, cerium and chromium were prepared through an aqueous sol–gel route. Aluminum nitrate nonahydrate ($Al(NO_3)_3\cdot 9H_2O$, Aldrich, 99.9%), terbium nitrate pentahydrate ($Tb(NO_3)_3\bullet 5H_2O$, Aldrich, 99.9%), cerium nitrate hexahydrate ($Ce(NO_3)_3\cdot 6H_2O$, Aldrich 99.9%), tetraethoxysilane (TEOS, Aldrich, 98%) and absolute ethanol (Carlo Erba, 99.8%) were used as reactants for the preparation. To this end, aqueous solutions containing appropriate concentrations of aluminum and dopant nitrates were mixed with an ethanolic solution of TEOS and acidified with nitric acid (pH 1). The resulting transparent sols were stirred for 180 min at room temperature and then allowed to gel at 50 °C for three days. The prepared gels were successively powdered in an agate mortar and gradually thermally treated (4 °C min^{-1}) up to 1250 °C, leaving the samples at this final temperature for 24 h. The final concentration of dopants in the whole set of characterized ASO sample was Ce = 1% atm, Tb = 5% atm. and Cr = 0.1%.

2.2. Experimental set up

Raman scattering measurements were carried out in backscattering geometry using a 532.0 nm line by a wavelength stabilized diode module (LASOS DPSS series) coupled with a Reflecting Bragg Grating (Optigrate–Braggrade 405) to narrow the laser line. Measurements were performed at room temperature with a triple spectrometer Jobin-Yvon Dilor integrated system with a spectral resolution of about 1 cm^{-1}. Spectra were recorded in the Stokes region by a 1200 groove/mm grating monochromator and a LN-cooled charge coupled device (CCD) detector system.

Time-resolved photoluminescence measurements (TRPL) in the ns domain were performed using an optical parametric oscillator with a frequency doubler device, excited by the third harmonic (355 nm) of a pulsed Nd:YAG laser (Quanta-Ray Pro 730). The excitation pulse width at half-maximum was 8 ns with 10 Hz of repetition rate, and spectral bandwidth less than 0.3 cm^{-1}. The PL signal was dispersed by a spectrograph (ARC-SpectraPro 300i) with a spectral bandpass $<$2.5 nm and detected by a gateable intensified CCD (PI MAX Princeton Inst.). TRPL in the sub ns domain were performed with a PicoQuant pulsed diode laser with excitation wavelength at 355 nm and 200 ps pulse duration. Detection was obtained by 200 ps time resolution with a Hamamatsu streak camera (mod. M5676 S-20).

Transmission electron microscopy (TEM) images were collected using a Hitachi 7000 microscope equipped with a W thermoionic gun and operating at 125 kV. Images were collected with a AMT DVC (2048 × 2048 pixel) CCD Camera. Prior to observation, the finely ground powders were deposited on a carbon coated copper grid.

X-ray diffraction (XRD) patterns were collected on a Panalytical Empyrean diffractometer using a Cu-Kα tube operating at 40 kV and 40 mA, coupled with a graphite monochromator on the diffracted beam and an X-Celerator linear detector. XRD data were collected in Bragg–Brentano geometry scanning over an angular 2θ range from 10° to 90° while spinning the sample holder at a speed of 1 Hz in order to reduce any preferred orientation effect. Phase identification was performed using the PDF-2 database (PDF-2 JCPDS International Centre for Diffraction Data, Swarthmore, PA).

3. Results and discussion

The crystal structure of the samples was studied through XRD diffraction as well Raman spectroscopy. Fig. 1 reports the XRD diffraction pattern of the undoped ASO sample. The plot presents

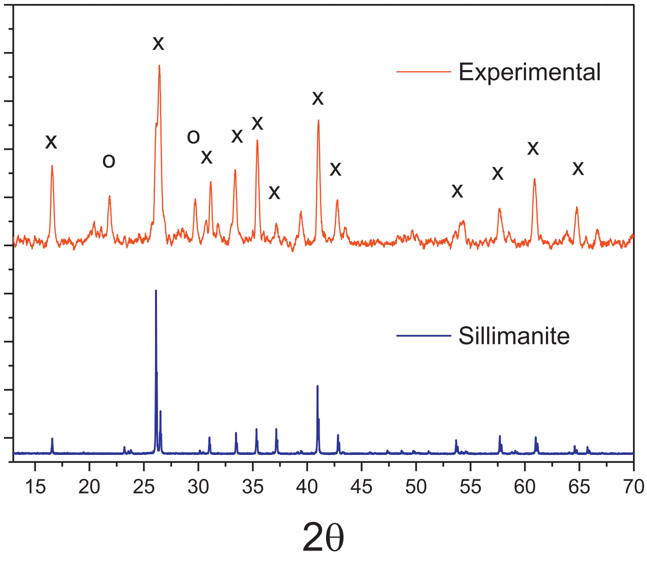

Fig. 1. XRD pattern for Al_2SiO_5 sample. For reference the XRD pattern of Sillimanite is reported. The main peak of sillimanite (x) and impurities (o) are marked.