CHAPTER II

LITERATURE REVIEWS

Structure of ZrO_2

ZrO_2 can exist in three different crystalline structures that are cubic, tetragonal and monoclinic polymorphs. These crystal structures undergo phase transition with increasing temperature [30]. The monoclinic is stable at low temperature. It transforms into a tetragonal phase when it is heated to 1170 °C. This tetragonal structure transform into a cubic one when the samples are further heated to 2370 °C as shown in Figure 13. Both cubic and tetragonal crystalline phases are unstable at ambient temperature. However these phases are more favorable for the technological applications than the monoclinic one due to their high photoluminescence efficiency [31]. So the crystal structure stabilization is very important for improving photoluminescence efficiency of this class of phosphor.

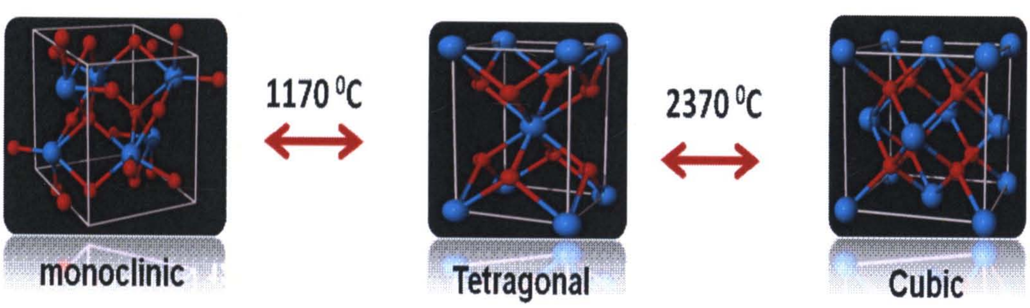

Figure 13 Phase transition of ZrO_2 crystals [32]

The ZrO_2 crystal structure stabilization

Previous studies were focused on ZrO_2 stabilization by different kinds of additive. Cations with lower valence than Zr^{4+} such as MgO, CaO and Y_2O_3 [33-38], and even oxides such as CeO_2, SiO_2, Cr_2O_3 and TiO_2 [39, 40] whose cations have the same valence with that of the host were used. These cations were introduced into the lattice of ZrO_2 to make cubic and tetragonal structure that is stable at room temperature. The cationic species added to ZrO_2 for tetragonal and cubic phase stabilization can affect the luminescence of RE^{3+} ion. These low-valent cations incorporate into ZrO_2 crystalline structure and substitute the zirconium cations. The ability to stabilize each crystalline phase of ZrO_2 at ambient temperature provides an opportunity for correlating the optical properties of rare-earth ions with the crystalline structure.

Figure 14 shows the example of yttrium oxide for doping into the pure ZrO_2 structure. The addition of yttrium oxide to pure ZrO_2 replaces some of the Zr^{4+} ions in the ZrO_2 lattice with Y^{3+} ions. This produces oxygen vacancies, as three O^{2-} ions replace four O^{2-} ions. It also permits yttrium stabilized zirconium dioxide to conduct O^{2-} ions.

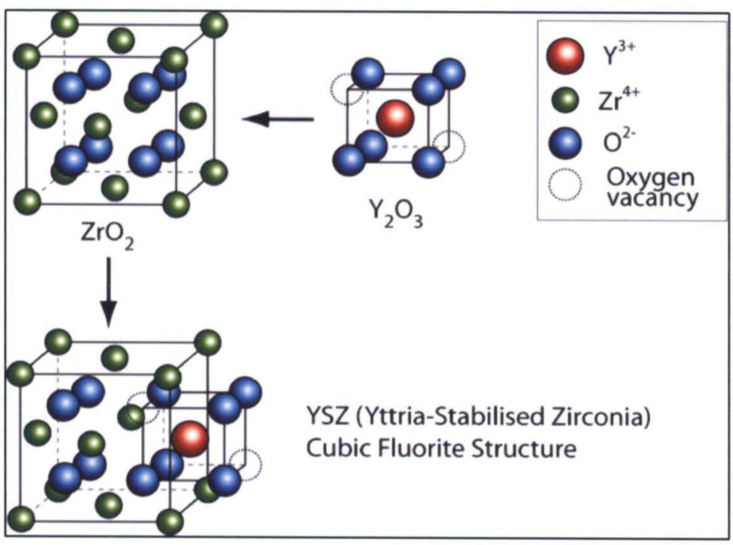

Figure 14 Stabilization of ZrO_2 structure with yttrium oxide (Y_2O_3) [41]

