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Stabilised Ziconia and Luminescence of Ziconia Doped with Cerium $(Zro_2):Ce^{3+}$.

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Abstract: *One big disadvantage of pure Zirconis is polymorphism, during heating process it undergoes phase transformation and this makes the usage of pure Zirconia (ZrO_2) in many applications very difficult. This phase transformation leads researchers to focus on the modification of ZrO_2. The addition of some oxides e.g. CaO, Y_2O_5 etc into Zirconia (ZrO_2) results into modification that do not undergo phase transformation during heating, hence can be used in many applications. Y_2O_3 was used in this research as a stabiliser to prepare the modifications known i.e. monoclinic, cubic and tetragonal and it was doped with a rare earth trivalent metal. Precipitation method was used to obtain Zirconia hydroxide from $ZrOCl_2$. $8H_2O$ and 25% NH_4OH. This was then heated in an oven to obtain the desired modification. To measure it luminescence, ZrO_2 was doped with 1% Ce_2O_3 using heating method. The results of using a stabilizer showed that with 8% Y_2O_3, cubic phase of zirconia (mixed a bit with some monoclinic) was obtained and with 4% Y_2O_3, a mixed phase was also obtained. The results of doping Zirconia (ZrO_2) with 1% Ce_2O_3 showed luminescence spectra with two peaks, one at 22000cm^{-1} (454.5nm) which is due to Zirconia and the second peak at 16400cm^{-1} (609.8nm) which can be attributed to a fd-transition in Ce^{3+} in accordance with literatures.*

Keywords: *Cerium, Doping, Luminescence, Phase transformation, Stabilized Zirconia.*

I. Introduction

Zirconia (ZrO_2) exists in a monoclinic phase at room temperature inverting into a tetragonal phase above approximately 1200°C, it is available in a wide variety of shapes and sizes and also amenable to a wide variety of cold and hot forming techniques [1]. Zirconia is stable in oxidising and mildly reducing atmosphere, in its pure form it has a high melting point (about 2,700°C) and a low thermal conductivity. One big disadvantage of pure Zirconis is polymorphism, during heating process it undergoes phase transformation and this makes the usage of pure Zirconia (ZrO_2) in many applications very difficult [2]. This phase transformation leads researchers to focus on the modification of ZrO_2 [3]. The addition of some oxides e.g. CaO, Y_2O_5 etc into Zirconia (ZrO_2) results into modification that do not undergo phase transformation during heating, hence can be used in many applications. This research aims at using Y_2O_3 as a stabiliser to prepare the modifications known i.e. monoclinic, cubic and tetragonal and try to dope in a rare earth trivalent metal. Precipitation method is used to obtain Zirconia hydroxide which is then heated in an oven to obtain the desired modification. Doping Zirconia with 1% Ce_2O_3 was done using heating method.

II. Experimental

2.1 Preparation of Stabilised Zirconia:

To prepare stabilised zirconia, 3g of $ZrOCl_2$. $8H_2O$ was weighed and 8% mol of Y_2O_3 was added. The mixture was dissolved in hot water with stirring at 80°C with addition of small amount of HCl. The clear solution was precipitated using 25% NH_4OH and filtered. The hydroxide formed was washed with distil water and then washed several times with 1% NH_4OH to get Cl-free hydroxide. The Cl^- free hydroxide was heated for one day at 120°C to obtain the cubic phase modification of zirconium.

To get the tetragonal phase, 4.5% mol Y_2O_3 was used in the same procedure as above; the only exception was that after heating to 120^{o}C the product was cooled down slowly.

2.2 Doping with Ce_2O_3:

For the doping procedure, 3g ZrO_3 and 1% Ce_2O_3 was weighed and mixed well in a mortar. The mixture was heated at 1000°C for 14 days, and then cooled down slowly.

III. Results

3.1 ZrO_2:8%Y_2O_3.

With 8% Y_2O_3, cubic phase of zirconium (mixed a bit with some monoclinic) was obtained. The x-ray powder diffraction pattern of the prepared modification seen in blue fitted into the theoretical cubic pattern seen in red, as shown in fig 1. Some few peaks can be seen to belong to monoclinic phase, but the cubic fit the measured much better.

