Structural studies of zirconia and yttria doped zirconia for analysing its phase stabilization criteria

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Abstract: In this work, the target of zirconia with 2-inch diameter is prepared from the powder form having a particle size 5 µm by giving 4 tonnes of pressure in the hydraulic press. The prepared target is sintered at 1000-degree Celsius for 10 hrs. Yttria-stabilized zirconia target is also obtained in a similar process. The structural properties of both targets are investigated using θ-2θ geometry of X-ray diffractometer system. The changes in structure are studied in doped and undoped zirconia. The structural findings are showing the transformation of phase with doping. These studies help to understand the structural properties of zirconia with and without doping for technological application.

1. Introduction
Zirconia (ZrO2) shows versatile physicochemical properties, such as high ionic conductivity, low thermal conductivity, superior chemical stability, high hardness and prominent optical properties [1-4]. Because of these properties zirconia has a wide range of applications, such as medical implants, oxygen detector and thermal barrier coatings. The structural studies of zirconia have shown that it is a polymorphous, which occurs in three crystallographic phases (i) monoclinic (m), lowest symmetry structure with thermodynamically stable up to 1170 °C; (ii) tetragonal (t), appears from 1170 °C to 2370 °C; (iii) cubic (c), from 2370 °C to 2715 °C (melting temperature) [5]. Under these changes in symmetry, its physicochemical properties get improved, which means that high-temperature phases are extra suitable for industrial applications. Stabilization of such high symmetry phases has been a vigorous topic and can be done either by doping the oxide with divalent or trivalent cations, such as MgO, CaO, Y2O3 or by keeping the crystallite size below 10 nm where minimum surface energy could be achieved by higher symmetry phases [6].

As compared to other fluorite oxides (MO2), zirconia does not sustain the cubic structure at room temperature. Usually, the size of these tetravalent cations (M) is big enough to sustain the cubic (fluorite) structure. However, in the case of zirconia (ZrO2), the size of Zr4+ is not big enough to sustain the cubic phase at room temperatures. Therefore, to stabilize the cubic structure, it has to be partly substituted with a larger cation than Zr4+. For this purpose, since more than ninety years, to stabilize the cubic phase of zirconia at lower temperature range is achieved by doping in zirconia with larger cations of lower valence than Zr4+, e.g., by incorporating Y3+, Ca2+, or Mg2+ in the ZrO2 lattice. This strategy was initially testified by Ruff et. al. [7] in 1929. It has been reported by Gaudon, et. al.
[8] that by doping around and above 7 mol% of yttria (Y$_2$O$_3$), the c-phase of zirconia can be stabilized at room temperature. This material is known as yttria-stabilized zirconia (YSZ) [5]. On the other hand, doping by 2-7 mol% of yttria leads to the stabilization of the tetragonal phase also known as partially stabilized zirconia. Below 2 mol% of yttria doping, the monoclinic phase is present. It was further reported by Gravie [9] that if the grain size of zirconia is in the range of 11-17 nm then 100% tetragonal phase is present. However, if the grain size ranges from 17-30 nm, a mixture of tetragonal and monoclinic phases is present. Beyond 30 nm only monoclinic phase exists.

The main aim of the present work is to synthesize zirconia target from powder form and to compare the structural studies with yttria-stabilized zirconia target. The phase analysis has been characterized by XRD.

