Abstract

BaO–ZrO₂ nanocrystals were synthesized using the chemical bath deposition technique and then subjected to post-synthesis annealing between 500 and 900 °C. X-ray diffraction patterns showed the amorphous structure for as-synthesized sample, while annealed samples show either disordered tetragonal phase or a mixture of tetragonal and monoclinic phases at high temperatures. The emission spectrum displays blue emission band for the as-synthesized sample with peak maximum at 434 nm. All annealed samples showed both blue (434 nm) and red (710 nm) emission bands upon excitation at 248 and 360 nm. Samples excited at 310 nm produced only the red emission band centered at 710 nm, which decreased monotonically with increasing temperature and was completely quenched at 900 °C. CIE results show the phosphor is capable of producing blue, red and white light depending on the excitation wavelength chosen and the post-synthesis heat treatment temperature. The synthesized phosphor is cost-effective and can be applied in display and other lighting technologies.

1. Introduction

Zirconia is a very important ceramic for various applications because of its excellent mechanical, chemical, optical properties [1, 2] and its abundance in the Earth crust. Zirconia has three polymorphs which occur at different temperature regimes; cubic (c- ZrO₂), tetragonal (t- ZrO₂) and monoclinic (m- ZrO₂) phases [3]. The transformations between these three polymorphic phases limit the application of zirconia. Fortunately, the control and manipulation of these phases can be achieved by either one or a combination of the following: heating zirconia at elevated temperature, changing the crystallite size at certain thresholds and addition of various oxides of transition or rare-earth ions [4]. The most common oxides used for stabilizing zirconia are yttrium and cerium oxides [5]. Besides, the inclusion of rare-earth ions such as Eu³⁺, Tb³⁺, and La³⁺ also facilitates phase stabilization in addition to harnessing their optical potentials [6, 7]. Few reports are found for Ba²⁺ stabilized zirconia [5, 8] but none was focused on the luminescence properties of Ba²⁺ stabilized zirconia. In this work, we report the stabilizing potentials of BaO and the unusual optical properties of zirconia when incorporated with BaO (at its solubility limit) followed by annealing at varying temperatures. The BaO–ZrO₂ nanocrystals show tunable emission from red light to white light (of different hue) when annealed at different temperatures. This tunable emission is unique to BaO–ZrO₂ nanocrystals than the component oxides (BaO and ZrO₂).

2. Experiments

The BaO–ZrO₂ nanocrystals were prepared using the chemical bath deposition technique. The samples were then annealed at varying temperatures between 500 and 900 °C. Typically, a predetermined amount of C₁₆H₃₆O₄Zr and Ba(NO₃)₂ solutions in Ba/Zr molar ratio of 0.25 were mixed in a beaker. The mixture was then
transferred to a pre-heated water bath set at 80 °C with continuous stirring. A mixture of NH₃ and H₂O₂ solutions was drop-wise added to the above mixture resulting in a white precipitate which was aged for 24 h. The precipitate was filtered and washed several times with deionized water and ethanol, followed by drying at 110 °C for 12 h. The dried solid was grinded with pestle and mortar into fine powder and then separated into equal masses which were annealed at the various temperatures (500, 600, 700, 800 and 900 °C) for 3 h.

The powders were characterized using a Bruker AXS D8 Advance powder x-ray diffractometer with Cu Kα radiation. The JEOL JSM-7800F Field Emission Scanning Electron Microscope (FESEM) equipped with Oxford Xmax⁵ Energy Dispersive Spectrometer (EDS) was used to study the morphology and composition of BaO–ZrO₂ nanocrystalline phosphors. Similarly, the morphology and microstructure of the BaO–ZrO₂ nanocrystalline phosphors were obtained from Transmission Electron Microscope (TEM), high resolution TEM (HRTEM) and selected area electron diffraction (SAED) using JEOL-JEM 2100 Transmission Microscope. TEM analysis was carried with the aid of CrystBox analytical tool developed by Klinger [9]. The PerkinElmer Lambda 950 UV–vis spectrophotometer was used to obtain diffuse reflectance data. Room temperature photoluminescence was measured using an Edinburgh instrument FLS980 spectrometer with double monochromators.

