

## Study of ZrO<sub>2</sub> Cubic Phase Stabilization as a Function of the Yttrium and Rare Earth Oxides Mixtures at Low Temperature

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**Abstract** This work reports and discusses the results for the crystalline cubic phase formation and stabilization of zirconia as a function of the temperature and yttrium and rare earth oxides mixture (YRE) content. The raw materials were of Brazilian origin. The powder mixtures were obtained from the yttrium and rare earth hydroxides and hydrous zirconia coprecipitation. These powder mixtures were dried at 100 °C in air. The DTA/TGA analyses showed that the temperature of the formation of ZrO<sub>2</sub> crystalline phases was a function of the YRE content. The crystalline phase evolution of these powders as function of the treatment temperature was studied by X-ray diffraction. It is concluded that for this studied YRE-ZrO<sub>2</sub> system, the zirconia cubic phase can be stabilized in the temperature of 500 °C and remains stable at 1400°C.

### Introduction

Zirconia (ZrO<sub>2</sub>) is a very important ceramic material. The most notable zirconia characteristics are the phase transitions. The transition between tetragonal and monoclinic phases occurs at approximately 1170 °C and it is similar a martensitic transition type. A second phase transition to a simple-cubic fluorite structure (as CaF<sub>2</sub> type) occurs around 2370 °C. This cubic structure can be stabilized at lower temperatures by adding adequate amounts of stabilizer oxides, like Y<sub>2</sub>O<sub>3</sub>, MgO, CaO and rare earth oxides [1-3]. Generally, addition of more than 16 mole % of CaO (7.9 wt.%), 16 mole % MgO (5.86 wt.%), or 8 mole % of Y<sub>2</sub>O<sub>3</sub> (13.75 wt.%), into zirconia structure is needed to form a fully stabilized cubic zirconia. These additions into the zirconia structure promote a stable cubic solid solution, which has no phase transformation during heating and cooling. Cubic zirconia is a good solid electrolyte and is used as oxygen sensors. In this investigation hydrated amorphous zirconium oxide obtained by coprecipitation has been studied. Zirconia is commonly produced by calcination of the hydrated oxide precipitated in the hydrolysis of zirconil salts solutions. It is important to emphasize that this method is the most convenient way to prepare fine powder from aqueous solution. Thus, the major aim is the preparation of cubic ZrO<sub>2</sub> solid solution at lower temperatures.

### Experimental Procedure

The present study is focused on the powder characteristics prepared by the coprecipitation method [4]. Chemical and physical powder characteristics were determined by the initial powder preparation and by subsequent thermal treatments. The coprecipitated powders were dried in a rotary vacuum evaporator device at 50 and 100 °C. After the drying step of the precipitates,

thermogravimetry and differential thermal analysis (DTA and TGA) were carried out between room temperature and 1200°C, with heating rate of 10 °C min<sup>-1</sup>. All these samples were calcinated at temperatures ranging from 400 to 800 °C. Calcination was performed in a tubular furnace in air at a heating rate of 10 °C.min<sup>-1</sup> and cooled at same rate to room temperature. The structure evolution from amorphous to crystalline zirconia was studied by X-ray diffraction analysis (XRD) in the selected specimens (CuK $\alpha$  radiation and 20°≤2θ≤90°) and the indexing of diffraction patterns was done according to the standard data listed in the JCPDS files [5,6]. Scanning electron microscopy (SEM) was performed in the coprecipitated and calcinated powders.

### Results and Discussion

The DTA/TGA results (Fig.1) for some mixtures of coprecipitated powders showed as the result an endothermic effect due the loss of the adsorbed on the surface and structural water molecules. The exothermic effect was due to zirconia crystallization. It was evidenced that the temperature of crystallization ( $T_p$ ) increase and the exothermic effect decrease continuously with the increase of YRE content. The crystallization peak changed from 461 to 490 °C, for 15.5 and 34.8 wt.% YRE content, respectively. After this exothermic peak no other thermal effect was observed up to 1200 °C. The similar phenomenon was found for the coprecipitates in the ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>-MgO systems [7-9].

