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RESEARCH ARTICLE

Synthesis and Characterization of Zirconia (ZrO_2) by simple Sol-Gel Route

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Abstract

It is well known that sol-gel technique is a simple and cost effective method to produce ceramic powders. The present study deals with the synthesis and characterization of ZrO_2 nanopowders. Since ZrO_2 possesses diverse electronic and optical properties, it is potentially utilized in the applications of gas sensors, solid fuel cells, high durability coating, catalytic agents, etc. Based on sol-gel technique, the synthesis of ZrO_2 is carried out using Zirconium alkoxide as the starting material followed by drying the gel and heat treated at 700 ^oC for 1 hour. Structural characterization and crystalinity were studied using X-ray diffraction. Microstructural and morphological characterization was performed using electron-microscopic technique - scanning electron microscopy (SEM).

1. INTRODUCTION

Zirconia (ZrO_2) is a material of great technological potential importance due to its outstanding mechanical and electrical properties, high dielectric constant and wide band gap. Among the wide spectral ZrO_2 applications, a few includes the use in gas sensors, solid fuel cells, high durability coating, catalytic agents, etc. In recent years, its energy gap ($Eg \approx 6$ eV) and dielectric properties suggested its potential to replace SiO_2 in advanced metal oxide semiconductor (MOS) devices in gate stack, dynamic access memory devices, and optical applications. [1–3]. The sol-gel method is based on the phase transformation of a sol obtained from metallic alkoxides or organo-metallic precursors [4]. This sol which is a solution containing particles in suspension is polymerized at room temperature, in order to form a wet gel where the particles are prevented from agglomeration by mutual repulsion of similar charges at the particle surface and uses metal-organic precursors in alcoholic media, where the polymeric particles remain as separated particles in solution because of their small size. Depending on the synthesis route and the reaction conditions, oligomers or particles, with a dimension ranging from 1 nm – 1 μm, are formed in the solution [5-7]. The transition from sol into gel in colloidal systems is a result of electrolytic effects that also determine the particle distance at the gelation point, thereby influencing the capability of a gel to remain monolithic during the drying process. On the other hand, gelation of sols that contain oligomers occurs as a result of a polymerization reaction. The nature and kinetics of these reactions determine the properties of the gel. The solvent is removed by drying the gel and the next step is a proper heat treatment to obtain a desirable coating/ thin/ film/ powder.

Some of the advantages of the sol-gel method are its versatility and the possibility to obtain high purity materials, the provision of an easy way for the introduction of trace elements, allowance of the synthesis of special materials and energy savings by using low processing temperature. The aim of the present paper is to prepare zirconia by sol–gel method, starting from different chemical nature precursors. It is expected that the obtained zirconia powders have nanometric dimensions and can be utilized for wide variety of applications. Unlike other ceramic materials, zirconium oxide (ZrO_2 – also known as zirconia) is a material with very high resistance to crack propagation.

Zirconium oxide ceramics also have very high thermal expansion and are therefore often the material of choice for joining ceramic and steel. For this reason extensive research is being done on ZrO_2.

2. EXPERIMENTAL

2.1. Materials used:

Zirconium (IV) propoxide (Sigma-Aldrich), Acetic acid (Sigma-Aldrich), Isopropanol, Nitric acid (SD Fine) chemicals received and used as such without further purifications. Double distilled water is used for the preparation.

2.2 Preparation:

The precursor used in the synthesis of ZrO_2 by sol-gel method was Zirconium (IV) propoxide (Sigma-Aldrich) with acetic acid (Sigma-Aldrich) as chelating agent and isopropanol as solvent. To reduce the viscosity of the alkoxide solution and reactivity with moisture, the alkoxide solution was prepared by stirring zirconium propoxide and isopropanol at room temperature in the molar ratio 1 Zr: 15 isopropanol. Catalyst solution was prepared with molar composition of 1.0 H_2O: 0.6 HNO_3: 7.5 isopropanol was prepared with distilled water, nitric acid (sigma-Aldrich) and isopropanol. Acetic acid was added drop-wise to the stirred alkoxide solution until the molar ratio of acetic acid to Zr became 2.0, and the solution was mixed with the above solution to produce a zirconia sol until the molar ratio of $Zr:CH_3COOH:HNO_3:H_2O:C_3H_7OH$ became 1.0:2.0:3.0 and was kept for stirring for 2 hours [8].