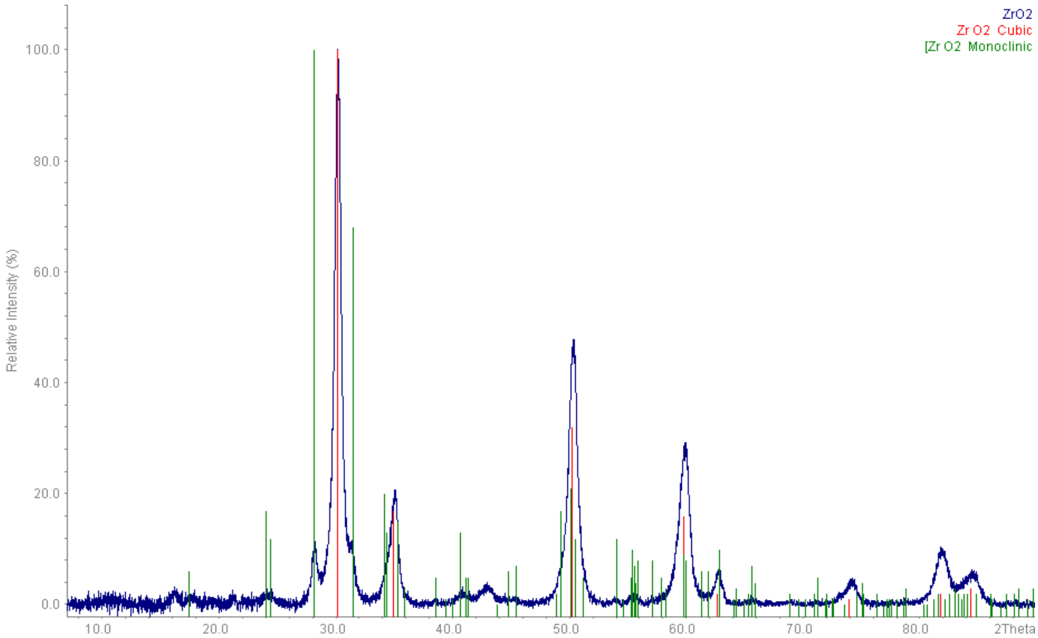

Fig 1. X-ray Powder Diffraction Pattern for Cubic phase ZrO_2.

3.2 ZrO_2:4%Y_2O_3:

A mixed phase was obtained with 4% Y_2O_3, i.e. cubic and tetragonal as shown in fig 2, blue peaks are the prepared tetragonal modification and green the theoretical tetragonal modification and can be seen to fit to certain degree. The experiment was repeated and cooled very slowly at 1^{o}C per hour, yet a pure tetragonal phase was not obtained, but obtained alongside some mixed phses. As can be seen from the X-ray diffraction pattern, the product obtained does not have high symmetry character when compared to the theoretical cubic pattern, although some peaks fit, but not completely split as is the case in the theoretical, this support the fact that the tetragonal was prepared even though with some amount of cubic phase. Since the peaks from the obtained results do not split completely, the process of complete conversion from cubic to tetragonal is not yet completed. Fitting the obtained with the monoclinic phase, one can see that the monoclinic phase was also obtained in the measured to a certain degree but not as much as the tetragonal and cubic. The cubic peaks position is similar to the tetragonal only that the symmetry is higher in the cubic, so the tetragonal peaks are more split than the cubic.

