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Investigations on the low voltage cathodoluminescence stability and surface chemical behaviour using Auger and X-ray photoelectron spectroscopy on $LiSrBO_3:Sm^{3+}$ phosphor

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ABSTRACT

Orange-red emissive $LiSrBO_3:Sm^{3+}$ phosphors were synthesized through the solid-state reaction method. Under UV radiation (221 nm) and low-voltage electron beam (2 keV, 12 mA/cm^2) excitation, the Sm^{3+} doped $LiSrBO_3$ phosphor shows emission corresponding to the characteristic $^4G_{5/2}$-$^6H_{7/2}$ transitions of Sm^{3+} with the strongest emission at 601 nm. A high stability of cathodoluminescence (CL) emission during prolong electron bombardment with low-energy electrons was observed. Surface sensitive diagnostic tools such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to study the surface chemistry. AES results revealed modifications in the surface concentrations of Li, Sr, B, O and C on the surface of the $LiSrBO_3:Sm^{3+}$ phosphor as indicated by the changes in their Auger peak to peak heights (APPH) as a function of electron dose. Observed changes in the high resolution XPS spectra of the $LiSrBO_3:Sm^{3+}$ surface irradiated with the low energy electron beam provide evidence of compositional and structural changes as a result of the electron beam stimulated surface chemical reactions (ESSCRs). Additional SrO_2 was identified by XPS on the phosphor surface after it received an electron dose of 300 C/cm^2 together with the increase in the concentrations of chemical species containing the B–C–O bonding. The new surface chemical species formed during electron beam bombardment are possibly responsible for the stability of the CL in the $LiSrBO_3:Sm^{3+}$ phosphor.

1. Introduction

In the field of display phosphors, the pure oxides and mixed oxide phosphors have gained special attention due to their high vacuum stability and absence of corrosive gas emission. Among the several hosts registered as display phosphors within the domain of oxide related lattices, borates offer a large band gap, thermal and chemical stability, and low synthesis cost [1,2]. The first report on the synthesis and single crystal structural determinations for mixed alkali and alkaline-earth metal orthoborates ($LiMBO_3$ where M = Sr, Ca) by Cheng et al. [3], initiated considerable research efforts on these materials due to their interesting optical properties. Since then, the hosts related to the alkali alkaline-earth orthoborate family has emerged for various luminescence applications such as thermoluminescence [4], white light emitting diodes [5] etc. However, there is a lack of information on the cathodoluminescence (CL) property of the $LiSrBO_3$ and its suitability as a display device phosphor. The stability and efficiency of the cathodoluminescence (CL) process is a characteristic that is often used to assess the potential of a phosphor for use in flat-panel display applications such as field emission displays (FEDs) where the prime operating conditions are the low electron beam accelerating voltage and the high current densities. The CL characterization of a phosphor in a vacuum chamber is important for preliminary evaluation and chemical stability testing of phosphor powders under continuous electron beam exposure prior to its incorporation into an actual display device. Especially, for low voltage display applications, the surface chemical behaviour of a phosphor turns out to be a key criterion for its usability [6], whereby, it is critical to constantly consider potential electron-beam degradation effects such as electron-stimulated desorption and adsorption (ESD and ESA, respectively). Therefore, there is a serious pursuit globally for newer oxide based materials which remain chemically stable under a prolonged exposure with a low energy electron beam. The chemical passivation of CL phosphors by inorganic oxides (Al_2O_3, SiO_2, MgO, SnO_2 etc.) may aid, to some extent, to their surface chemical stability and consequently ensures the longevity of the display device [7–9]. However, an external surface protection of the phosphor by the above mentioned protective inorganic oxides may become

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susceptible to the processing complexities and cost ineffectiveness. To circumvent such complexities, the ESD and ESA processes, together called as electron stimulated surface chemical reaction (ESSCR) [10,11] hereafter, may well come to the rescue in terms of modifying the phosphor's surface under a given vacuum environment during continuous electron beam exposure. Concomitant investigations previously conducted on the oxide based phosphor systems in this laboratory showed the role of ESSCR in ascertaining surface chemical stabilities for the potential CL phosphors [12]. Therefore, to validate the ESSCR mechanisms further in borate hosts the surface chemical states and the CL response resulting from the low energy electron irradiation of $LiSrBO_3:Sm^{3+}$ were monitored using experimental techniques such as CL spectroscopy, Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