2. Experimental Details
To develop the target of a 2-inch diameter of undoped zirconia, we used 99.999% pure zirconia in powder form which is marked by Sigma-Aldrich and having a particle size of 5 µm. First powder of zirconia was grinded for 5 hours in mortar and pestle. Polyvinyl alcohol (PVA) was added as a binding agent to the powder to increase the strength and decrease the chances of a breakdown of the target. The finely grinded powder was put into the 2-inch die set under the pressure of 4 tonnes in the hydraulic press. The prepared target was sintered to various temperature for different periods to make it stronger. First, it was sintered to 450 °C for 5 hours and then to 1000 °C for 10 hours with heating and cooling rates of 3 °C/min and 2 °C/min, respectively. The prepared sample had a thickness of around 3 mm. Flow chart showing these steps is shown in the figure. 1. Whereas, Yttria-stabilized Zirconia [ZrO$_2$/Y$_2$O$_3$ (90:10 wt%)] target with 2-inch diameter target is also obtained in a similar process. The prepared targets have been characterized through X-Ray Diffractometer (XRD) performed at Central Facility SLIET, Longowal, Punjab using Bruker D8 advanced diffractometer of Cu K$_\alpha$ source and by recording the patterns in 2θ range of 20°-50° at step size and a scan speed of 0.02° and 2 sec/step, respectively.

![Flow chart showing steps of making Zirconia target](image)

3. Results and Discussions
The XRD patterns recorded for the pure and doped zirconia have been shown in the figure. 2. For the zirconia target, peaks at 28.3° and 31.6° correspond to Monoclinic phase of zirconia as matches with JCPDS No. [01-086-1451]. A strong peak appeared in YSZ target at 30.3° indexed as (1 0 1) plane of tetragonal-ZrO$_2$ (JCPDS No.01-088-1007) with a well-resolved doublet of weak intensity at 34.6° and
35.0° as (0 0 2) and (1 1 0) planes, signifying the structural symmetry of tetragonal phase. Whereas peaks at 28.3° and 31.6° show the presence of monoclinic phase also [6].

Data obtained from XRD is useful to find the crystallite size with peak broadening [10]. The crystallite size of both the targets was determined using the X-ray line broadening method with the use of the Scherrer equation:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

where \( D \) represents the particle size in nanometers, \( \lambda \) is the wavelength of the radiation (1.54056 Å for CuKα radiation), \( k \) is a constant equal to 0.94, \( \beta \) is the peak width at the half-maximum intensity and \( \theta \) is the peak position [11].

Using the equation (1), particle size for main peak positions is calculated and the variation of peak width (\( \beta \)) with peak position (\( \theta \)) for both targets are given in Table 1 and Table 2.

**Table 1: Main peak positions and their FWHM for zirconia target**

| 2\( \theta \) (in degree) | (hkl) values | FWHM(\( \beta \)) | Particle size(nm) |
|---------------------------|--------------|-------------------|-------------------|
| 28.3                      | (-1,1,1)     | 0.19              | 45.05             |
| 31.6                      | (1,1,1)      | 0.23              | 37.51             |
Table 2: Main peak positions and their FWHM for YSZ target

| 2\(\theta\) (in degree) | (hkl) values | FWHM(\(\beta\)) | Particle size(nm) |
|------------------------|--------------|----------------|------------------|
| 28.3                   | (-1,1,1)     | 0.40           | 21.40            |
| 30.3                   | (1,0,1)      | 0.34           | 25.29            |
| 31.6                   | (1,1,1)      | 0.37           | 23.32            |

From the above data, the average crystallite size of Zirconia is found to be \((41.2 \pm 1.9)\) nm which is greater than 30 nm which indicates it is in monoclinic phase whereas average crystallite size of Yttria stabilized zirconia is found to be \((23.3 \pm 1.1)\) nm which is between 17-30 nm which shows this target has a mixture of tetragonal and monoclinic phases. This result represents that the high-temperature phase i.e. the tetragonal phase of zirconia which exists from 1170 °C to 2370 °C can be stabilized at room temperature by doping zirconia with yttrium [12].

4. Conclusion

In the present work, the zirconia target has been prepared for the purpose to compare the structural studies with yttria-stabilized zirconia target. The prepared target is found to be in the monoclinic phase as analyzed through XRD. Further, it was also confirmed with crystallite size. The yttria-stabilized target found to have a mixture of tetragonal and monoclinic phases. All the results lead to the conclusion that the high-temperature phase of zirconia can be achieved at room temperature by doping it with yttrium.

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