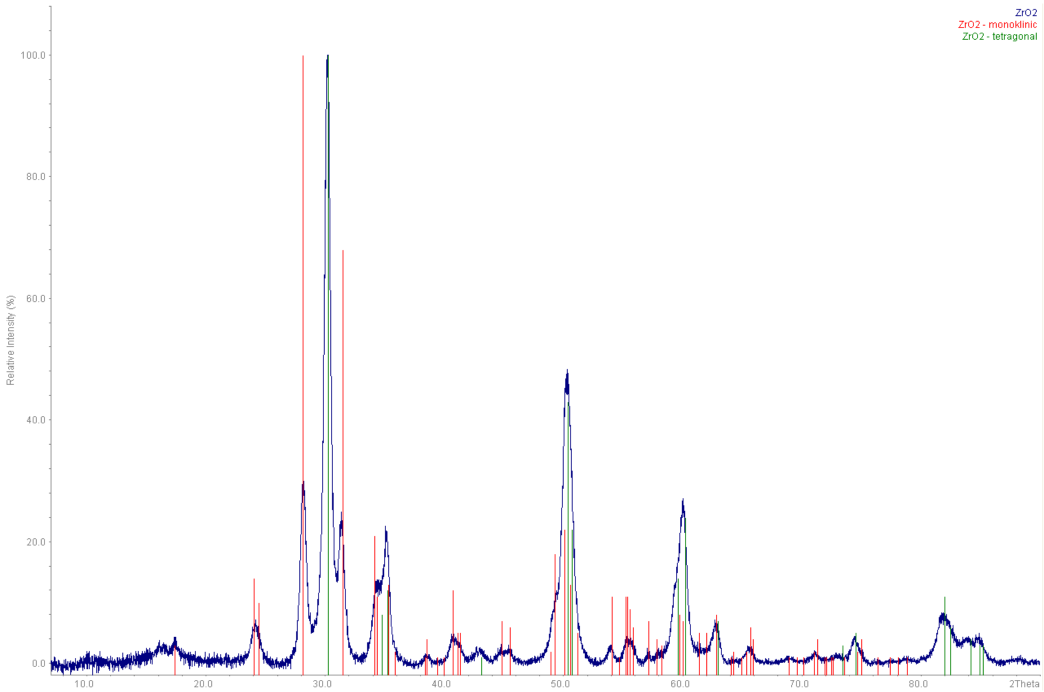

Fig 2 X-ray powder diffraction pattern for mixed phase ZrO_2

3.3 Luminescence of Ziconia doped with Cerium (ZrO_2):Ce^{3+} ZrO_2:Ce^{3+}:

The x-ray powder diffraction pattern showed some peaks due to ZrO_2 and some extra peaks which could be attributed to Ce ions as can be seen from fig 3.

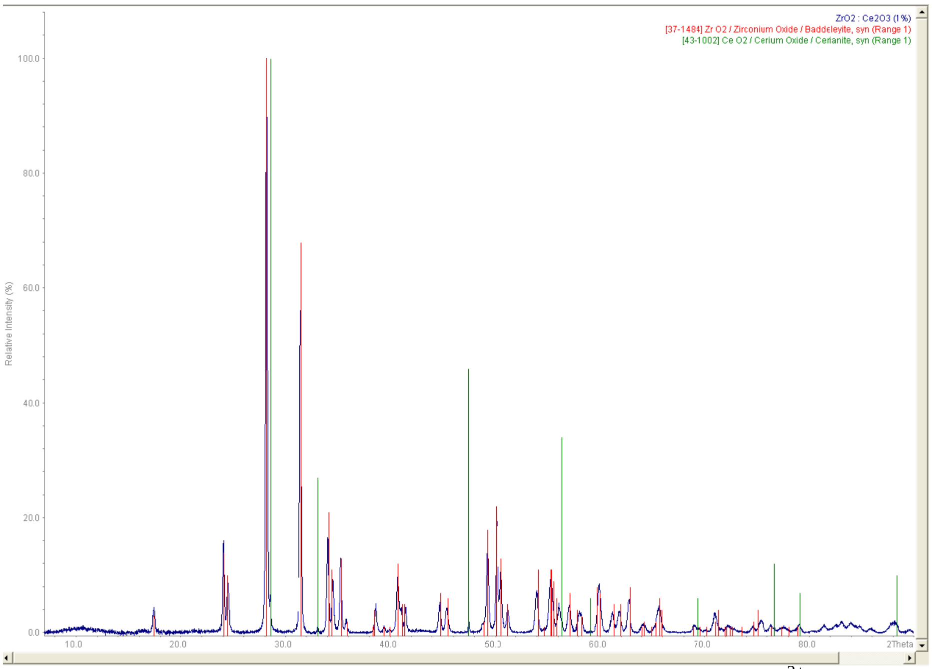

Fig 3. X-ray powder diffraction pattern of ZrO_2 doped with Ce^{3+}.