The $LiSrBO_3$: Sm^{3+} (3 mol.%) was synthesized using a conventional solid-state reaction method at 700 °C for 2 h as described in ref [5] by using $LiCO_3$, $SrCO_3$, H_3BO_3 and $Sm(NO_3)_3{\cdot}6H_2O$ as raw materials. A Cary Varian Eclipse spectrometer was used for the Photoluminescence (PL) measurements. A Shimadzu UV–vis 1700 spectrophotometer was used to perform the diffuse reflectance measurements. CL and AES measurements were carried out using a singular electron beam excitation of 2 keV and 12 μA beam current at a pressure of 1×10^{-6} Torr O_2. CL data was collected using an Ocean Optics Inc. PC2000 spectrometer. The surface chemical elements were identified using AES before and after an electron dose of 300 C/cm^2. A PHI 549 AES system was used for the CL and APPH measurements and a PHI 700 Scanning Auger Nanoprobe (5 keV, 10 nA, a beam diameter ≈50 nm) was used for AES spot analyses. Variations, both in Auger peak to peak height (APPH) of the identified chemical constituents and the CL emission intensity for prominent Sm^{3+} emission were recorded simultaneously to determine the effect of the electron beam on the surface and the corresponding CL output of the phosphor. For a precise determination of the surface chemical state changes before and after electron beam exposure, XPS analysis was carried out using a PHI 5000 Versaprobe spectrometer (analyser resolution ≤0.5 eV) using monochromatic Al Kα radiation ($h\nu$ = 1253.6 eV). The charging of samples during the X-ray irradiation was taken care of by neutralizing with slow electrons and ions during the data acquisition. The charge over compensation resulting in shifts in

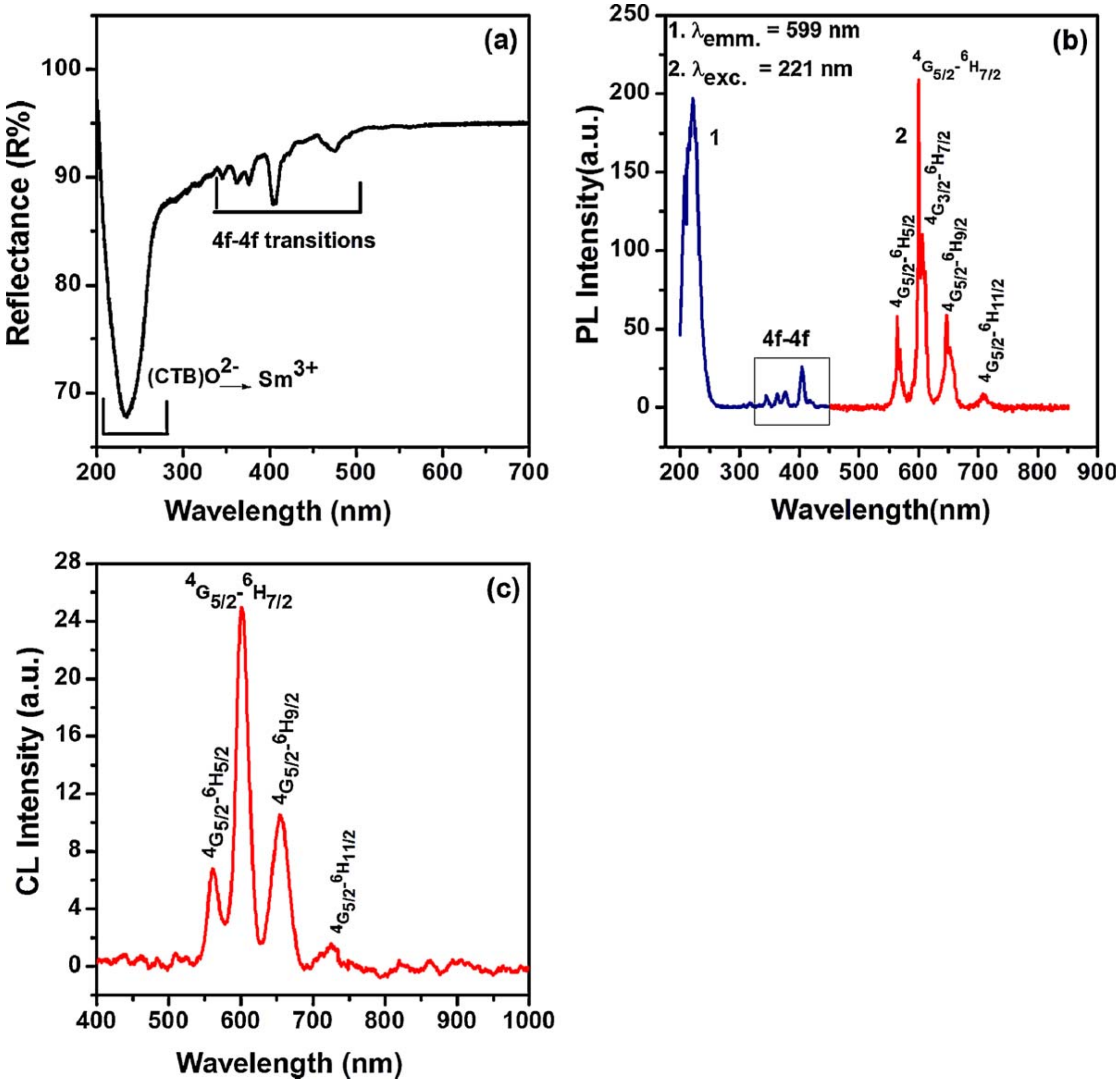

Fig. 1. (a) Diffuse reflectance spectra, (b) the PL emission (λ_{exc} = 221 nm) and excitation (λ_{em} = 599 nm) spectra and (c) the CL output of $LiSrBO_3:Sm^{3+}$ (3 mol.%) under electron beam excitation with primary beam voltage and beam current of 2 keV and 12 μA respectively.