



## Formation of metastable tetragonal zirconia nanoparticles: Competitive influence of the dopants and surface state



Oksana Gorban<sup>a,\*</sup>, Susanna Synyakina<sup>a</sup>, Galina Volkova<sup>a</sup>, Sergey Gorban<sup>a</sup>, Tetyana Konstantiova<sup>a</sup>, Svetlana Lyubchik<sup>b</sup>

<sup>a</sup> Donetsk Institute for Physics and Engineering named after A.A. Galkin of the NAS of Ukraine, Nauki av. 46, Kyiv 03680, Ukraine

<sup>b</sup> REQUIMTE, Universidade de Nova de Lisboa, 2829-516 Caparica, Portugal

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### ABSTRACT

The effect of the surface modification of the nanoparticles of amorphous and crystalline partially stabilized zirconia by fluoride ions on stability of the metastable tetragonal phase was investigated. Based on the DSC, titrimetry and FTIR spectroscopy data it was proven that surface modification of the xerogel resulted from an exchange of the fluoride ions with the basic OH groups. The effect of the powder pre-calcination temperature before modification on the formation of metastable tetragonal phase in partially stabilized zirconia was investigated. It was shown that the main factor of tetragonal zirconia stabilization is the state of nanoparticles surface at pre-crystallization temperatures.

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### 1. Introduction

Zirconia in nanosize is one of the most popular materials in modern materials science due to its promising properties for the application in catalysis, the technologies of ceramics production for functional, structural and medical application, photonics, etc. [1–4]. The key point of effective development of these technologies is the phase stability control of zirconia nanoparticles, since this material is characterized by polymorphic transformations under temperature, pressure or others energetic impact [5–8]. It is considered that the monoclinic phase of pure zirconia is a stable modification up to 950–1200 °C [9]. Above this temperature, the tetragonal phase is forming, which is thermodynamically stable in the bulk of zirconia up to 2380 °C [10]. Tetragonal zirconia widely used in practice due to its active surface and smaller grain size [11,12]. This explains abundant investigations aimed at the mechanisms and development of the approaches to the high-temperature tetragonal phase stabilization zirconia at low temperatures. To explain the reasons of the metastable tetragonal phase formation in the zirconia at low temperatures a number of mechanisms was offered. These mechanisms based on either (i) the kinetic factors caused by various impurities [13], lattice defects [14], vacancies and nonstoichiometry [15,16] and structural

similarity to the amorphous precursor [17,18] or (ii) the thermodynamic factors associated with small particle size [19], high apparent surface area and high surface tension [20,21]. Despite the numerous publications devoted to the tetragonal phase stabilization and suggested mechanisms, the reasons of the metastable tetragonal phase formation at low temperatures are still debatable [22]. In addition, the metastable phase formation in nanoscale zirconia should be considered not only in term of the vacancy defects in the oxide lattice but also the vacancy defects in a surface state due to impurities and others external factors [22]. Although a dominant role of the oxygen vacancies in the tetragonal zirconia stabilization is still uncertain (contrary to a cubic zirconia [16,22]), the lattice concentration of oxygen vacancies requiring for the tetragonal phase stabilization in a pure zirconia is assessed as  $ZrO_{1.97}$  [23] and  $ZrO_{1.98}$  for rare-earth doped tetragonal zirconia, in particular, by yttrium [24]. The metastable phase formation occurs along with the oxide crystal lattice formation. Furthermore, treatment of a pure zirconia by surface-active additives like water, fluoride or sulfate ions can significantly affect the metastable phase formation [22,25–27]. It is shown [28], that the surface treatment of a high-dispersed amorphous pure zirconia by  $NH_4HF_2$  solution of 8 wt% inhibits the tetragonal phase formation at its crystallization. Therefore, it was concluded a decisive role of the surface impurities on the metastable phase formation [22]. However, the questions of competitive effect of doping rare earths such as yttrium, and fluoride ions as surface-active agents on the metastable tetragonal phase formation in zirconia is not considered in the literature. It is suggested, that an yttrium

\* Corresponding author.

