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Full Length Article

The effect of the host lattice on the optical properties of Bi^{3+}in $Ca_{1-x}O$:Bi and $Ca_{1-x}(OH)_2$:Bi phosphors

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ABSTRACT

The present work refers to the structural and luminescence changes in $Ca_{1-x}O$:Bi ($x = 0.5\%$) phosphor due to the reaction of the $Ca_{1-x}O$: Bi ($x = 0.5\%$) phosphor with atmospheric air. The X-ray diffraction (XRD) patterns of the as-annealed sample (at 1200 °C) showed the characteristic peaks of CaO, while high-intensity peaks of $Ca(OH)_2$ were also observed for the same samples that were kept in the air after annealing. Indicating that mixed phases of $Ca_{1-x}O$:Bi ($x = 0.5\%$) and $Ca(OH)_2$:Bi were present in the exposed samples. It was clear that the observed optical properties (excitation and emission) of the Bi^{3+} depended strongly on the reaction of the CaO with the environment due to the host lattice structure changes and therefore a big challenge for practical applications.

1. Introduction

The luminescence properties of the Bi^{3+} ($6s^2$) ions as an activator in oxides host lattices have been reported by many researchers [1]. Excitation occurs from the $^1S_0$ ground state to the $^3P_1$ or $^1P_1$ excited states. The transitions $^3P_1 \rightarrow {}^1S_0$ yield, usually, a single broadband emission [2–4]. A strong dependence of the excitation and emission bands of the Bi^{3+} ions on the host was found and ascribed to the coordination characteristics of the activator site, i.e., the number of ligands and distance of Bi^{3+} to ligands [2,3]. They are extensively used to probe the host matrix due to the high sensitivity to the actions in the surrounding environment [3]. CaO is one of the alkaline-earth oxides groups, which exhibits properties typical of an insulator, with a wide band gap of 7.0 eV [5]. During the exposure to water or atmospheric air, CaO forms a $Ca(OH)_2$ compound [6]. The process can be reverted by annealing at higher temperatures (800 °C) by thermal decomposition [7]. Many researchers have studied the reaction of CaO with atmospheric air [6]. In the field of luminescent materials, the CaO matrix has been doped successfully with rare-earths, such as in the case of CaO:Tb^{3+} [8], CaO:Eu^{3+} [9] and CaO:Sm^{3+} [10]. But the CaO activated by Bi^{3+} is poorly studied. The chemical bonds in the CaO material is mostly of an ionic nature [11]. However, when this material is in contact with watermolecules, some of the ionic bonds will be re-arranged owing to the insertion of the covalent nature of the water molecules in the CaO structure. Therefore, in this host, the ionic and the covalent bonds both are existing by oxygen (O^-) and hydroxyl (OH) anion connections, respectively [11]. It may change the sensitivity of the Bi^{3+} ions via the variation in crystal structure and hence the luminescence emission. Therefore, the present research work aims at finding the conjugate effect of covalent and ionic bonds on the sensitivity for the Bi^{3+} ions and crystal structure via estimation of the structural variation (chemical bonds) correlated luminescence properties of the Bi^{3+} ion. It is impossible by doping the CaO materials with rare earth elements due to the shielding effect [12]. However, numerous techniques are used for the synthesis of different phosphors for versatile applications [13,14]. The $Ca_{1-x}O$:Bi ($x = 0.5\%$) phosphor powder was synthesized by the sol-gel combustion method. The structural and photoluminescence (PL) properties of the freshly annealed and exposed to atmospheric conditions, samples are reported.

2. Experiment

CaO:Bi^{3+} was synthesized by the sol-gel combustion method. Full details of the synthesizing process can be found in reference [25]. The resulting product was a light gray $Ca_{1-x}O$:Bi ($x = 0.5\%$) powder. The powder was then annealed in air at 1200 °C for 2 h.

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Table 1
Refinement parameters.

Elements	X	Y	z
Ca	0.0000	0.0000	0.0000
O	0.5000	0.5000	0.5000
a = b = c	4.81050 Å		
$\alpha=\beta=\gamma$	90°		
Space group	Fm−3 m (225)		

These samples are called the freshly annealed samples. Some of the samples were also left in air under controlled clean conditions for three months. These samples are called air-exposed samples. A BrukerD8 Advance diffractometer (40 kV, 40 mA) with CuK_α x-rays (1.54 Å) was used for x-ray diffraction (XRD) measurements in order to determine the phase composition of the materials. Photoluminescence (PL) measurements were made using the PL Cary Eclipse system. All measurements were done at room temperature. High-resolution X-ray photoelectron spectroscopy (XPS) spectra of the Bi ion on the surface of the freshly annealed and air-exposed samples as well as in the bulk of these samples after sputtering were obtained. A PHI 5000 Versaprobe-Scanning ESCA Microprobe was used. The x-ray beam used was a 100 μm diameter monochromatic Al K_αX-ray beam ($h\nu$ = 1486.6 eV) generated by a 25 W, 15 kV electron beam. The pass energy of the hemispherical analyzer was maintained at 11 eV. An Ar ion gun (2 kV energy ions) at the rate of 18 nm/min was used to clean/sputter the powder samples. The estimated sputter rate was determined by using standard SiO_2 samples with known thicknesses.

