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Strong ultraviolet luminescence from cerium- and gadolinium-doped cubic boron nitride

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Abstract

Cubic boron nitride has been successfully activated by Gd^{3+} and Ce^{3+} and routinely fabricated under high pressure–high temperature conditions as micropowders, ceramic samples and polycrystalline compacts when doped with appropriate Ce or Gd compounds. Strong UV photoluminescence under 244 and 325 nm laser excitation from the Gd- and Ce-doped cBN is found to be stable over the temperature range of 7–300 K. A remarkable feature in the 244 nm excited spectrum of the Gd-doped ceramic and polycrystalline samples is strong and relatively sharp emission peaking at 315.4 nm assigned to $^8S_{7/2}$–$^6P_{7/2}$ electronic transitions of the Gd^{3+} ions. A very strong bright and blue-colored photoluminescence is observed from the Ce-doped cBN resulting from two structured bands peaking at ~390 and ~290 nm that is ascribed to electronic transitions of the Ce^{3+} ion coupled with lattice vibrations of cBN. Efficient emitters have been created with broad bands in the UVB (280–315 nm) and UVA1 (340–400 nm) regions of the electromagnetic spectrum.

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1. Introduction

There is considerable interest in ultraviolet-emitting materials for a wide range of applications such as the development of more efficient white-light phosphors, purification of air and water, the detection of organic molecules, conversion of short wave UV light into longer wave UV and improvement of the sensitivity of radiation-sensitive materials. In addition, phosphors based on cubic boron nitride (cBN) are capable of withstanding extreme environmental temperature, radiation, high electric power and high electric field conditions.

Two decades ago it was discovered that doping semiconductors with lanthanides is a way to realize light emitters with luminescence arising from radiative intra-4f electron transitions of triply ionized ions doped into these semiconductors [1].

The development of lanthanide implanted semiconductors has been mainly aimed at using them in highly efficient light emitters and solid-state lasers. GaN, as a direct, wide band-gap semiconductor, has been doped by lanthanides giving luminescence from the infra-red to the blue region of the electromagnetic spectrum combined with resistance to thermal quenching. However, the band-gap energy of GaN (3.3 eV), being smaller than the lowest energy optical transitions of gadolinium or cerium, is not able to act as a useful host for activating their luminescence, although their emission could be effective for white-light conversion phosphors. There are very few phosphor materials that efficiently convert UV-blue emission from a LED into green or, in particular, to red light. Red-emitting phosphors that can be efficiently pumped by UV-blue LEDs are very scarce. As regards the presently used phosphors, YAG:Ce^{3+}-based phosphors, exhibit reduced efficiency because of thermal quenching and reduced lifetime due to the phosphor deterioration. Therefore, it is important to explore new phosphor

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materials with improved properties for use in white-light LEDs. The critical challenges to be faced for solid-state wavelength converters are the development of new inorganic phosphors for the near UV (360–410 nm), improvement of the absorption of the LED light (blue or UV) by the various phosphors, achievement of >90% internal quantum efficiency in blue, green, and red phosphors (or other luminescent materials), exploration of quantum dots and nanoclusters for wavelength conversion, and the control of degradation mechanisms under high-current, high temperature operating conditions. We review the situation with regard to Ce and Gd doping.

The dominant oxidation state of cerium ion is 3+, although 2+ can be found in some compounds and the 4+ state is also known as well. It is well-known that Ce^{3+} ions show 4f↔5d transitions resulting in a broad band emission in the UV to visible range. Since electrons in the 5d state take part in the formation of chemical bonds (in the excited state), the position of the excitation and emission bands depends strongly on the host lattice, i.e., the crystal structure and composition [2]. The Ce^{3+} ion has an $^4f_1$ electronic ground state configuration. The luminescence of the Ce^{3+} ion originates from a transition from the lowest 5d level to the ground states that are split by the spin-orbit coupling into two components, $^2F_{5/2}$ and $^2F_{7/2}$, separated by $\sim 2000\ cm^{-1}$. Since the position of the lowest 5d levels is strongly influenced by local coordination, the emission wavelengths of Ce^{3+} vary for different host lattices from UV to the visible region. According to previous works on Ce^{3+} in various fluoride hosts ($LiLuF_4$, $LiYF_4$, LaF_3, LuF_3) the related light emission is concentrated in bands at around 300 nm and 320 nm [3,4]. Lasing is reported at 325 nm in $LiYF_4$ [5]. Other works, mainly on silicates and silicon aluminum oxynitrides, did however give much broader luminescence bands centered at 390 nm [6,7]. All Ce^{3+} activated phosphors, with the exception of YAG, show the maximum of their emission in the UV or blue region (<410 nm). This emission is ascribed to the Ce^{3+} 5d–4f transition and has a decay time shorter than 100 ns [8]. Ce-doped lanthanide–oxynitride glasses show very interesting luminescence properties, and the Ce^{3+} emission can be varied over a large spectral interval (380–500 nm) with changes in the chemical compositions of the compound and with Ce concentration [9]. In oxide host lattices, the emission of Ce^{3+} is generally located in the UV to blue (300–500 nm) spectral range [2]. For example, for an α-Al_2O_3 host, it was discovered that Ce implantation effects on "luminescence" appear at 390 and 420 nm [10].