The luminescence spectra given in fig 4, below showed two peaks, one at 22000cm^{-1} (454.5nm) which is due to Zirconia and the second peak at 16400cm^{-1} (609.8nm) which can be attributed to a fd-transition in Ce^{3+} in accordance with literatures. The emission spectra of Ce_2O_3 fig 5 showed a broad peak which is mainly due to the big band gap of the oxide and two other broad peaks which is typical broad band emission of Ce^{3+}, which is a transition of a 5d orbital to the 4f orbital. This 4f configuration yields two levels i.e. $^2F^{5/2}$ and $^2F^{7/2}$. The emission occurs from the lowest crystal field component of the $5d^1$ configuration to the above mentioned two levels of the ground state. In the emission of the doped ZrO_2:Ce^{3+}, the second of these double peak at 17600cm^{-1} did not appear, perhaps due to the host lattice effect, but the peak at 16400cm^{-1} is clearly seen in the result. A broad shoulder at 25200cm^{-1} may be seen if the slit was narrowed. At 2200cm^{-1} a peak is seen which coincide with that seen in pure ZrO_2 emission.

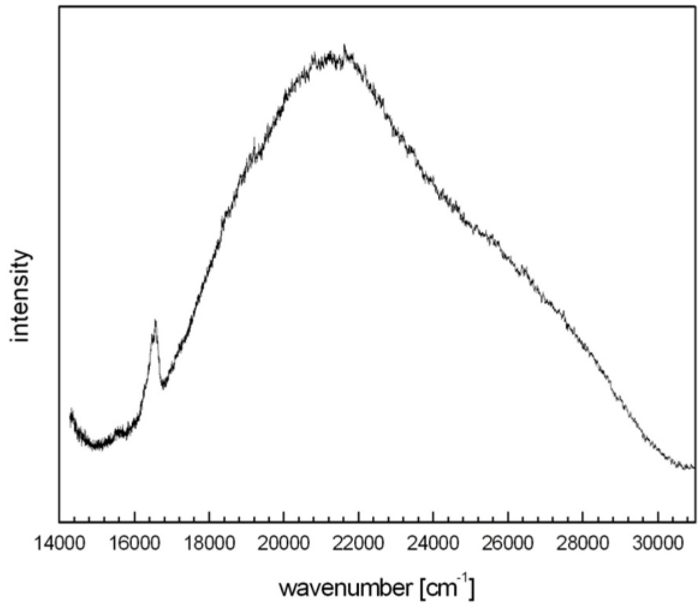

Figure 4. Emission spectra of ZrO_2:Ce^{3+} measured at 300k

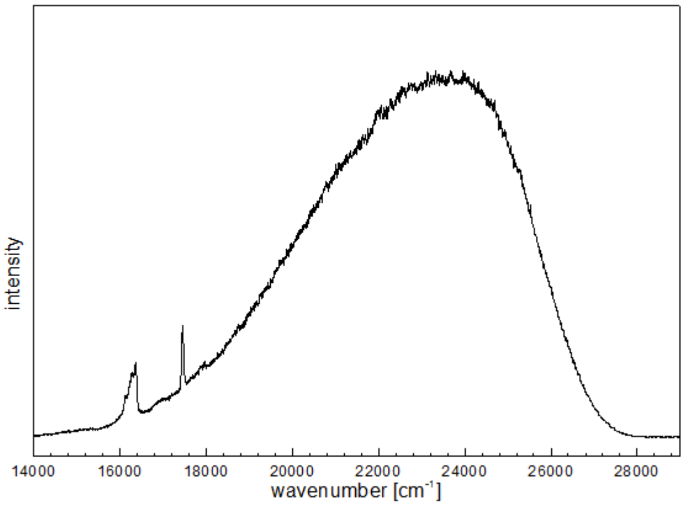

Figure 5 Emission Spectra of Ce_2O_3 Measured at 300k

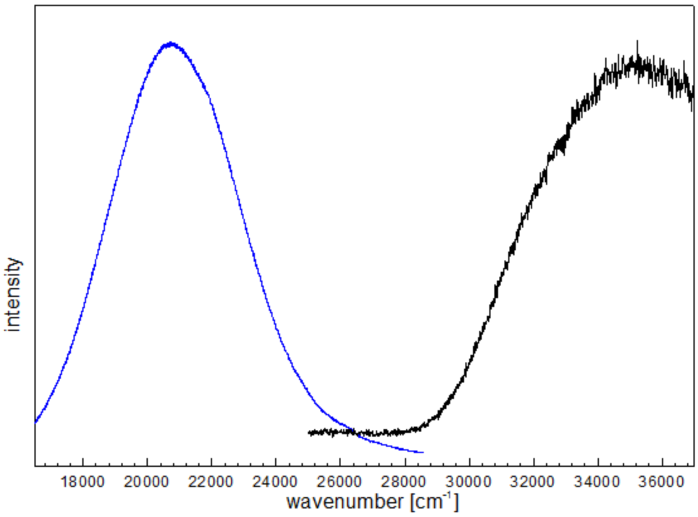

Figure 6 Emission (in blue) and Excitation (in black) spectra of ZrO_2(m) measured at 300k

IV. Discussion

The result obtained showed that the disruptive tetragonal transformation into monoclinic phase which occurs at 1000°C (or a range of 800°C to 1200°C) must have occurred during the cooling. The transformation cubic-monoclinic is not so much as problematic as monoclinic-tetragonal- monoclinic transformation, hence the cubic could be obtained with much ease compared to the tetragonal phase. That means for the cubic phase, the solid solution formed with Y_2O_3 is stable, which is Comparable with other result obtained by different researchers, one can conclude that what was obtained here is partially stabilized Zirconia. 