3. Result and discussion

The XRD data were incorporated into the X'Pert High Score software associated with the JCPDS PDF 2 to match the existing data. The XRD pattern of the freshly annealed sample matches well with the CaO structure (JCPDS 078-0649). However, for the air-exposed samples, the XRD pattern matches with JCPDS 078-0649 along with the presence of some extra peaks of the $Ca(OH)_2$ structure (JCPDS 076-0570). The refinement of the freshly annealed CaO XRD pattern was carried out using the FullProf software and the weighted R factors R_p (profile factor) and R_{wp} (weighted profile factor) converged to the reliable values of 3.4% and 7.2%, respectively. It indicated that the pure CaO phase formed without any impurity in the freshly annealed CaO sample. The phase was identified as cubic with the space group Fm−3 m (225) having lattice parameters of 4.81050 Å. Table 1 shows the refinement parameters for the freshly annealed CaO sample.

Due to the adsorption and reaction of water (and possibly oxygen content from ambient air) on the surface of the CaO from the ambient atmosphere as per formula $CaO + H_2O{=}Ca(OH)_2$, the XRD pattern exhibits the presence of both the phases [6]. The relative humidity during that time of year was in between 50 and 60%. No peak corresponding to the dopant ion was observed in any of the patterns owing to the low doping concentration of the Bi^{3+} ions. As the ionic radii of Ca^{2+} (114 pm) with Bi^{3+} (117 pm) were about the same, the doping did not visibly affect the original crystal structure. The cubic structure of the prepared CaO was drawn using the VESTA software [15] as shown in Fig. 1(b). It illustrates that the Bi^{3+} has substituted in the octahedron sites (CaO_6) of the Ca^{2+}. The oxygen atoms are shown as a red color and the Ca atom is shown in a green color. When water molecules adsorbed from the atmosphere they would mainly attach to the surface side, as illustrated clearly in Fig. 1(b). The hydrogen atoms are shown in a sky blue color.

The chemical nature of the $Ca(OH)_2$ that developed on the freshly annealed sample during exposure to air was investigated. The detail XPS of the O-1s and Ca-2p peaks were measured for these samples, which gave similar trends in the XPS results that have been reported previously by Yousif et al. [24] on another degradation study, and therefore only shown as Supporting material in Fig. S1. Only the XPS depth profiles are given, that differ from the previous study, as shown in Fig. 2(a) and (b). The XPS results were plotted, Fig. S1, as a function of profile numbers (each profile represent acquisition data after 3 nm sputtering deeper into the bulk sample). The XPS investigation represents the chemical information about the sample's surface as well as inside (bulk) of the sample. The change in shape and position of the O-1s peaks, Fig. S1, during sputtering for both samples indicated the formation of a different phase during air exposure. The O-1s peaks on the surface and inside the bulk of the samples were attributed to the O-1 in $Ca(OH)_2$ [16] and CaO [16,17], respectively. The Ca-2p peaks have shifted to a higher binding energy compared to the same peaks in the bulk of the samples, Fig. S1.

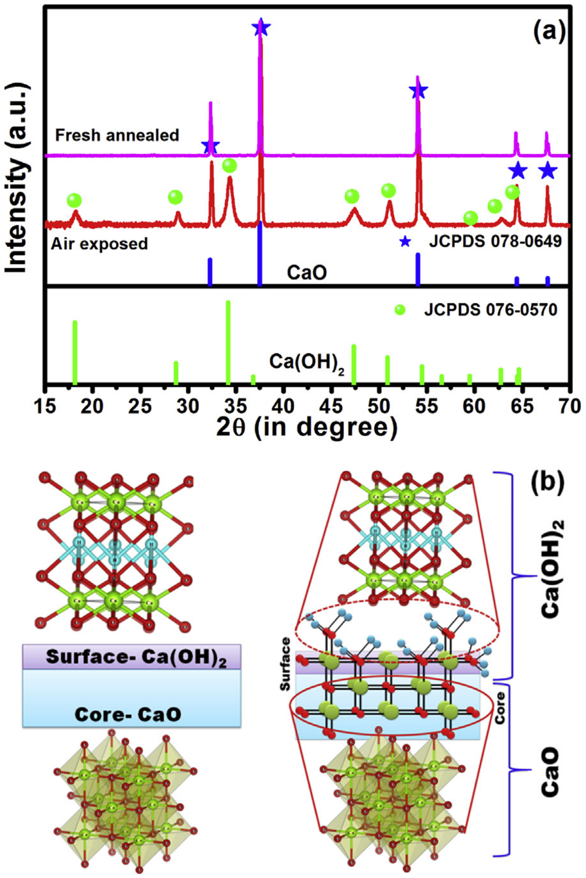

Fig. 1. (a) Shows the X-ray diffraction patterns of the freshly annealed and air-exposed samples as well as the standard patterns of the CaO and $Ca(OH)_2$ (b) The schematic representation of the CaO structure and the attachment of the $Ca(OH)_2$ as drawn with the VESTA software. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

The interpretation of these results may be possible by keeping the nature of this material in mind. As mentioned earlier, in the presence of water or atmospheric air the CaO forms a $Ca(OH)_2$ compound [6]. Therefore, according to this nature of the material and referring to the literature, all the peaks on the sample's surface were an indication of the $Ca(OH)_2$ compound [18], while the other peaks indicated the formation of the original CaO compound. Mierwaldt et. al. [19] investigated the behavior of the O-1s and Ca-2p XPS peaks during ultra-high vacuum (UHV) conditions and exposure to an H_2O vapor atmosphere. Their results showed that the O-1s and Ca-2p that were related to the $Ca(OH)_2$ compound