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Materials Research Bulletin 41 (2006) 724–731
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Luminescent host lattices, $LaInO_3$ and $LaGaO_3$—A reinvestigation of luminescence of d^{10} metal ions

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Received 10 February 2005; received in revised form 21 September 2005; accepted 10 October 2005
Available online 2 November 2005

Abstract

The phosphor $LaInO_3:Eu^{3+}$ exhibits, in addition to the weak orange-red emission of Eu^{3+}, a broad blue emission whose origin formed the basis for the reinvestigation of luminescence of $LaInO_3$ and the analogous $LaGaO_3$, well known host lattices for luminescent centers. The results are analyzed based on the luminescence observed for In^{3+} and Ga^{3+} in various host lattices. An attempt is made to understand the mechanism of the luminescence of d^{10} ions In^{3+} and Ga^{3+}.

Keywords: A. Ceramics; A. Oxides; A. Optical materials; C. X-ray diffraction; D. Luminescence

1. Introduction

Recent developments in the display device technology has resulted in various types of displays such as electroluminescent (EL) displays, field emission displays (FEDs), plasma display panels (PDPs) and vacuum fluorescent displays (VFDs) and current research interest in the area of luminescence is in the development of phosphors for such applications. One among them is the development of phosphors for low-voltage ($\leq$1 kV) emissive flat-panel displays. The requirement of phosphors for each display device application is different. For example, a phosphor with intrinsic electronic conductivity is suitable for field emission displays in order to prevent the buildup of the space charges at the surface of phosphors. Recent reports on the semiconductors $CaIn_2O_4$ and $SrIn_2O_4$ as host lattices for the red emitting Pr^{3+} make it possible to think of different host lattices in the oxides regime that are semiconductors [1,2]. $LaInO_3$ is a narrow-band semiconductor [3] and hence it may find application as a host lattice for field emission displays. Eu^{3+} luminescence has been studied under cathode ray excitation in $(Lu_{1-x}La_x)InO_3:Eu^{3+}$ and it was found that the intensity of Eu^{3+} emission peak at 610 nm increases with decrease in x. This has been attributed to the formation of a solid solution of $LaInO_3$ and $LuInO_3$ with increase in x [4]. $Lu_{1-x}La_xInO_3:Eu^{3+}$ showed a brighter emission than $Y_2O_3:Eu^{3+}$ with added In_2O_3 (necessary to improve the conductivity of phosphor and increase the excitation efficiency under cathode ray excitation) and the reason for this is the inherent In_2O_3 present in the former one. Bi^{3+} luminescence has been reported in $LaInO_3$ and $LaGaO_3$ host lattices and the difference in the energy of $^1S_0$–$^3P_1$ transition of Bi^{3+} luminescence in the two lattices has been explained based on the difference in the covalent nature of the host lattices [5–8]. Bi^{3+} is a well-known sensitizer of rare earth ions in various lattices [9–11]. With this in

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0025-5408/$ – see front matter
doi:10.1016/j.materresbull.2005.10.010

mind, we have investigated the $LaInO_3:Eu^{3+}$, Bi^{3+} system to observe the energy transfer process that could improve the efficiency of this phosphor to find application in field emission displays [12]. During the course of our study, we observed a strong blue emission in the phase that contained no Bi^{3+}. This induced us to reinvestigate the luminescence of $LaInO_3$ and analogous $LaGaO_3$ host lattices. Both $LaInO_3$ and $LaGaO_3$ belong to the perovskite structure with orthorhombic distortion. The structure consists of three dimensional sublattice of corner connected $In(Ga)O_6$ octahedra and the La^{3+} is in eight-fold coordination of oxide ions. We report here the observed luminescence of $LaInO_3$ and $LaGaO_3$ and a possible mechanism for the origin of luminescence in these compounds.

2. Experimental

2.1. Synthesis

The compounds $LaInO_3$, $La_{0.95}Eu_{0.05}InO_3$, $La_{0.995}Bi_{0.005}InO_3$ and $LaGaO_3$ were synthesized by high temperature solid-state reaction from La_2O_3 (Indian Rare Earths, 99.9%), Eu_2O_3 (Indian Rare Earths, 99.9%), Bi_2O_3 (Cerac, 99.9%), In_2O_3 (Cerac, 99.5%) and Ga_2O_3 (Alfa Aesar, 99.999%). La_2O_3 and Ga_2O_3 were preheated at 1100 °C overnight to remove the absorbed moisture and carbonates. Stoichiometric amounts of the reactants were ground well and heated at 950 °C for 24 h and finally sintered at 1250 °C for 24 h with an intermittent grinding. In the case of Bi^{3+} containing sample, the mixture was heated in a covered alumina crucible in order to avoid Bi^{3+} volatilization.

2.2. Characterization

The compounds were characterized by powder X-ray diffraction (XRD) (P3000, Rich Seifert) using Cu $K\alpha_1$ radiation. The diffraction pattern of $LaInO_3$ was indexed based on a theoretically generated pattern (from the atomic coordinates given in Ref. [13]) using the Lazy Pulverix program [14]. In the case of $LaGaO_3$, the diffraction pattern was indexed based on the pattern reported in JCPDS (file no. 24–1102). X-ray fluorescence (XRF) analysis was carried out (axs, Bruker) for $LaInO_3$ and $LaGaO_3$ to find out qualitatively the presence of Bi^{3+}, if any, by contamination from furnace during synthesis. The room temperature photoluminescence excitation and emission spectra were recorded for the powder samples using a spectrofluorometer (FP-6500, Jasco) operating in the range 220–720 nm.

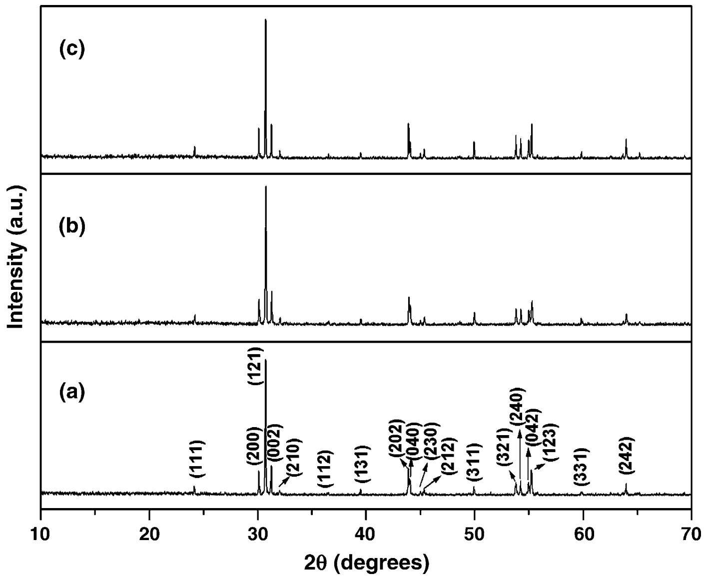

Fig. 1. Powder XRD patterns of (a) $LaInO_3$, (b) $La_{0.95}Eu_{0.05}InO_3$ and (c) $La_{0.995}Bi_{0.005}InO_3$.