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Synthesis, characterization and photoluminescent properties of $BaZr_xNd_{1-x}O_3$ perovskites

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ABSTRACT

$BaZr_xNd_{1-x}O_3$ perovskites were prepared by the conventional solid state ceramic route for $x = 0.85$, 0.9, 0.95, 0.99, 0.995 and 0.999. The powders were calcined at 1250 °C. X-ray diffraction patterns of the samples confirmed the cubic phase formation and no considerable additional peaks were found. The absorption spectra of doped samples showed strong absorption around 225 nm, a shoulder at 250 nm and a broad peak around 330 nm. The samples with higher concentrations of neodymium show peaks around 750 and 800 nm. The absorption at 250 nm was due to the absorption by the host $BaZrO_3$ and others can be attributed to that of Nd^{3+}. The emission spectra of the samples were recorded for different excitations and strong emissions were observed around 344 nm, 360 nm, 401 nm, 527 nm and 901 nm. Chromaticity values of the samples measured using CIE chromaticity diagram were also discussed.

1. Introduction

The recent development of materials with optical properties such as electroluminescence and photoluminescence can lead to new high performance optoelectronic devices [1]. The study of luminescence properties of rare earth elements hosted in several crystalline matrices such as metal oxides, phosphors, metal-organo complexes and variety of semiconductor materials is strongly motivated because of their applications in optoelectronic devices and flat panel displays such as electroluminescent displays, field emission displays, plasma display panels, and vacuum fluorescent displays [2]. The requirement of phosphors for each application is different and the searches for new materials with improved properties are in progress. The photoluminescent properties of Bi, Ga, In and Al materials doped with various lanthanides such as Ce, Pr, Nd, Sm, Gd, Tb, Eu, Yb, and Er are reported. Depending upon the dopants and host materials used, luminescent spectra can be obtained in different regions of electromagnetic spectra.

Among various lanthanides, neodymium (Nd^{3+}) is of technological importance due to its various applications in commercial red phosphors and active laser components [3]. Nd^{3+} possesses intense luminescence at 1.06 μm [4–6]. A number of reports are available on the up-conversion properties of Nd^{3+} [7–10]. Due to the low luminescent efficiency, very little reports are available on the luminescence properties of Nd doped crystals in the visible region, most of the reports are concentrated in the 1.06 μm region. The photoluminescent emission of Nd^{3+} strongly depends on the host materials used. It was reported that choosing appropriate host materials for Nd^{3+} activators, allow the occurrence of visible transitions under ultra violet excitation conditions [11,12]. Mizoguchi et al. [13] reported that on changing the host environment, the emission from Sn^{2+} ion in $BaSnO_3$ shifts from NIR region further into the infrared region. In the case of neodymium, the emission was observed around 1070 nm in Nd:YAG [14], 876 nm and 1070 nm in $BaTiO_3$ host [15], 900 nm and 1060 nm in $LaGaO_3$ [16] and ZrO_2 host [17]. Besides the above mentioned emissions of Nd^{3+}, Yamanoi et al. [18] reported the vacuum ultraviolet (VUV) fluorescence of Nd^{3+} in APLF glass host around 185 nm due to the $4f^25d$ to $4f^3$ transitions of Nd^{3+}. Only a few reports are available on the emission properties of Nd^{3+} based materials in the visible region. Liu and Kuang [19] reported intense visible luminescence from Nd^{3+} in Yttrium oxysulfide host. They observed strong emission in blue region with 261 nm pumping and is attributed to the $^2P_{1/2}$ to $^4I_{9/2}$ transitions of Nd^{3+}. A bright red luminescence at 613 nm is reported for $Nd_x(Ca_{1-x-y-z}Ba_ySr_z)TiO_3$ system under excitation at 335 nm [20].

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Recently, considerable interest has been given in the area of materials science and research in doped perovskite structures, owing to their wide variety of unique electronic, magnetic and optical properties [21]. Perovskite type oxides are a class of materials that have been investigated extensively since 1940s, since these materials display a plethora of physical and chemical properties of technological interest that depend on the processing conditions, oxygen content, order, particle size, etc. Due to their excellent capability of hosting functional ions of various dimensions and types, perovskite materials offers a wide area for fundamental and technological research especially for their attractive optical properties. Zirconia based perovskites are very promising refractory structural materials with a very high melting points, low chemical reactivity with corrosion compounds and better phase consistency over a wide range of temperature [22]. Among these $BaZrO_3$ possess excellent phase consistency that they may not undergo any phase transitions even up to their melting temperatures [23]. These properties of $BaZrO_3$ make it a promising candidate for its potential applications as host materials for lanthanides in optoelectronic applications. In the present paper, we report the visible luminescence of Nd^{3+} activated in $BaZrO_3$ host material.

2. Materials and methods

Conventional solid state ceramic route were used for the preparation of $BaZr_xNd_{1-x}O_3$ compounds. High pure $BaCO_3$, ZrO_2 and Nd_2O_3 (Hi-media Chemicals, India) were taken in stoichiometric ratios and mixed thoroughly in acetone medium in an agate mortar for about 2 h. Nd_2O_3 was annealed at 1000 °C for 1 h in order to eliminate any presence of additional impurities. The samples were dried and calcined at 1250 °C for about 6 h in an electrically heated furnace. The powders were ground well and calcined powder samples were used for X-ray diffraction studies (Philips XPERT PRO) using Cu-Kα radiation. The absorption and reflectance spectra of the calcined samples were measured using a Jasco UV–Visible spectrophotometer. The Photoluminescence spectra of the samples were measured using Flurolog@-3 Spectrofluorometer. The CIE colour co-ordinates based on CIE 1931 chromaticity calculations of the PL spectra was calculated using the colour calculator program developed by Radiant Imaging.