The RE^{3+} ions also stabilize crystal structure of ZrO_2 because the RE^{3+} ions are divalent and trivalent cationic species (the charge state 2+ or 3+). The oxygen vacancy is involved for charge compensation. Therefore, it is expected that the ZrO_2 doped with RE^{3+} ions could result in tetragonal and cubic phase stabilization. The relationship between structure of the materials and photoluminescence efficiency is explored. The materials are prepared by new route involving chemical method.

Many efforts stabilized the tetragonal or cubic phase at low temperature. Among additives, yttrium oxide (Y_2O_3) was an effective stabilizer and was widely used. Bokhimi, et al. [42] studied yttrium oxide-doped ZrO_2 nanopowders with various concentration of Y_2O_3 ion ranging from 0 to 10 mol% prepared by hydrolysis. The results indicated that the pure ZrO_2 exhibited the monoclinic phase. The addition of small amount of Y_2O_3 (2.5 and 5.0 mol%) into ZrO_2 resulted in tetragonal structure. Further increasing Y_2O_3 concentration to 7.5 and 10.0 mol% caused the formation of cubic phase as shown in Figure 15.

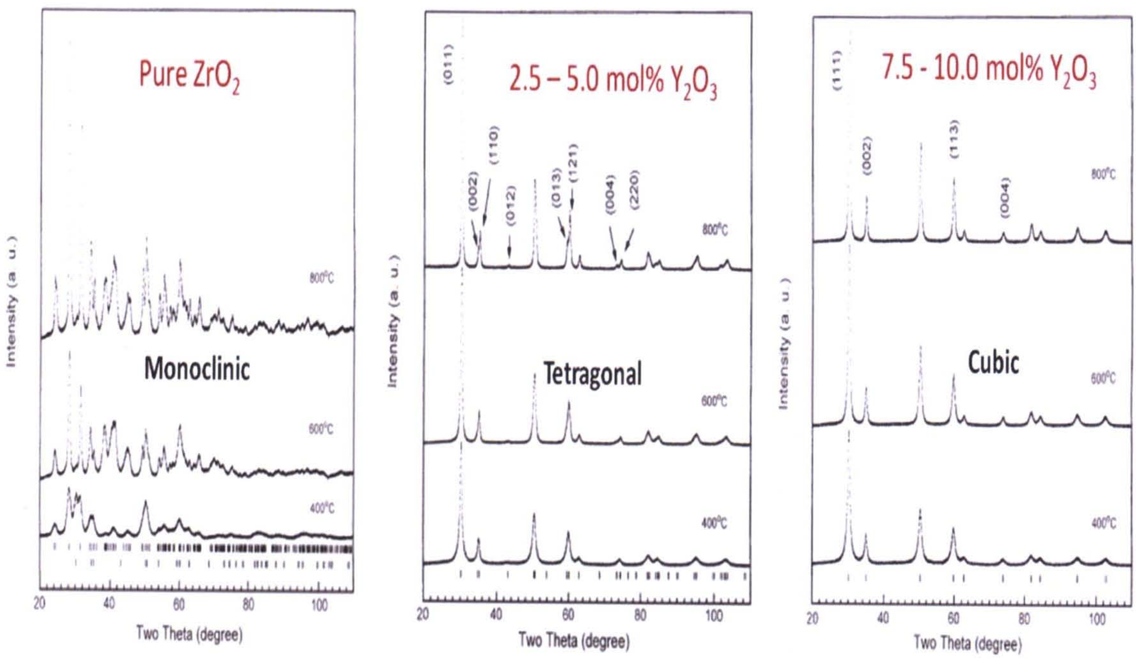

Figure 15 X-ray diffraction patterns of the ZrO_2 with various concentration of Y_2O_3 from 0 to 7.5 mol% [42]

Yang, et al. [43] studied yttrium oxide-doped ZrO_2 nanopowders with various concentration of Y_2O_3 ion ranging from 0 to 4 mol% prepared by solvothermal method. The tetragonal and cubic structures were obtained when the concentration of added Y_2O_3 was 2.5 and 4 mol%, respectively (see Figure 16). The particles had spherical shape with an average crystal size of 10 nm as shown in Figure 17.