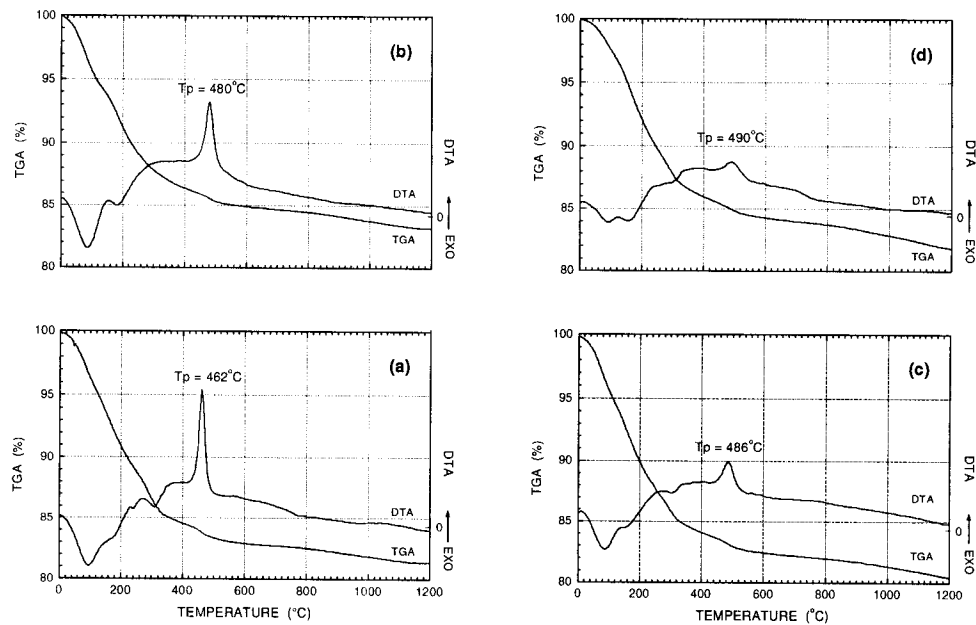


Figure.1. DTA/TGA curves of the precipitated powder mixtures as a function of the YRE content: (a) 15.50 wt.% (7.16 mole %), (b) 22.50 wt.% (10.88 mole %), (c) 27.70 wt.% (13.87 mole %) and (d) 34.80 wt.% (18.23 mole %).

In Fig.2 are showed the XRD patterns obtained from different thermal treatments. The XRD patterns of all YRE-ZrO<sub>2</sub> samples did not present any significant difference. These results showed a

representative behavior for all studied compositions. The coprecipitated powders were amorphous and transformed to the cubic/tetragonal crystalline structure at 400 °C. However, their diffraction pattern indicated a poor crystallinity. This phase transformation was consistent with the exothermic effects found in the DTA. These powder mixtures presented the same crystalline phases when they were calcinated at 1440 °C in air [4]. These results indicated that the stable cubic phase was formed at a low temperature (near 400 °C) and remained stable at high temperatures for the powder mixtures studied in this work.

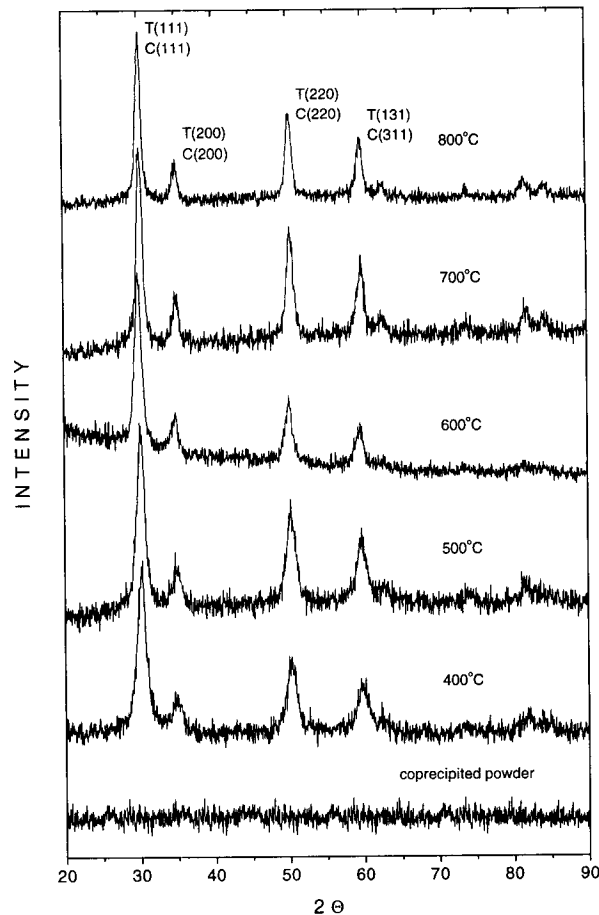


Figure.2. Representative evolution of amorphous and crystalline zirconia as a function of the calcination temperature.