3. Results and discussion

Fig. 1 shows the XRD patterns of $BaZr_xNd_{1-x}O_3$ compounds for ($x = 0.85$, 0.9, 0.95, 0.99, 0.999, 0.995 and 1). All the samples crystallizes in the cubic phase of $BaZrO_3$ and were compared with the standard JCPDS file (JCPDS 06-0399). It is evident from the XRD patterns that there is no considerable phase change for the doped samples compared with that of pure samples. Secondary phases $BaNd_2O_4$ (JCPDS 86-0679) has been observed in $BaZr_{0.85}Nd_{0.15}O_3$ samples. The ionic radii of Nd^{3+} is 1.109 Å, which is comparable with that of Zr^{4+} (0.84 Å) and hence may replace Zr in crystal lattice site, which may be the reason for the absence of any secondary or impurity phase up to $BaZr_{0.9}Nd_{0.1}O_3$.

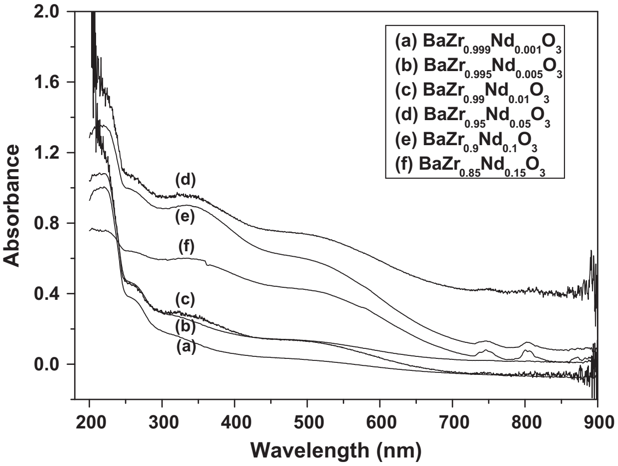

Fig. 2a. Absorbance spectra of Nd^{3+} doped $BaZrO_3$.

Figs. 2a and 2b shows the absorbance spectra of Nd^{3+} doped and undoped $BaZrO_3$ compounds respectively. All the Nd^{3+} doped samples show strong absorption at 225 nm, a shoulder at 250 nm and a broad peak around 330 nm. The samples with higher concentrations of neodymium show peaks around 750 and 800 nm. The band gap reported for undoped $BaZrO_3$ is around 4.8 eV [24]. The peak around 250 nm can be attributed to band edge absorption of $BaZrO_3$. The absorption at 330 nm in the spectra of doped samples, which was absent in the undoped samples can be due to the electrical transitions of Nd^{3+} ($^4I_{9/2}$ to $^4D_{1/2}$) [25]. The peaks around 750 and 800 nm is due to the transitions from $^4I_{9/2}$ to $^4S^{3/2}$ and $^4F_{7/2}$, $^4F_{5/2}$ and $^2H_{9/2}$ respectively [26].

Fig. 3 shows the Tauc's plot of $BaZr_xNd_{1-x}O_3$ for $x = 0.999$, 0.995, 0.99, 0.95, 0.9 and 0.85 respectively. The variation of band gap with the doping concentration of Nd^{3+} is shown in Fig. 4. The band gap of BZN samples shows a decrease in band gap with increasing concentration of Nd^{3+}. Doping introduces additional energy levels near to the conduction and valance band of the material leading to band edge tailing. The evidences of small phase change for higher doping concentration ($x = 0.85$) corroborates the XRD results.

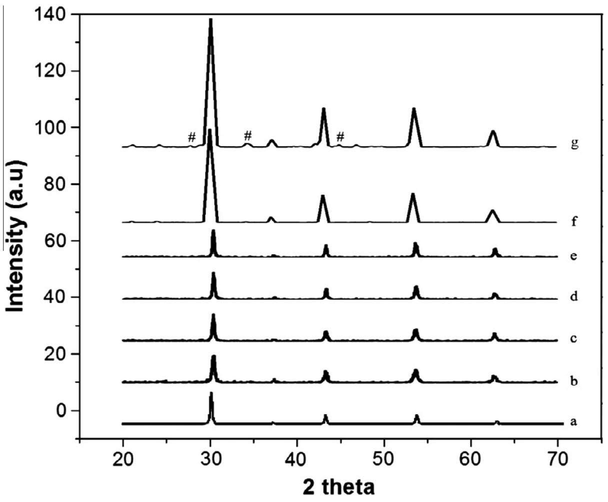

Fig. 1. XRD patterns of $BaZr_xNd_{1-x}O_3$ compounds.

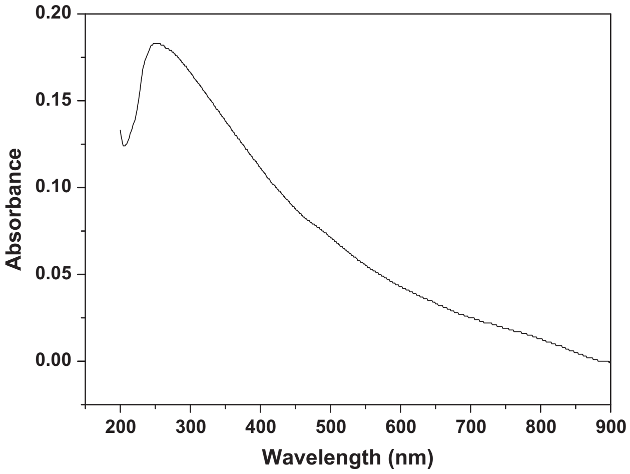

Fig. 2b. Absorbance spectra of undoped $BaZrO_3$.