### 3. Results and discussion

#### 3.1. Structural analysis

X-ray diffraction patterns of BaO–ZrO₂ nanocrystals after post-synthesis heat treatment at various temperatures are displayed in figure 1. The as-synthesized sample showed a broad amorphous structure and samples annealed at 500–700 °C displayed mainly the deformed tetragonal structure of ZrO₂ according to JCPDS card No. 81-1545. After heat treatment at 800 °C, the monoclinic phase (JCPDS card No. 86-1451) emerged and turned out to be dominant after annealing at 900 °C. These results show that BaO is capable of stabilizing zirconia in the tetragonal phase at temperatures up to 700 °C. We also observed the dominance of the 112 reflection in the tetragonal phase. Both Jones and Mee [10] and Pradhan *et al* [8] showed that mixed phases of monoclinic-cubic/
tetragonal coexist in baria-zirconia at low BaO concentrations and certain synthesis methods, respectively. According to Garvie, tetragonal zirconia is stabilized when the crystallite size is less than 10 nm. A complete conversion from tetragonal phase to monoclinic phase is achieved at 30 nm. In 1978, Garvie gave calcination temperature ranges and corresponding crystallite sizes at which tetragonal to monoclinic transformation could occur; 800–900 °C has crystallite size at 22 nm with a trace amount of monoclinic phase. In the range 900 to 1000 °C, the crystallite grew to 26 nm and a complete conversion to monoclinic phase. However, in this research the average crystallite size of the synthesized BaO–ZrO₂ obtained from Scherer formula range from 9 nm to 16 nm; samples annealed at 500–700 °C have average crystallite size of about 9 nm, and those samples annealed at 800 and 900 °C have sizes around 15 nm and 16 nm, respectively. The tetragonal to monoclinic phase conversion started quite earlier (800 °C) than proposed by Garvie. This may not be unconnected to the presence of BaO in the crystal lattice of zirconia. According to Wei-ping et al the solubility of BaO is quite low (0.025 in molar percent) in c-ZrO₂ and t-ZrO₂. Though, this level of solubility was thought to be of great benefit to the enhancement of mechanical strength of ZrO₂, it was considered to be too small to effectively stabilize it in the t-ZrO₂ phase at low temperatures. However, we have demonstrated that in addition to post-synthesis heat treatment, BaO could effectively stabilize zirconia in the tetragonal phase up to 700 °C.

3.2. Morphology
The scanning electron micrographs of BaO–ZrO₂ nanocrystals annealed at 600 °C and 900 °C are presented in figures 2(a), (b), respectively. Both micrographs show fractured particles of irregular size distribution. The jagged edges and small particles still present in the sample annealed at the elevated temperature (900 °C), as compared to the same sample annealed at 600 °C, suggest that segregation and grain growth was minimal. The EDS spectra in figures 2(c), (d) show the same percentage by weight of the Ba²⁺ ion (0.3 Wt%) in the zirconia matrix. This value of weight percent translate into 0.26 mol% of Ba to Zr ratio. No impurity elements were recorded in either sample.

The morphology and microstructure of BaO–ZrO₂ nanocrystals are further explained by TEM, high resolution TEM (HRTEM) and selected area electron diffraction (SAED) all shown in figure 3. Analysis of HRTEM images in figures 3(a) and (c) shows the particles are ellipsoidal in shape and partially agglomerated with well-defined lattice fringes (yellow encircles). In figure 3(a), an isolated micrograph of a single particle of BaO–ZrO₂ (annealed at 600 °C) with a lattice spacing of 0.2957 nm corresponding to the (100) plane of tetragonal ZrO₂. The SEAD for the corresponding sample also shows single-phase tetragonal ZrO₂ structure.
yellow rings. The fringes contain planes of both tetragonal and monoclinic phases of ZrO$_2$. Similar result can be seen in the corresponding SAED pattern shown in figure 3(d). In both figures, the monoclinic phase dominates which is consistent with the XRD results presented in figure 1. The disorder caused by both high temperature treatment and tetragonal-monoclinic phase transformation can immediately be seen in figure 3(b).