The SEM micrographs of the coprecipitated and calcinated powders did not show apparent differences in the physical characteristics of YRE-ZrO<sub>2</sub> powders (Fig.3). The particle and agglomerate sizes and agglomerate density showed no significant influence due to the increase of the

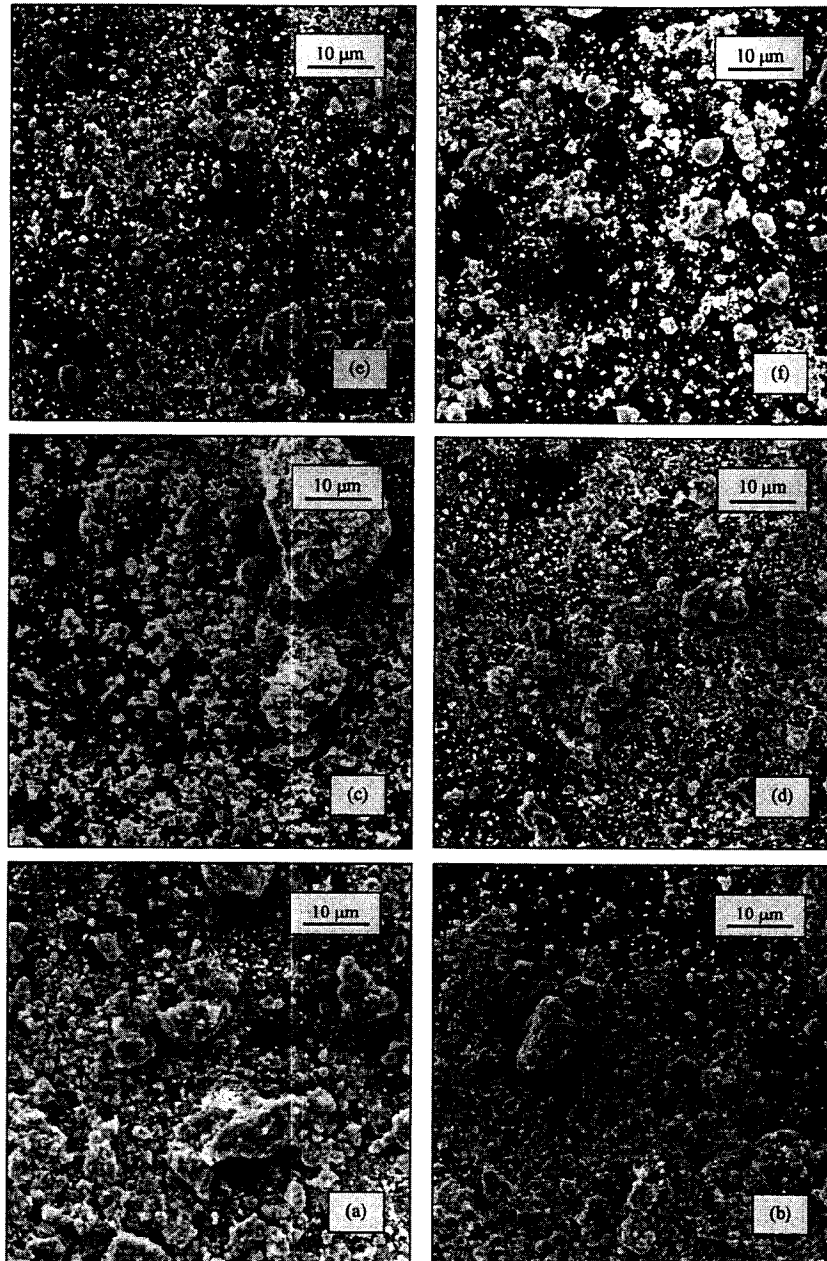


Figure.3. SEM photomicrographs of YRE-ZrO<sub>2</sub> powders: (a) Coprecipitated and dried, (b) calcinated at 400°C, (c) calcinated at 500°C, (d) calcinated at 600°C, (e) calcinated at 700°C and (f) calcinated at 800°C.

calcination temperature. In the further stages of compaction will be very important to avoid the use of powders with hard agglomerates to prevent the formation of dense packed zones. These regions

promote a non-homogeneity of the ceramic densification and consequently they will affect the sintered ceramic properties. In the case of ceramic to use as oxygen sensors, the microstructure voids reduce the ionic conductivity values.

### Conclusion

These results indicate that the formation process of cubic zirconia solid solution starts at 400°C and remains stable to 1400°C. The main powder chemical and physical characteristics depend on the starting powder and processing steps. During the powder synthesis, agglomerates were formed in the early stages of the preparation and during the precipitation. The particle shape, size and size distribution were influenced mainly by the precipitation parameters. This study was very important because, in some cases, the thermal treatment can promote a significant increase of the powder agglomeration state. In our opinion, the thermal treatment did not present great effect on agglomerate density of reactive fine powders. However, it can be concluded that for these YRE-ZrO<sub>2</sub> powders the more adequate calcination temperature appears to be at 500 °C.

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