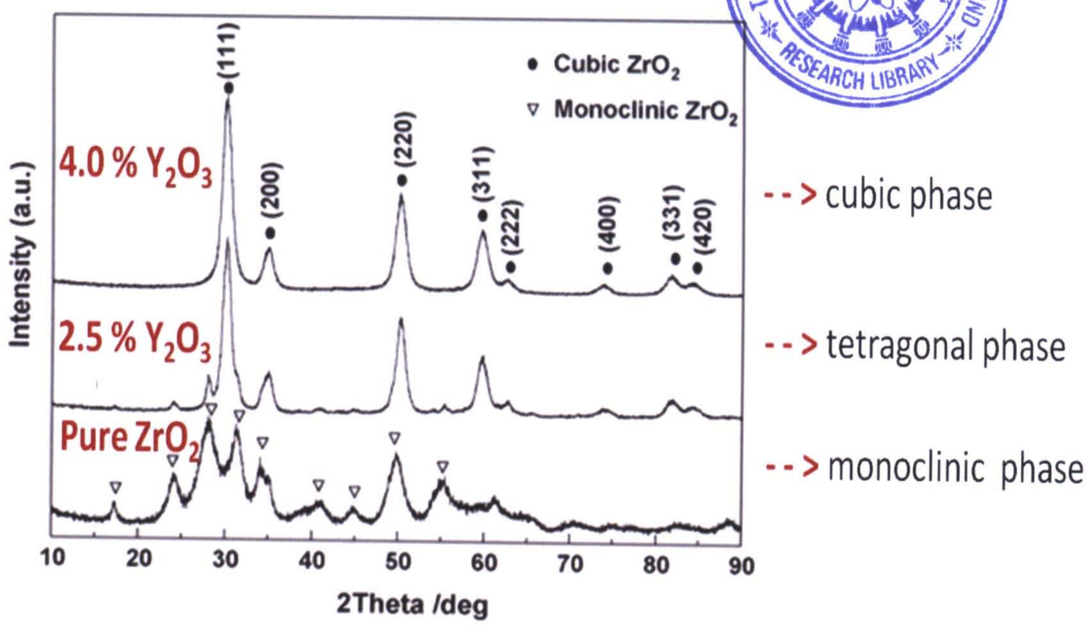

Figure 16 X-ray diffraction patterns of the ZrO_2 with various concentrations of Y_2O_3 [43]

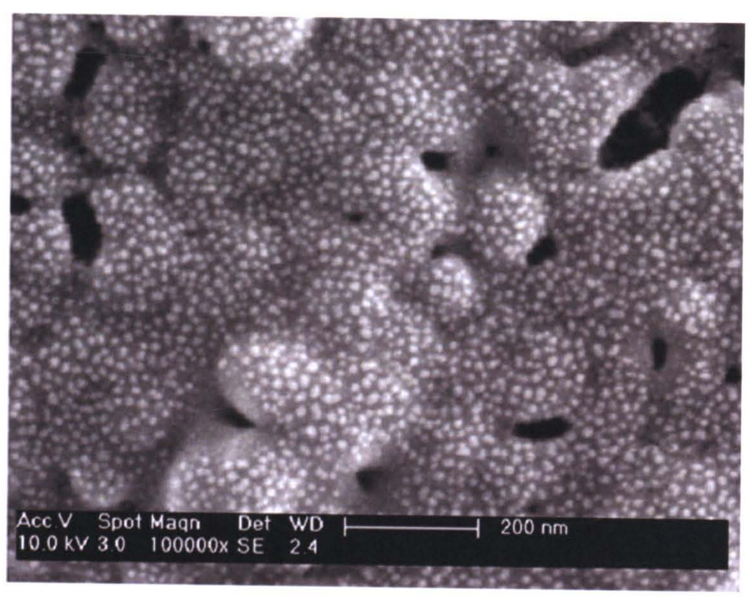

Figure 17 SEM image of the ZrO_2 with doping 4 mol% Y_2O_3 [43]

In addition, Wang, et al. [44] synthesized the Eu^{3+} ion doped zirconium dioxide nanocrystals with different doping concentration of CaO. From the XRD pattern of ZrO_2 with 2 mol% of Eu, phase of ZrO_2 changes from monoclinic to tetragonal and cubic phase as shown in Figure 18. The emission intensity of the phosphor increased with increasing of Ca^{2+} ion.