3.3. Optical analysis

The representative diffuse reflectance spectra (DRS) of as-synthesized and annealed BaO–ZrO$_2$ nanocrystals are displayed in figure 4(a). Other patterns have the same characteristics as the spectra presented in figure 4. The as-synthesized sample show prominent absorption peaks at 212.9 nm (5.82 eV), 291.6 nm (4.25 eV), and 360.1 nm (3.44 eV) (figure 4(a)). Meanwhile, the annealed samples show absorption peaks at 214.8 nm (5.77 eV), 341.6 nm (3.63 eV), 360.1 nm (3.44 eV), 457.7 nm (2.71 eV) and 494.0 nm (2.51 eV) (figure 3(a)). The peak at 212.9/214.8 nm is due to the zirconia band to band transition [8, 14–16]. The 291.2 nm and 341.6 nm absorption peaks are assigned to the d-d transition states of impurity Ti$^{3+}$ ion [17]. However, peaks at wavelength above 341 nm are assigned to BaO absorption, which becomes more prominent after annealing them. A combination of Kubelka-Munk remission formula [18] and the Tauc’s relation [19, 20] was used to obtain the energy bands for the samples as shown in figure 4(b). The as-synthesized BaO–ZrO$_2$ (0 °C) has energies at; a = 2.92 eV (424.7 nm), b = 3.42 eV (362.7 nm), c = 5.05 eV (245.5 nm) and the annealed sample (800 °C) has energies positioned at; d = 2.23 eV (556.1 nm), e = 3.44 eV (360.5 nm), f = 4.42 eV (280.5 nm) and g = 4.97 eV (249.5 nm). Though the energy at 5.05 eV coincides with the separation between the valence band and vacuum level in BaO as suggested by Taft et al in 1959 [21], in this case it is best ascribed to the band gap energy of the ZrO$_2$ [8, 16]. The band gap energy decreased to 4.97 eV after annealing to 800 °C. The rest of the energies coincide with reported values for BaO [21].

Figure 5(a) displays photoluminescence excitation (PLE) spectra for as-synthesized sample obtained by monitoring the 434 nm emission wavelength, and annealed sample (600 °C) obtained at 434 and 710 nm emission wavelengths. The PLE spectrum of as-synthesized sample shows strong excitation band at 240 nm and a low intensity band in the range 300–370 nm. The excitation spectra for the annealed samples show strong broad band covering the 236–370 nm range and their spectra vary with emission wavelength; at 434 nm emission wavelength, the excitation spectrum show bands at 241, 257, 287, 305, 310, 319, 342 and 360 nm with the dominant wavelength at 360 nm. The absorption peaks at 287 nm, 305 and 310 nm have already been...
Figure 4. (a) Diffuse reflectance spectra of as-synthesized and annealed (800 °C) samples, and (b) the energy band diagram of BaO–ZrO$_2$ nanocrystals.

Figure 5. Photoluminescence Excitation spectra (a) and emission spectra (b)–(d) BaO–ZrO$_2$ nanocrystals.
ascribed to exciton formation in BaO [10]. The bands at 319 nm and 342 nm are ascribed to the inherent Ti$^{3+}$ ion in ZrO$_2$ [17, 22]. The excitation spectrum obtained by monitoring the 710 nm emission wavelength presents the same bands listed above (obtained by probing 434 nm emission wavelength), except that the 310 nm band is now dominant. These extra bands for annealed samples, when compared to the as-synthesized sample, may be due to structural defects as well as the prominence of BaO states after annealing them. Besides, the excitation peaks corresponds largely to the absorption peaks shown in figure 3.

Photoluminescence emission spectra of BaO–ZrO$_2$ nanocrystals annealed at different temperatures and excited at 248, 310, and 360 nm are displayed in figures 5(b)–(d). Unique PL characteristics are obtained at excitation wavelengths of 310 and 360 nm. When BaO–ZrO$_2$ nanocrystals were excited by a 310 nm source (figure 5(c)), the emission spectra show broad red spectrum centered at 710 nm. No other significant band was observed at lower wavelength. Besides, the red band decreases monotonically with increasing annealing temperature, reaching a minimum at 900 °C. On the other hand, both blue and red bands were obtained for the annealed samples after exciting them at 248 nm and 360 nm. In this case also, the red emission band decreased monotonically with increasing temperature and reaches minimum at 900 °C. However, unlike the former case, the intensity of blue band became stronger than the red band at 800 °C and 900 °C. These are the two temperatures at which the tetragonal phase transformed to the monoclinic phase of zirconia. This result clearly shows that the red band from BaO–ZrO$_2$ nanocrystals is favoured when ZrO$_2$ structure is in the tetragonal phase. It also shows that excitation at 248 and 360 nm are indirect excitations via the host ZrO$_2$, while the 310 nm is a direct excitation of the BaO. One other point to note is that, while in the Jones and Mee report (1965) the 310 nm wavelength stimulated predominantly the blue emission band for BaO, in the present work, this wavelength stimulated only the red emission band. This is likely due to structural modification of barium oxide by the deformed ZrO$_2$ matrix. Deconvolutions of the broad emission peaks (not shown) display the presence of bands at 412, 434, 482 and 551 nm. The green emission bands at 482 and 550 nm may originate from Ti$^{3+}$ ion. This ion is known to be a major impurity that serves as primary activator in ZrO$_2$ [17, 22–25]. According to [17], the blue emission band is temperature and phase dependent; varying from blue (at low temperature and tetragonal phase of ZrO$_2$) to green (at $>800$ °C and monoclinic phase). However, in this work we did not observe this kind of variation, probably because of the presence of Barium ions which could quench the Ti$^{3+}$ emission like it is the case for Fe. Figure 6 shows the Ti$^{3+}$ energy levels and the transition producing the blue and green emissions.