E-mail addresses: [matscidp@aim.com](mailto:matscidp@aim.com) (O. Gorban), [s\\_lyubchik@yahoo.com](mailto:s_lyubchik@yahoo.com) (S. Lyubchik).

introduction into zirconia leads to the vacancies generation in a crystal lattice, while the presence of fluoride ions alters the surface state. Resolving these issues is important not only for understanding the mechanism of the metastable phase formation in nanosized zirconia at low temperatures, but also for predicting those systems degradation under operation conditions.

## 2. Material and methods

Hydrogel nanopowders of a doping zirconia were synthesized by chemical precipitation. For the synthesis, the zirconium oxonitrate [ $ZrO(NO_3)_2$ ] of 2 mol/l and the yttrium nitrate [ $Y(NO_3)_3$ ] of 0.044 mol/l solutions in distilled water were used. The ammonia of 6 wt% solution was used for a chemical precipitation. Precipitation was carried out at pH 10–11, followed by precipitate washing to pH 7. The microwave irradiation (MW) with power of 700 W and a frequency of 2.45 GHz was used for the xerogel synthesis from hydrogel. Then the xerogel was calcinated at 120, 150, 185, 200, 250, 300, 400, 500, 700 and 1000° C. Surface post-treatment of the xerogel and oxides (annealing temperature ranged from 120 to 700° C) by fluoride ions were carried out by 5 wt% solutions of  $NH_4F$  in a Teflon beaker. Then the xerogel was dried at a microwave power of 700 W to remove moisture. The modified by fluoride ions system was calcinated at 500, 700, 850° C and 1000° C. Samples obtained were named as: (i) Z3Y, Z3Y120, Z3Y150, Z3Y185, Z3Y250, Z3Y300, Z3Y400, Z3Y500, Z3Y700 and Z3Y1000 in a case of the original systems; and as Z3YF, Z3Y120F, Z3Y150F, Z3Y185F, Z3Y250F, Z3Y300F, Z3Y400F, Z3Y700F and Z3YF', Z3Y120F', Z3Y150F', Z3Y185F', Z3Y250F', Z3Y300F', Z3Y400F', Z3Y700F' in a case of the fluoride-modified systems (where a numeral index indicates a calcinations temperature of the samples and index (')) indicates that the system after modification was annealed at 700° C). The Z0 xerogel is a pure zirconia xerogel ( $ZrO_2$ ).

For detection of the terminal OH-group titrimetry method was used [29]. The XRD pattern was measured with a diffractometer DRON3, using  $CuK\alpha$  radiation. FTIR spectra of the zirconia nanopowders were registered within a range of 400–4000  $cm^{-1}$  with a resolution of 4  $cm^{-1}$  using Fourier IR spectrometer «Tensor 27» made by «Bruker». The thermal decomposition behavior of xerogel was performed at heating rate of 5° C in air using Linceise STA PT1600 equipment. EPR studies of xerogels were carried out at room temperature using a standard radiospectrometer CMS8400 with a high-frequency modulation at 9 GHz. The fifth CTC line of two-valent manganese ion in cubic magnesium oxide of a calibration sample was chosen as a reference of the paramagnetic centers concentration (PMC). The total intensity of the studied spectral peaks was considered as a ratio of the areas of samples absorption profile and the reference peak calculated by double integration of the derivatives of the absorption profile. The relative measurement error did not exceed 20%.

## 3. Results

### 3.1. Hydrate shell structure evolution of $ZrO_2$ -3 mol% $Y_2O_3$ under F-anion modifications and temperature

FTIR spectrum of the initial xerogel and xerogels modified by fluoride ions by solution with 5 wt% concentration are present in Fig. 1. According to the FTIR spectroscopy data the xerogel structure of the Z3Y system has developed hydration shell. There is a wide sub-maximum at 3700–2500  $cm^{-1}$ , which corresponds to the stretching vibrations of hydroxyl groups of water and others hydroxyls of different binding strength. The peaks at 1626  $cm^{-1}$