3.4wt% and 2.4wt% of stabilizer was used by Bansai and Hever [4 & 5], which is relatively lower than what was used here. Other people recommended that the addition of small quantity of stabilizer to pure Zirconia will bring its structure in to tetragonal phase [6]. 4mol% of Y_2O_3 used here appears to be high compared to values from some literature [7]. At temperature higher than 1000°C one could say the tetragonal phase is obtained, but to get this at room temperature is where the Problem lies. In particular, the stabilized Zirconia as obtained from the result of addition of 4mol% is a mixture of cubic and tetragonal phase.

ZrO_2 Doped with Ce^{3+}. As can be seen in fig 4, two broad peaks at 22000cm^{-1} (454.5nm) and 16400cm^{-1} (609nm) were obtained. From the literatures [8,9], the luminescence spectra of Ce^{3+} extends from 20000cm^{-1} (500nm) to 15384.6cm^{-1} (650nm), therefore the peak at 609nm can be attributed to Ce^{3+} doped in the ZrO_2. It can be seen from the spectra obtained from ZrO_2 alone given in fig 6, that the broad peak in fig 4 is from ZrO_2 and the small peak at 16400 cm^{-1} from Ce^{+3}, although it is a little shifted to the right which could be the effect of the host lattice on $Ce^{+3.}$ The broad shoulder seen at 25200cm^{-1} may or may not come from the broad band gap of the oxide since this is at a higher energy than that seen in the Ce_2O_3 spectra in fig 5. The intensity of the peak due to ZrO_2 is very high compared to that due to the Ce^{3+}; this can be as a result of the composition of the compound as only 1% of Ce_2O_3 was added.

V. Conclusion

From the results obtained, the modifications of ZrO_2 were successfully prepared, although mostly mixed phases were obtained, which could be improved upon in future research by reducing the stabilizer. This is in accordance with some literature, therefore with a little controlled amount of stabilizer used and cooling slowly the pure tetragonal phase can be prepared. The result of doping with Ce_2O_3 showed that Ce^{3+} was present in ZrO_2.The spectra agree with literature to be due to Ce^{3+}, as such if stabilised ZrO_2 is used as a host lattice for doping, it can be a good luminescence material.

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