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Employing one crystalline phase to gain different phosphor emissions for distinctive applications: Preparation, crystallization and luminescence of $SrAl_2B_2O_7$ with different additions via glass ceramic technique

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ABSTRACT

$SrAl_2B_2O_7$ phosphor was crystallized via glass-ceramic technique. The effect of adding TiO_2, Eu_2O_3, Dy_2O_3 and CeO_2 on both crystallization process and luminescent properties were studied using differential thermal analysis (DTA), X-Ray diffraction analysis (XRD), scanning electron microscope (SEM), Fourier-Transform infrared absorption spectra (FT-IR), optical ultra violet (UV) -visible near infrared (NIR) absorption and fluorescence spectrophotometer. The batches were melted around 1450 °C. New method to revealed reducing atmosphere was applied. DTA results show broad exothermic peak revealing surface crystallization. The XRD patterns depict crystallization of pure $SrAl_2B_2O_7$ in hexagonal form. Presence of CeO_2 enhances the crystallization of $SrAl_2B_2O_7$ phase while TiO_2 inhibit it. Increasing the time or temperature of heat treatment didn't affect the nature of the crystalline phase. Optical UV–visible NIR absorption and luminescent properties clarified the presence of titanium and cerium ions as Ti^{4+} and Ce^{3+} form, while europium present in both Eu^{2+} and Eu^{3+}. The resulting phosphor revealed different colors depending on the excited wavelength used and heat treatment applied.

1. Introduction

During the most recent decade, phosphorescence materials have attracted a lot of interest due to the fact they have huge reasonable and potential applications in several fields, e.g., emergent lighting, LED displays, optical amplifiers, markers for biomolecules, and carried out in a large scale as sensors for ultraviolet, x-ray, and β-ray identification [1].

Each phosphorescence color has its importance in the applied technology; for example blue-emitting materials which resulted from fast-decay luminescence are used in fluorescent lamps, plasma display systems or UV-emitting phosphors used in lamps for medical applications and skin tanning [2].

The most important application for blue phosphor is in white LEDs. White LEDs are generated by one of the following two techniques; the first is to match a blue chip with a yellow phosphor. This previous methodology leading to disadvantages like low color-rendering index (CRI), low luminous performance, and high color temperature [3–5]. The second one method is to apply red, green, and blue light emitting phosphors to generate the white light and such method is carried out by pumping the emitted tricolors by ultraviolet (UV) spectra emitted from InGaN chips. The latter approach has been focused in recent researches about the fluorescence materials due to its unique characteristics, including excellent color temperature, stable, and high energy performance [1,6,7].

The observed defects in the previous methodology may be existing due to differences in the properties of tri-color phosphor. For instance, the absorption of blue emissions occurs easily by green or red emissions that resulting in a weakness in the yield performance of white light emissions. Hence, the method of applying single host phosphors excited by ultraviolet spectrum to generate the white light has gain much interest between scientists [8]

The materials used in this field are huge, most of them prepared via solid state reaction which revealed disadvantages than glass method as presence of pores and incomplete homogeny throughout the sample. Borate glasses attract attention because their optical properties as: special optical damage threshold, ability to resist the cruel conditions in vacuum discharge lamps or screens [9] beside its large band gap [10–14]. Consequently, borate glasses can be used as host lattices for luminescent ions. Glass-ceramics are taken into consideration as an efficient and good candidate for the photoluminescence emissions especially during the control of non-irradiative losses over the lower limit of the excited states relaxations of luminescent ions of such materials [15].

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From different phases crystallized within borate glasses, $SrAl_2B_2O_7$ shows particularly importance; it can obtain by crystallization of aluminoborate glasses [16]. This phase was found in two crystalline forms, cubic and a hexagonal unit cell [2]. $SrAl_2B_2O_7$ and their derivatives are characterized as nonlinear optical materials and their crystalline structures are known as anti-centrosymmetric space group in the trigonal structural forms [17]. Doping aluminoborates phases with rare earth ions expect to give high UV transparency and non-linear properties [2].

Europium ions attract more interest of the scientists in luminescent field. Eu^{3+} containing materials are successfully excited by ~ 395 nm near ultraviolet as a result of $^7F_0$-$^5L_6$ transition and emit red light at ~615 nm due to the $^5D_0$-$^7F_2$ transition of Eu^{3+} ions [18,19]. Sulfides containing Eu^{3+} ions also have been represented in a wide scale as $Y_2O_2S:Eu^{3+}$ etc [20], but their main implementations were limited due to their poor chemical durability etc. On the other hands, the luminescence study of Eu^{2+} revealed variation in the positions of emission bands from ultraviolet to visible regions, according to the composition and structure of host lattice [21–24]. In most aluminates phases the emission of Eu^{2+} lies in the visible range as in $SrAl_2B_2O_7$ doped with Eu^{2+} lies in blue region. Combination of Eu^{2+} and Dy^{3+} gave interesting results where Eu^{2+} act as the emitter and also as an electron trapping center whereas Dy^{3+} act as the hole trap [25] giving emission peak around 520 or 400 nm depending on the crystal host [25,26]. Also combination of Cerium ions with other rare earth ion improved the luminescent properties [1].

