Synthesis of Lithium-doped Zirconia Nanoceramics of Controlled Oxygen Vacancies

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ABSTRACT

Doping of lithium (Li⁺) cations results in stabilised zirconia, especially in tetragonal (t) crystal structure, i.e., Li⁺: t-ZrO₂. It is useful to vary oxygen vacancies in Li⁺: ZrO₂ powders. The Li⁺: t-ZrO₂ powder having 1-5 mol per cent Li⁺, are obtained by using a novel chemical method of a polymer precursor, which consists of Li⁺ and Zr⁴⁺ cations capping in polymer molecules of polyvinyl alcohol (PVA) and sucrose. The results are analysed in terms of XRD and microstructure of Li⁺: t-ZrO₂ powders prepared under specific conditions of heating the precursor in air at elevated temperatures. The polymer precursor consists of fibrils of average 120  m length and 0.5–1.0  m dia. A refined Li⁺: t-ZrO₂ powder (15-25 nm crystallite size) occurs after heating the precursor at 500–600 °C for 2 h in air.

Keywords: Stabilised zirconia, ceramics, nanoceramics, microstructure, synthesis, cationic doping

1. INTRODUCTION

Interest in nanocrystalline zirconia (ZrO₂) ceramics, of average diameter in the 2–100 nm range, has increased during recent years, because of their properties (e.g., sintering ability, mechanical toughness, superplastic behaviour) are significantly different from those in a coarse grained structure. At atmospheric pressure, pure ZrO₂ exists in three well known polymorphs of P2₁/c monoclinic (m), P4₂/1nnc tetragonal (t), and F m₃m cubic fluoride (c) crystal structures, where m-ZrO₂ is the equilibrium bulk structure at low temperatures. Efforts have been made to obtain the high temperature phase t-ZrO₂ or c-ZrO₂ in a thermodynamically stable state at low temperatures using doping of MgO, CaO, Y₂O₃, or other similar oxides. Emphasis has been given for the synthesis of such phases either by undersized or oversized cationic doping using hydrothermal processes, and sol-gel processes.

In this study, synthesis of a nanoceramic t-ZrO₂ powder has been carried out using doping of undersized cations such as Li⁺. Murata et al. reported that Li⁺–modified ZrO₂ offers specific catalytic activity in oxidative coupling of methane to give C₂ hydrocarbon. A forced hydrolysis (by adding NH₄OH) of dispersed Li⁺ and Zr⁴⁺ cations via polymer molecules of polyvinyl alcohol (PVA) and sucrose in water was used to obtain a polymer precursor. For Li⁺ limited to 5.0 mol per cent, no Zr⁴⁺–Li⁺ phase separation encountered during the reaction. Otherwise, Li⁺ hardly dissolves in zirconium hydroxides. A reconstructive decomposition follows on heating the polymer gel (dried and pulverised into a powder) in air, forming a refined Li⁺: t-ZrO₂ powder at temperatures as low as 500–600 °C.
The results are analysed in terms of XRD and microstructure of the Li+: t-ZrO₂ powders.

2. EXPERIMENTAL DETAILS

Separate solutions were obtained for ZrOCl₂.8H₂O in distilled water and Li₂CO₃ in diluted HCl each of 1.0 M concentration. A transparent colourless solution appeared in homogeneous mixing in two components. A similar mixed solution was obtained in 3.0 g/dl PVA and 30.0 g/dl sucrose in distilled water. To form a polymer precursor, the PVA-sucrose solution was added dropwise to the aqueous solution in ZrOCl₂.8H₂O and LiCl (Li₂CO₃ dissolved in HCl) at room temperature. The obtained sample was transferred to a water-cooled bath (Julabo model HD-4) in part to hydrolyse the metal cations by reacting with cold NH₄OH (25 %) at 2–5 °C average temperature. A transparent gel occurred of hydrolysed metal cations as Li⁺-doped ZrO(OH)₂·αH₂O. As much as 5.0 mol per cent Li⁺ (as per the final Li+: ZrO₂ product) could be incorporated in ZrO(OH)₂·αH₂O in a mixed hydroxyl gel (amorphous). Requisite amounts of the reagents used in forming a typical polymer gel (3.0 mol % Li₄O) are given in Table 1. It was observed that, in the solution, the product Li⁺:ZrO(OH)₂·αH₂O continues to react with the water by polycondensation and polymerisation processes. Average pH at this stage had been reduced to 3.5 as we observed and modelled in the case of a monolithic ZrO(OH)₂·αH₂O gel. Washing in cold water separated byproduct chlorides, resulting in a colorless transparent hydroxyl gel, which was then dried at 90-100 °C over a sand bath (Fig. 1).