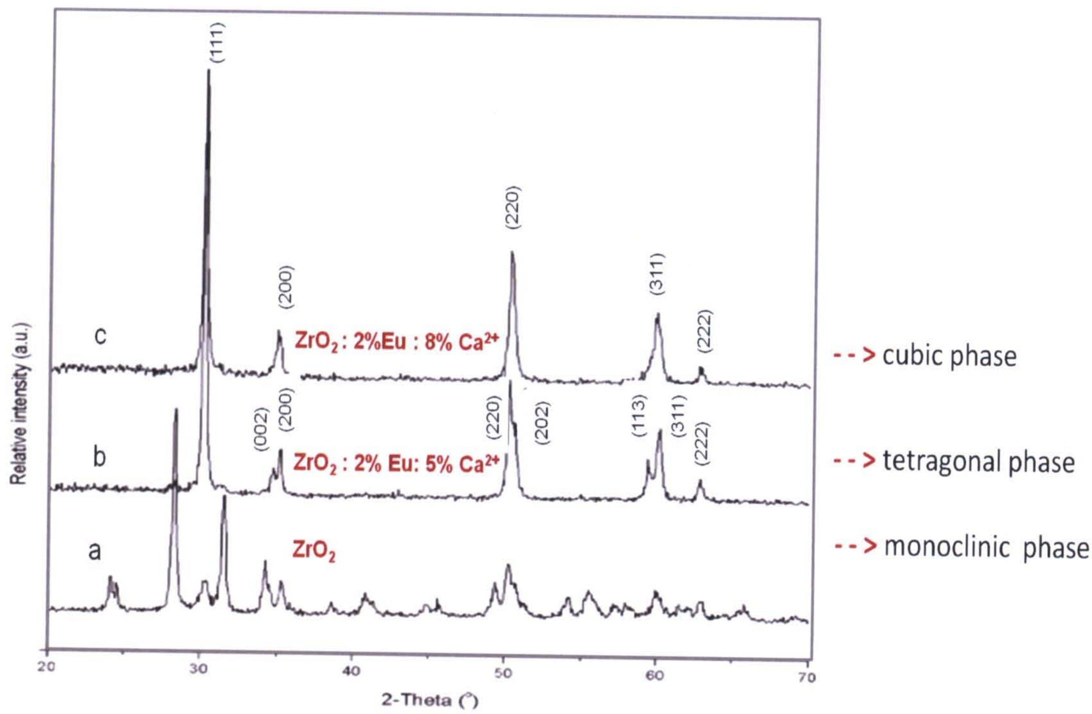

Figure 18 X-ray diffraction patterns of the ZrO_2 with various concentration of CaO from 0, 5 and 8 mol% [44]

In recent years, there are many reports on rare earth ion (RE) doped ZrO_2 nanocrystals by chemical method such as ZrO_2: Sm [45], ZrO_2: Dy [46], ZrO_2: Pr [47], ZrO_2: Tb [48], ZrO_2: Eu [49] and ZrO_2: Er [50, 51]. In addition, the transition metal (TM) doped ZrO_2 nanocrystals can be seen that these phosphor compounds emitted color such as ZrO_2: Mn [52, 53] and ZrO_2: Ni [8]. Diaz-Torres, et al. [46] studied the ZrO_2 nanocrystal doped with various concentrations of Dy, prepared by sol-gel method. The results indicated that the phosphor emitted yellow color and exhibited highest efficiency photoluminescence at 0.5 mol% of Dy concentration in ZrO_2. Its structure was a mixture of tetragonal and monoclinic crystalline phases. Gu, et al. [15] prepared the ZrO_2: Dy by co-precipitation method. The highest photoluminescence intensity was obtained when the concentration of Dy in ZrO_2 was 2 mol%. The structure still was a mixture of tetragonal and monoclinic phase. From both methods, it is clear that the efficiency photoluminescence of Dy doped ZrO_2 related with the tetragonal and monoclinic crystal structure.