Recent study by Rojas-Hernandez et al. [27] depicts methods that are designed to prepare inorganic ($SrAl_2O_4$) phosphor containing rare earths (Dy and Eu) including hydrothermal, co-precipitation, microemulsion, sol–gel method and combustion method and they reached to a new strategies to obtain micrometric phosphor particles avoiding the high cost and insufficient methods of preparations for industrial applications that can be occurred by starting from bulk material, proceed synthesis directly sub-microparticles and avoid the impacts of high energy during milling to retain crystallinity [27].

The wide objective of our study is utilizing one crystalline phase to get phosphor via industrial technique as glass method; this phosphor is characterized by safety and can emit different color for different applications. Consequently, in this study $SrAl_2B_2O_7$ phosphor was crystallized via glass-ceramic technique. The effect of adding TiO_2, Europium ions, Dy^{3+} and CeO_2 on both crystallization process and luminescent properties were studied using DTA, XRD, SEM, FT –infrared absorption spectra, Optical UV–visible NIR absorption and fluorescence spectrophotometer.

2. Experimental

2.1. Preparation of glasses

Table 1 represents the chemical composition of aluminoborate glasses in mole %. About 25 g powder of reagent grade as $SrCO_3$, Al_2O_3, H_3BO_3, TiO_2, Eu_2O_3 Dy_2O_3 and CeO_2 were thoroughly mixed. The compositions were denoted as **ST**, **SED**, **STED** and **SEDC** where S = sample, T = TiO_2, E = Eu_2O_3, D = Dy_2O_3 and C = CeO_2. After thoroughly mixing, the batches were placed in a platinum crucible and melted in an electric furnace at 1400–1500 °C for 1hr with occasional swirling every 15 min to ensure homogenization. The melting process was done under flow of N_2 gas to prevent the presence of O_2 gas from oxidizing Eu^{2+} ions; this new method is an attempt to replace the reduction process with hydrogen gas by replacing oxidizing atmosphere by inactive N_2 gas. The melts were quenched into cold stainless-steel plate to ascertain its glassy nature.

Table 1
Chemical composition of the designed glasses in mol%.

Sample no.	SrO	Al_2O_3	B_2O_3	TiO_2	Eu_2O_3	Dy_2O_3	CeO_2
ST	40	30	30	3	–	–	–
SED	40	30	30	–	0.05	0.05	–
STED	40	30	30	3	0.05	0.05	–
SEDC	40	30	30	–	0.05	0.05	3

2.2. Crystallization of glasses

Differential thermal analysis (DTA), using SDTQ600 instrumentation under inert gas was utilized to determine the temperatures of the glass transition (T_g) and crystallization (T_c) of the glass samples. The heating rate was 10 °C/min and alumina was used as blank reference material. The results obtained were used as a guide for determining the required heat-treatment temperatures needed to induce crystallization in the samples.

2.3. Characterization

Glass-ceramics were subjected to powder X-ray diffraction using Ni-filled Cu-Kα radiation for determination of the types and contents of the crystalline phases precipitated in them. X-ray diffraction (XRD) was performed using Bruker D8, an advanced instrument. The reference data for the interpretation of the XRD patterns was obtained from ASTM X-ray diffraction card files.

The morphology of glass-ceramics samples were examined with a scanning electron microscope, SEM model Philips XL30 attached with EDX unit, using an accelerating voltage of 30 K.V., magnification 10x up to 400,000x, and resolution for wavelength (3.5 nm).

2.4. Optical UV–visible NIR absorption measurements

The optical absorption spectra of perfectly polished samples of equal thickness (2 mm ± 0.1 mm) were recorded at room temperature using a recording spectrophotometer type (JASCO Crop., V-570, Rel-00, Japan) in the range 200–2600 nm.

2.5. FTIR absorption spectra

FT –infrared absorption spectra were recorded for powder samples at room temperature in the range 4000–400 cm^{-1} by FT infrared spectrometer (type JASCO – 4600 FTIR) using potassium bromide pellets for fine powdered samples.

2.6. Luminescence properties

Luminescence spectra were measured on a spectrofluorometer instrument model Jasco FP-6500 (Japan) with UV- cut filter to avoid scattering. The light source was Xenon arc lamp (150 W) and the excitation and emission slit band widths were 5, 5 nm, respectively. The phosphorescence lifetimes were measured also using Jasco spectrofluorometer and were calculated using the software supplied with the instrument. All the samples were measured under the same geometrical conditions and at room temperature.

2.7. CIE 1931 chromaticity diagram

Any color with its hue, saturation, and luminance can be specified by the tristimulus values X, Y, and Z. Chromaticity coordinates are calculated from the spectral power distribution of the light source and the CIE color-matching functions in the range 380–370 nm at intervals of 5 nm. The tristimulus values for a nonmonochromatic light source with spectral relative power P(λ) are given by [28,29]:

$$X = \int P(\lambda)\bar{x}(\lambda)d\lambda \tag{1}$$