The process of forming Li⁺:ZrO(OH)₂·αH₂O gel and derived Li⁺: t-ZrO₂ powder is summarised in Fig. 1. The Li⁺ stabilised t-ZrO₂ occurred of nanoparticles by reconstructive thermal decomposition of gel after heating in air at temperatures in the 500–600 °C range. Structures of precursor gels and of those transformed into Li⁺: t-ZrO₂ were studied in terms of XRD using Philips P.W.1710 diffractometer with filtered 0.15418 nm CuKα radiation. Microstructures of the samples were studied by scanning electron micrographs using a JEOL model JSM-5800 SEM. Average Li⁺: t-ZrO₂ crystallite

![Figure 1. Schematic diagram for preparing a Li⁺-modified Zr⁺⁺ polymer precursor and derived Li⁺: ZrO₂ powder.](image-url)
Table 1. Experimental conditions for forming a polymer precursor of Li+-modified ZrO2 hydroxyl gel with PVA-sucrose in cold water

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Solvent</th>
<th>Volume (ml)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrOCl2, 8H2O</td>
<td>Water</td>
<td>1470</td>
<td>1.0 M</td>
</tr>
<tr>
<td>Li2CO3</td>
<td>Dil HCl</td>
<td>45</td>
<td>1.0 M</td>
</tr>
<tr>
<td>PVA</td>
<td>Water</td>
<td>885</td>
<td>3.0 g/dl</td>
</tr>
<tr>
<td>Sucrose</td>
<td>Water</td>
<td>885</td>
<td>30.0 g/dl</td>
</tr>
</tbody>
</table>

A reaction batch of a 100 g sample in a typical Li+Zr1-xO2.15x composition, with x = 0.02 or 3.0 mol per cent Li+.

size (D) was calculated from fwhm-values (full width at half-maximum values) in the diffraction peaks using the Debye-Scherrer relation.

3. RESULTS AND DISCUSSION

3.1 Formation of Hydroxyl Gel and Derived Li+: t-ZrO2 Powder

Under favorable conditions of temperature and pH, dispersed Zr4+ and Li+ cations in an aqueous solution undergo hydrolysis reaction with the H2O molecules. The reaction, especially in the presence of NH2OH (having a high 12 pH value induces a local chemical potential between the reacting species) in cold condition, can be expressed in this example as follows:

\[ xLiCl + xH_2O \rightarrow xLi(OH) + xHCl \]

\[ (1-x)ZrOCl_2 + 2(1-x)H_2O \rightarrow (1-x)ZrO(OH)_2 + 2(1-x)HCl \]

\[ (1-x)ZrOCl_2 + xLiCl + (2-x)H_2O \rightarrow Li_xZr_{1-x}O_{1-x}(OH)_{2-x} + (2-x)HCl \] (1)

At room temperature, a hydroxyl compound formed in this reaction simultaneously encounters a thermal-induced disintegration as follows:

\[ Li_xZr_{1-x}O_{1-x}(OH)_{2-x} \rightarrow Li_{4x}Zr_{1-x}O_{2-1.5x} + (1-0.5x) H_2O \] (2)

At low temperature, an interbridging in LiZr1-xO1-x(OH)2-x molecules succeeds in support of mobile H2O molecules in solution, forming a polymer gel. It plays a crucial role in devising an amorphous gel, which can be expressed as LiZr1-xO1-x(OH)2-x·фH2O. A value of φ = 4–5 is estimated from thermogravimetric analysis of a dried sample at reduced pressure (1-5 mbar) at room temperature.