From many studies, the photoluminescence efficiency of the ZrO_2 nanocrystal doped with rare earth ion such as Eu^{3+} ion was highest when the material was tetragonal crystalline phase [54-56]. Moreover, Smits, et al. [57] studied the effect of and yttrium ion in ZrO_2: Eu nanocrystal prepared by microwave driven hydrothermal method. It was found that the structure of ZrO_2 doped 6 mol% of Y_2O_3 and 0.05 mol% of Eu was tetragonal crystalline. The luminescence intensity was higher than that of ZrO_2 doped 0.5mol% of Eu about 10 times as shown in Figure 19.

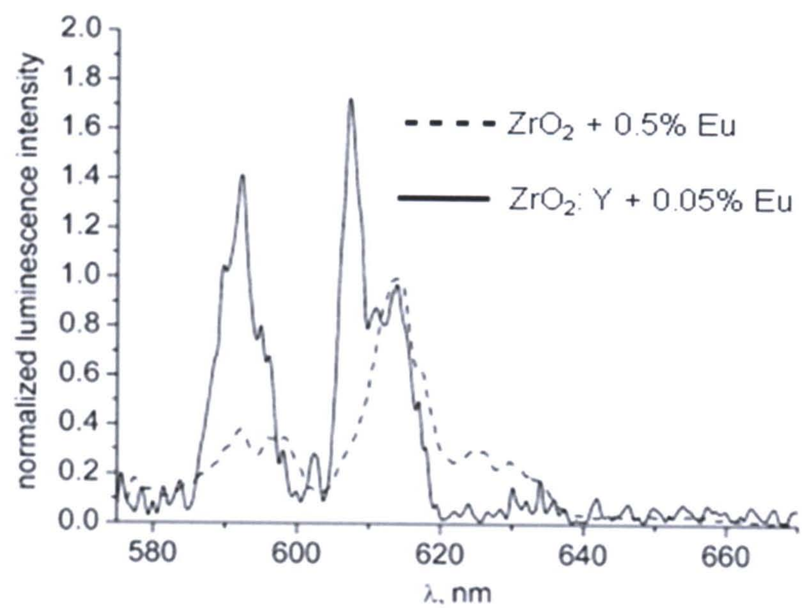

Figure 19 The luminescence spectrum of yttria-stabilized ZrO_2 containing 0.05% Eu [57]

However, adding of Y_2O_3 into the ZrO_2 nanocrystal doped with another RE was investigated by many groups. It was found that the photoluminescence efficiency was highest in tetragonal and cubic crystalline phase. Fu, et al. [58] studied photoluminescence of Dy^{3+} ions in yttrium-stabilized zirconium oxide. The ZrO_2 was added with 1% of Dy and varied the content of Y_2O_3 from 3 and 7 mol%. The structure transformed from monoclinic to tetragonal and cubic phases as shown in Figure 20. These phase transformations greatly affected the luminescence properties of

ZrO_2 co-doped with Y and Dy. It was found that the luminescent intensities in tetragonal and cubic phases were stronger than monoclinic phase as shown in Figure 21.