The mechanism of luminescence in BaO–ZrO$_2$ is quite complicated, but an attempt has made to explain the process leading to the blue and red emissions observed from the material. The energy level diagram in figure 6 is drawn from the diffuse reflectance measurement results and the excitation spectra obtained for the samples. It is established that visible emission from ZrO$_2$ is associated with localized defect levels with the energy band gap. These localized levels are caused by factors like particle size, morphology, crystallinity, oxygen vacancy concentration, temperature, residual stress and microstructural constraints imposed by inert transforming phases [1, 3, 26, 27]. These factors generally influence the photoluminescence of ZrO$_2$. The introduction of barium (with a larger ionic radius) into the ZrO$_2$ lattice would enhance these defects. The main sources of localized defect centers in ZrO$_2$ crystal lattice is oxygen vacancies/interstitials and Zr vacancies/interstitials.

Figure 6. Energy level diagram for BaO–ZrO$_2$ nanocrystals.
(Zr$^{3+}$ interstitials) [27–30]. These defects exist primarily on the surface of the ZrO$_2$ nanocrystals owing to their high-surface area at the nanoscale. The surface vacancies are the most active among the defect centers since they readily trap electrons.

The excitation of ZrO$_2$ beyond the energy band gap (5.87 eV) generates electron—hole pairs. The electron is captured very quickly at the surface of oxygen vacancy ($V_0$) or any other vacancy state in the lattice thereby creating F centers at the surface as well as the lattice. The Zr$^{4+}$ residing adjacent to the oxygen vacancy may capture the electrons to form Zr$^{3+}$ below the conduction band. Meanwhile, oxygen vacancies ($V_0$) are formed just above the valence band as shown in figure 6. Transition of electron from the Zr$^{3+}$ center to the $V_0^-$ is non-radiative. This transition is followed by the radiative relaxation of the electron to the low lying states or the valence band, giving out red and blue emissions, respectively. The recombination process is described by the following equations [28]:

\[
\text{ZrO}_2 + h\nu \rightarrow e^- + h^+ \quad (1)
\]

\[
V_0 + e^- \rightarrow F(Zr^{3+}) \quad (2)
\]

\[
F(Zr^{3+}) + h^+ \rightarrow (V_0)^+ \rightarrow V_0 + h\nu \quad (3)
\]

The blue and red emissions observed from BaO–ZrO$_2$ nanocrystals can also originate from the BaO. The mechanism for blue and red light emissions from isolated BaO has been explained by Jones and Mee [10]. However, Ba is a transition metal and when incorporated in ZrO$_2$ matrix, its luminescence configurations are influenced by the crystal field of the host. An example is the fact that excitation at 310 nm produces blue emission and excitation at 400 nm produces red emission, which is not the case when BaO is excited in isolation, see [10].

There is a general consensus on the existence of absorption peaks 4.30 eV (288 nm), 4.06 eV (305 nm) and 3.93 eV (311 nm) belonging to BaO [10, 21]. Similarly, Dueker & Hansy [31] suggested the existence of donor levels at about 4.0 eV (A), 3.6 eV (B), 3.0 eV (C) and 2.4 eV (D) below the vacuum level of BaO (5.0 eV). All these transition energies have been observed in the diffuse reflectance measurement results and the excitation spectra of our samples. It is on this basis that the energy band diagram for BaO in figure 6 was drawn by taking a cue from Jones and Mee [10], though with modifications. Now let us describe the red and blue luminescence with respect to transitions involving the BaO. We consider the two most prominent excitation peaks in figure 5(a); at 360 nm (3.4 eV) which produces both blue and red emissions, and excitation at 310 nm (4.0 eV) which produces only the red emission. The absorption of photons at 3.4 eV resulted in an electron transiting from the valence band of BaO (which in this case is drawn coincidence with that of ZrO$_2$) to a partially filled level at B above the valence band. From this level, two transitions emerged; radiative transition to a level F, at about 0.62 eV above the valence band. This transition gave rise to the blue emission at 3.02 eV (412 nm). The second transition involves an electron from level B been captured at the oxygen vacancy level ($V_0$) which is then followed by radiative relaxation to the valence band (blue emission at 434 nm), and to level E, 1.2 eV above the valence band (red emission). The energy level, E of BaO is at resonance with the oxygen vacancy level, hence electron transfer occurs between them.