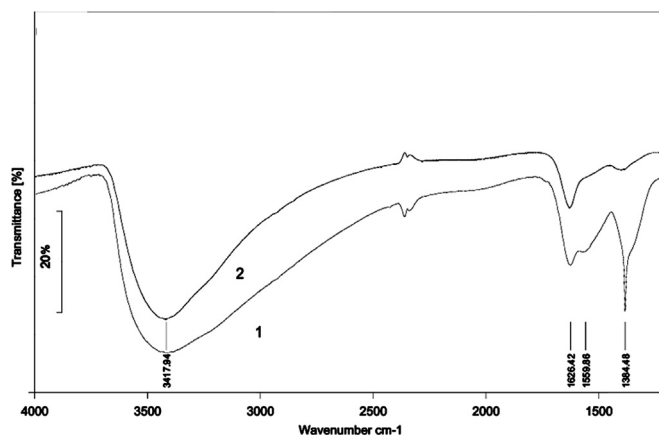


Fig. 1. FTIR spectrum of the initial xerogel (1); and xerogels modified by fluoride ions 5 wt% solution (2).

and 1560  $cm^{-1}$  correspond to the deformation vibrations of OH bonds of water and terminal hydroxyls ( $M-OH$ , where M is a Zr or Y atoms). Narrow absorption band with maximum at 1340–1380  $cm^{-1}$  belongs to the vibrations of  $NO_3$ -occluded groups on the Z3Y surface. Surface modification of Z3Y nanoparticles by fluoride ions leads to a change in a shape of the sub-maximum at 3700–2500  $cm^{-1}$ , which corresponds to the stretching vibrations of OH groups of water and hydroxyls of different degrees of binding. Changes in the FTIR spectrum are also observed at 1500–1700  $cm^{-1}$  corresponding to the deformation vibrations of the terminal hydroxyls and OH groups of water [30]. Changes of a hydrate shell structure after F-ions modification resulting in decrease of an intensity of those bands (Fig. 1). The annealing of these amorphous systems led to the oxide systems formation with different amount monoclinic phase. The monoclinic phase formation in the Z3YF500, Z3YF700, Z3YF1000 systems modified by 5 wt% F-anion solution is proven by FTIR spectroscopy (Fig. 2a). For comparison, a spectra of the parent Z3Y500, Z3Y700 and Z3Y1000 systems are also given (Fig. 2b). There are the stretching vibrations of OH bonds at 4000–2500  $cm^{-1}$  and the deformation vibrations at 1633  $cm^{-1}$  of the residual water and hydroxyl groups for all studied systems. A band at 1080  $cm^{-1}$  exhibits the lattice vibrations of Zr–O [30]. For the Z3Y500, Z3Y700 and Z3Y1000 systems there is a broad peak at 460  $cm^{-1}$ , which can be assigned to the vibrations of Zr–O lattice of the tetragonal structure. A band at 498  $cm^{-1}$  is assigned to the monoclinic and tetragonal phases; a band at 448  $cm^{-1}$  corresponds to the vibrations of Zr–O lattice of the tetragonal structure, other peaks at 421  $cm^{-1}$ , 592  $cm^{-1}$  and 734 (771 for 1000° C)  $cm^{-1}$  are the vibrations of Zr–O lattice of the monoclinic phase for the Z3YF500, Z3YF700 and Z3YF1000 systems [30]. Note, a position of the last absorption band depends on annealing temperature of the nanopowder. This fact could be due to the changes in a size and/or a form of the nanoparticles with increase of an annealing temperature. A spectra of the Z3Y150F', Z3Y200F', Z3Y300F', and Z3Y400F' systems, which were pre-calcinated before and thermally treated (at 700° C for 1 h) after the modification by fluoride ions, is presented in Fig. 3. As can be seen from the obtained results, a pre-calcination temperature affects an intensity of the OH bonds stretching vibrations at 4000–2500  $cm^{-1}$  and the bands intensity of deformation vibrations at 1500–1650  $cm^{-1}$  in the modified systems. The same tendency observed for the Zr–O lattice vibrations. Raise of a pre-calcination temperature from 150 to 400° C decrease an intensity of the corresponding vibrations bands of Zr–O monoclinic lattice. It should be noted that, a band at 771  $cm^{-1}$  identified as the vibrations of Zr–O monoclinic lattice in powder of modified xerogel hydroxide, shifts to a lower frequency

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