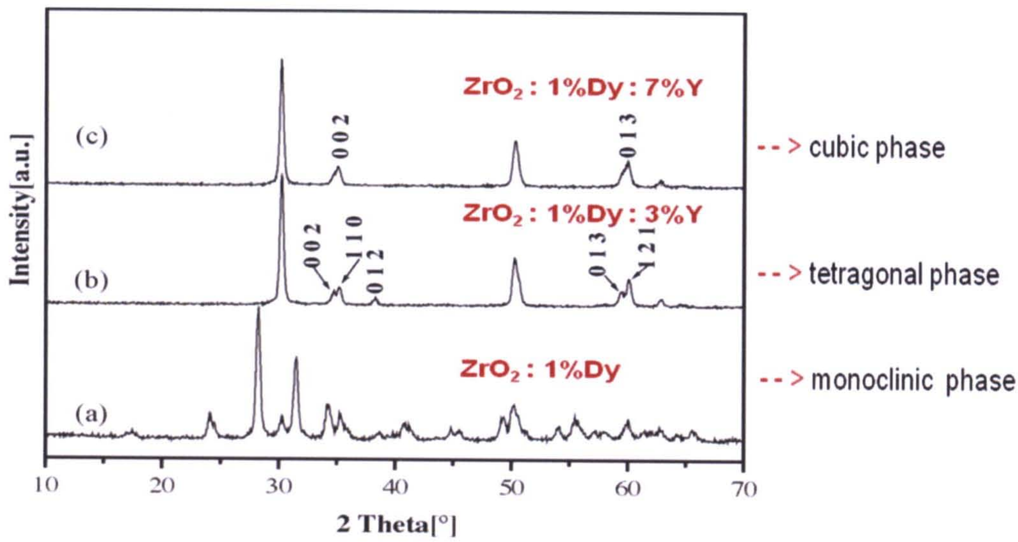

Figure 20 XRD patterns of ZrO_2: Dy particles with containing different content of Y (a) ZrO_2: 1%Dy (b) ZrO_2: 3%Y: 1%Dy and (c) ZrO_2: 7%Y: 1%Dy [58]

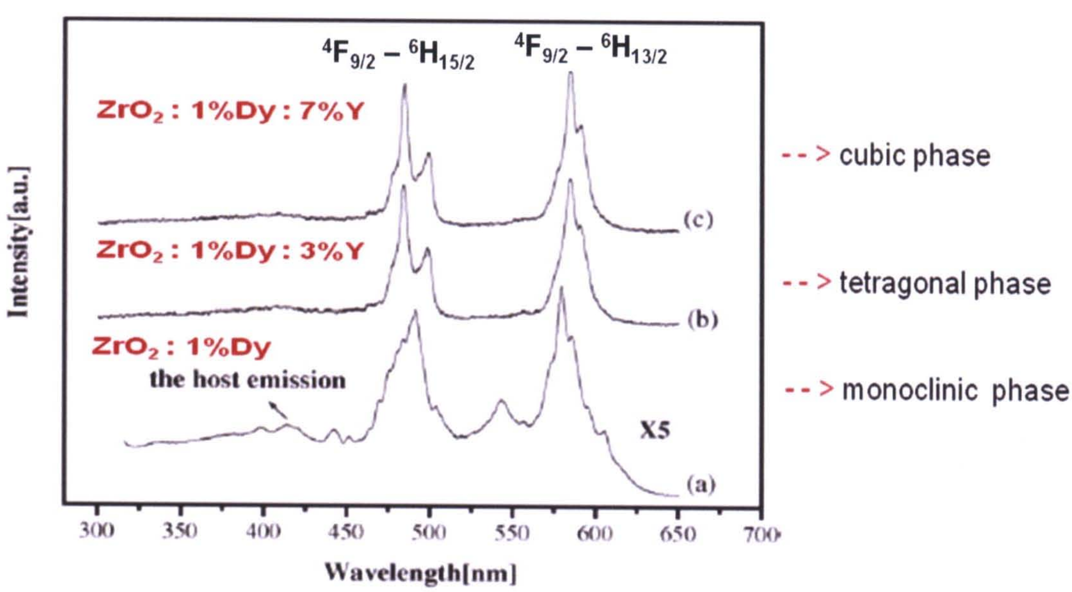

Figure 21 Photoluminescence of ZrO_2: Dy particles with containing different contents of Y (a) ZrO_2: 1%Dy (b) ZrO_2: 3%Y: 1%Dy and (c) ZrO_2:7%Y: 1%Dy [58]

In addition, the luminescence efficiency of Pr doped yttrium-stabilized zirconium oxide nanocrystal was investigated by Fidelus et al. [59]. The ZrO_2 nanocrystals were stabilized by 7 mol% of Y_2O_3. The luminescence intensities of the material improved significantly as shown in Figure 22.