Gd^{3+} is unique among triply ionized lanthanides in having an energy difference between the $^8S_{7/2}$ ground state and the first excited state $^6P_{7/2}$, which is the largest in the series. The expected transition probability for the $^6P_{7/2}$–$^8S_{7/2}$ transition is relatively small but larger compared to many of the transition probabilities from the higher-lying levels. Another interesting property of Gd^{3+} is a very small crystal field splitting of the ground state, which in many cases cannot be resolved by luminescence [11–13]. According to the mean free-ion parameters of Gd^{3+}, the excited state is predicted to be at ~3.99 eV above the ground state $^8S_{7/2}$. One can hence expect energetic transitions between the excited state and the ground state of the ion lying within the band gap since this is less than the band gap of the hosts like AlN and BN. In previous works, recently published, photoluminescence spectra were obtained from Gd^{3+} ions introduced into different hosts. For example, in Y_2SiO_5 Gd^{3+} emission occurred at 307 nm and 313 nm [14]. More recently, similar luminescence was observed for Gd^{3+}-doped $LiGdF_4$ and AlN [15,16]. Here it is quite clear that the luminescence observed originates from the Gd^{3+} ions themselves, although they are also able to transfer energy to their host [17]. A promising application of Gd^{3+}-doped materials is the implementation of light emitters operating down to the ultraviolet region of the electromagnetic spectrum [18].

A major motivation of the present work is to design novel luminescent materials based on Ce- and Gd-doped cubic boron nitride as promising conversion phosphors or as LEDs. To the knowledge of the authors, there is at present just one work on cathodoluminescence of Gd-doped AlN where the Gd was introduced into the material by ion implantation [17], but information is lacking about Gd-doped cBN and also about Ce-doped cBN or AlN.

2. Samples and measurements

The micropowders of cBN were synthesized in a growth system with nitrogen excess from hBN powder together with 1% of an appropriate Ce or Gd compound under high pressure–high temperature conditions (HP/HT) in a "thoroid" high pressure apparatus. The particle sizes of the micropowder were rather homogenous in the range 1–2 μm and they were very light yellow in color. Ceramic samples of cBN were also sintered without any additives and plasticizers directly from cBN micropowders under HP/HT. The polycrystalline samples were synthesized under HP/HT conditions from a mixture of hBN with 1, 2 or 5% of a Gd-based compound via a direct phase transition. Sintering was carried out under conditions of thermodynamic stability for cBN. After synthesis or sintering under high pressure–high temperature we did not expect any residual of the appropriate RE-based compounds in the samples. This conclusion was supported by X-ray diffraction of the final products which did not reveal any evidence of the original compounds. X-ray fluorescence analysis showed 0.3% of Ce in the ceramic formed using 1% of the added Ce compound. The polycrystalline samples activated by 1–5% of the added Gd-based compounds were found to contain from 0.5 to 2.5% of Gd and up to 0.05% of Ce. The ceramic and polycrystalline samples were 6 mm in diameter and were polished to a mirror finish using diamond polishing wheels. After polishing the samples were well treated in acids to remove any contaminations from their surfaces. All samples showed high mechanical characteristics and XRD analysis show no trace of hBN in any of them.

The photoluminescence experiments were performed using Renishaw micro-Raman spectrometers fitted with cold stages. One of the systems used 325 nm HeCd laser excitation and was fitted with an Oxford Instruments Microstat for cooling to temperatures ~7 K. The other used 244 nm excitation (488 nm argon ion laser frequency doubled) and was equipped with a Linkam Scientific Instruments THMS600/HF591 stage for