2.3. Solution A

$Zr(OC_3H_7)_4$ was mixed with C_3H_7OH in the molar ratio as discussed above with constant and rigorous stirring . A thorough stirring was continued for 60 minutes to ensure the effective coalescence.

2.4. Solution B

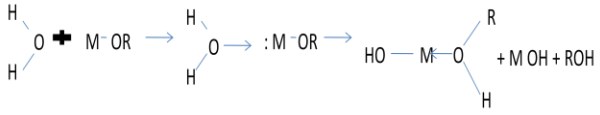
CH_3COOH was mixed with H_2O and conc. HNO_3 was then finally added drop-wise to the mixed solution. The solution was vigorously shaken continuously for about 60 minutes.

2.5. Synthesis of ZrO_2 powder

The stock solution A was added to the solution B and the pH was maintained to be 2.5. The solution was hydrolyzed and kept on a magnetic stirrer with the magnetic bit inside the beaker which continued for almost 12 hours. The resultant mixture was formed as a solution which on further heating resulted in the formation of a gel. Further heating with the drop-wise addition of conc. HNO_3 resulted in the production of fine powder.

2.6 Zirconia Sol formation

The formation of a sol from a precursor solution is initiated upon the addition or release of water, this leads to the initiation of hydrolysis and subsequent condensation reactions. The hydrolysis of an alkoxide leads to the formation of a reactive M-OH group.



For identifying the crystalline mineralogical phases of the powders obtained from gels, both by drying and heat treating, and bring information on their Synthesis and characterization of zirconia nano-powder obtained by sol-gel method, X-ray diffraction analysis was carried out on a Bruker D2 Phaser XRD - Ni-filtered CuKα (λ = 1.5406 Å) radiation, scanning speed of 0.04º/min, in 2θ = 10-70 deg. range. The micrographs were obtained using a Phenom desktop scanning electron microscope which had an optical zoom upto 24 X and electron image magnification of 24K X.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction