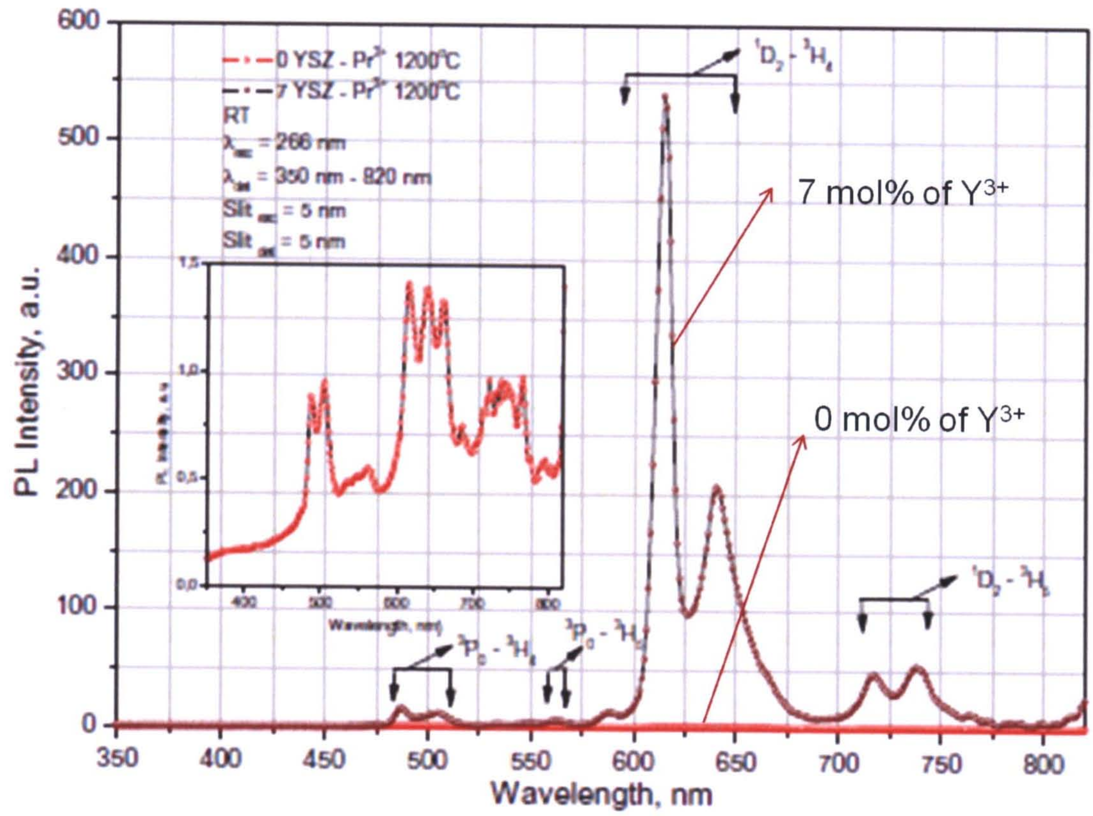

Figure 22 Photoluminescence of Pr in ZrO_2 and in sample stabilized by 7 mol% Y_2O_3 [59].

However, the luminescent properties of Eu^{3+} ions in different ZrO_2 phases modified by Y^{3+} ions are not well studied. Therefore, to be understand the effect of structural modifications on the photoluminescence spectra of the Eu^{3+}, Y^{3+} ions doped in ZrO_2 system.

Purpose of the Study

1. To synthesize the Eu doped yttria-stabilized zirconia nanocrystals by using chemical method

2. To study the effect of phase transformation on the luminescent properties of the Eu doped yttria-stabilized zirconia nanocrystals

Scope and Research Plan of the study

1. To synthesis the ZrO_2: Y: Eu phosphors by chemical process
2. The experimental parameter is varied as follow;
   2.1 The ratio of Y is varied from 0 to 7 mol%.
   2.2 The ratio of Eu is varied from 0 to 10 mol%.
   2.3 Different chelating agent will be used including citric acid, ethylenediaminetetraacetic acid (EDTA), malic acid and oxalic acid
   2.4 The effect of calcinations temperature is also investigated.
3. Preparation of ZrO_2: Y: Eu crystals in polymeric composite films
4. All samples will be characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and photoluminescence (PL) spectroscopy.