The red emission is also exclusively produced produced by exciting directly the BaO at the 4.0 eV level, A. This is followed by a radiative transition to a level, G at 2.3 eV above the top of the valence band. The emission level at G is associated with compositional changes of ZrO$_2$–ZrO$_4$ [31]. Since the red light emission emanated from transitions involving either oxygen vacancy states or compositional changes of ZrO$_2$, it validates the observed decrease in the luminescence intensity of the red component of the emitted light with increasing heat treatment. At high temperatures, the crystallite sizes become larger, crystallinity is enhanced, oxygen vacancy concentration reduces, and microstructural changes imposed by phase transformation begin to take place thereby quenching the red emission. Similar explanation could be valid for the blue emission line. However, the component of blue light coming from the BaO is not quenching as fast as the component from the defect states. Therefore, at higher temperatures, the magnitude of the blue emission remains nearly constant with increasing temperature, while the red component quenches spontaneously (figure 7).

Figure 8 shows CIE 1931 (Commission Internationale de l’Éclairage) colour coordinates of BaO–ZrO$_2$ nanocrystals annealed at a: As-synthesized, b: 500 °C, c: 600 °C, d: 700 °C, e: 800 °C and f: 900 °C. For the sample excited at 310 nm, the coordinates shift from white (the as-synthesized) to red (700 °C) and then shifted towards white light at 800 and 900 °C (figure 8(i)). This result is consistent with the decreasing red emission as temperature increases. On the other hand, when these samples were excited at 360 nm, the coordinates formed circle around the equal white region (figure 8(ii)). The result indicates that exciting the samples at 360 nm wavelength produced largely white light of different hues. White light ranging from cool white to warm white was obtained and are indicated by their respective correlated colour temperatures (CCT). Thus, the BaO–ZrO$_2$ nanocrystalline phosphor is capable of producing both red and white light. In order to determine the purity of the lights, the dominant wavelength/coordinates and the white point (D65) is plotted $(x_0, y_0)$ together with the
measured colour coordinates \((x_s, y_s)\) (the plotted points and coordinates of dominant wavelengths are not shown). A straight line was then drawn from the D65 point passing through the measurement point until it intersects the CIE 1931 gamut. The point coordinates at the intersection of the line to the gamut is the dominant wavelength/coordinates of the source \((x_d, y_d)\). The percentage purity of the phosphors were calculated using the formula [32]:

\[
Purity(\%) = \frac{\sqrt{(x_i - x_s)^2 + (y_i - y_s)^2}}{(x_d - x_i)^2 + (y_d - y_i)^2}
\]

The purity values of the phosphors are presented in table 1. Besides, the purity and CCT, the colour rendering index (CRI) was also determined from OSRAM colour calculator. The result shows low values of CRI because of the low intensity components of green light in the spectra. The obtained colorimetry parameters (CCT, CRI, colour purity & colour coordinate) show BaO–ZrO\(_2\) nanocrystals as a potential candidate for application in efficient display and lighting technologies. Besides, since the materials used for the preparation of BaO–ZrO\(_2\) nanocrystalline phosphors are inexpensive, it demonstrates that the phosphor will be cost-effective.
4. Conclusion

Nanocrystals of BaO–ZrO2 was synthesized using CBD method. Structural analysis shows tetragonal to monoclinic phase transformation at 800 °C. Blue and red emissions with broad bands were obtained at different excitation wavelengths. Blue emission originated from both BaO and ZrO2 and the red emission is defect mediated, hence decreases with enhanced crystallization at high temperatures. The red-emission band shows dependence on temperature and crystal phase, with the intensity decreasing as temperature increases. The red spectrum is completely quenched at the temperature (900 °C) at which the monoclinic phase became dominant; meanwhile, the blue emission spectrum was dominant at this temperature. The combination of the blue and red spectra gave under 360 nm excitation gave white light with relatively high purity but low CRI. The material is inexpensive and suitable for use for display and other lighting technologies.

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**Table 1.** CIE 1931 chromaticity diagram showing CIE coordinates, CRI, purity and nature of light BaO–ZrO2 nanocrystals and the standard D65 illuminant.

| Excitation wavelength | Annealed temperature | x     | y     | CCT  | CRI | Purity (%) | Nature of Light |
|-----------------------|----------------------|-------|-------|------|-----|------------|----------------|
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