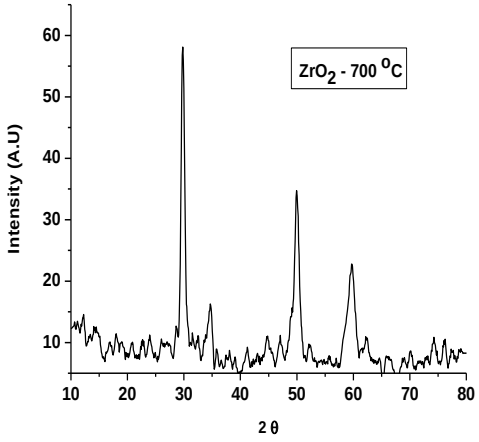


Fig. 1: XRD pattern of the as-synthesized ZrO2 powder by sol-gel route

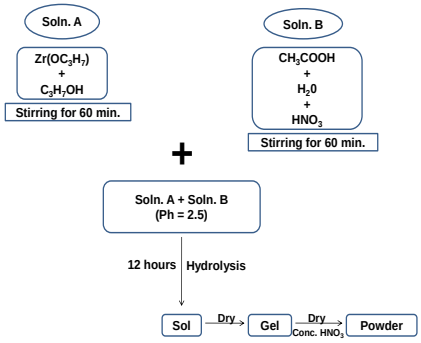


Figure 1 shows the XRD pattern of the crystalline zirconia powder heat treated at 700 ^{o}C for 1 hour. There are four strong diffraction peaks at 2θ = 29.87^{o}, 34.40^{o}, 49.97^{o}, and 59.69^{o}, which can be attributed to the formation of the zirconia [9-14]. It should be noticed that, when Zirconia powder is heat treated at 400^{0} and 500^{0} for one hour, XRD studies donot shown any prominent crystalline peaks. As the heat treatment temperature increases to 700^{0}, the crystalinity is formed in the synthesized zirconia powder. This is being more important in the case of the organic precursors used [15] for the preparation of inorganic zirconia. The average size of the zirconia particles can be calculated from the full width at half maximum (FWHM) values of the diffraction peaks using Debye-Scherrer formula.

$$D = \frac{0.97\lambda}{\beta cos\ \theta}$$

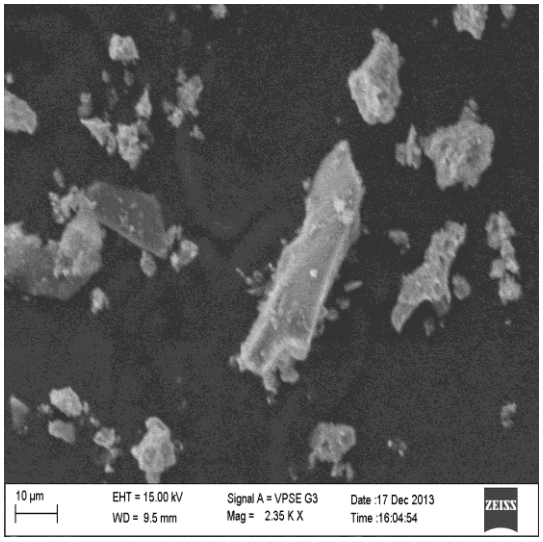
Where, 'D' is the average crystallite size, 'λ' is the wavelength of the x-rays used (CuKα of radiation λ = 0.154nm), 'Θ' is the diffraction angle and 'β' is the FWHM. The size of the nanoparticles are estimated at 2θ = 29.82°, 49.97^{o}, 59.69^{o}. The average crystalline size of the synthesized zirconia is 253.93A^{o} (25.39nm). By adopting a simple sol-gel technique average crystalline size of 25.39nm is achieved and it also reflected in the SEM results.

Table 1. Crystallite size of zirconia powder as calculated

2 theta	FWHM	Particle size (A^{0})
29.827	0.343	266.6
49.976	0.406	239.7
59.698	0.398	255.5

3.2 Scanning Electron Microscope (SEM)

Scanning electron microscopic image of the stabilized zirconia are presented in Figures 2. The analyses revealed that the particles are non-spherical in shape and without agglomeration and porosity. Furthermore, the average particle sizes for the stabilized zirconia solid solutions are determined from SEM with imaging software (SPIP). The particles are nearly spherical in shape and the distribution of the particles is such that they are well separated resulting in no-agglomeration of the Zr nanoparticles. The average particle size is determined from SEM micrographs using imaging software (SPIP) was found to be 28.85±4nm. The surface pictograph obtained from the synthesized ZrO2 is shown alongside. The particles are irregular in shape and the distribution of the particles is such that they are loosely packed giving rise to less porosity.



4. Conclusions

The sol-gel method synthesis of ZrO_2 powder starting from Zirconium alkoxide as precursor and acetic acid as chelating agent was carried out relatively easily. The resulting zirconia powders were characterized by X-ray diffraction, and scanning electron microscopy (SEM). Applying a heat treatment at temperatures higher than 700 ^oC leads in obtaining crystalline zirconia as single phase (monoclinic). Using sol-gel method and heat treatment at 700 ^oC for one hour zirconia powder of crystallite size 25.39 nm was obtained, both for the inorganic and organic precursor used. Zirconia powders obtained at the nanometric scale may have superior properties as compared to the powders of other ceramics and can be used extensively used for thermal shielding since it has very high resistance to crack propagation.

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