In the gelation process, Li+ as Li(OH) gets trapped in ZrO(OH)x·αH2O, forming a LiZr1-xO1-x(OH)2-x·фH2O glass gel. Notice ZrO(OH)x·αH2O is a glass gel former whereas Li(OH), which is an ionic compound, serves as a glass modifier. Presence of the polymer molecules of PVA-sucrose during the hydrolysis templates ZrO(OH)x·αH2O in a polymer of extended network over their molecular surfaces. The original sol-gel method involves alkoxides and is expensive one. The present method offers a simple process of hydrolysis type for processing a hydroxyl gel, especially involving the reactions in aqueous medium.

In this method, Li+-modified ZrO(OH)x·αH2O molecules interbridge by means of polycondensation or polymerisation in shape of fibrils (as evidenced from the microstructure in Fig. 2). It is a Li+: [ZrO(OH)x·фH2O]n polymer template in support over PVA-sucrose of effectively planar surfaces. In water, sucrose was hydrolysed to fructose and glucose, which was ultimately oxidised to gluconic acid. A metal-ion complex was formed in the reaction with Zr4+ and Li+ cations. It frames a co-branched polymer (planar) with PVA molecules (of otherwise linear structure), offering a multifunctional role in templateing Zr4+ and Li+ in a metal-ion complex over PVA-gluconic acid polymer molecules.

Another advantage of the organic polymer part is that it serves as a dispersoid and an internal fuel in producing Li+: t-ZrO2 by autocombusting Li+:[ZrO(OH)x·фH2O]n templates at moderate temperatures as low as 500-600 °C in air. Decomposition and in-situ combustion of the precursor evolve a plenty of heat of the combustion, which induces reconstructive Li+: t-ZrO2 nucleation and growth of limited particle sizes by reaction of small fragmented species of precursor over these temperatures. A high degree of gelation following the hydrolysis of the metal cations in reaction with NH2OH appears to be an important factor in this example of deriving Li+: t-ZrO2 of nanoparticles at such low temperatures. Virgin ZrO(OH)x·αH2O yields m-ZrO2 or a mixture
with $t$-$ZrO_2^{5,9,12,13}$, Marote$^9$, et al. reported a $t$-$m$-$ZrO_2$ mixture by heating $ZrOCl_2$, $8H_2O$ or $ZrCl_4$ in a molten $LiNO_3$ flux at 450 °C. As much $Li^+$ as 3.4 at per cent incorporates in $ZrO_2$ in this method. It is not a very viable way for producing $Li^+$: $ZrO_2$. Most of $Li^+$ involved in refluxing evaporates as a byproduct (toxic).

### 3.2 Microstructure and XRD

Figure 2(a) shows a typical SEM microstructure of polymer precursor gel $LiZr_{1-x}O_{1.5}\cdot(OH)_{x}$·$\varphi H_2O$ ($x = 0.02$), which has been dried at room temperature. It consists of a peculiar polymeric structure of fibrils or thin layers of average 0.5-1.0 μm dia. As long fibrils as 120 μm are present. These fibrils are developed in directional growth and by polycondensation of $LiZr_{1-x}O_{1.5}\cdot(OH)_{x}$·$\varphi H_2O$ molecules in an interconnected network structure (amorphous) over PVA-sucrose polymer molecules of effectively planar surfaces. This involves formation and $in situ$ polycondensation processes of dispersed $LiZr_{1-x}O_{1.5}\cdot(OH)_{x}$·$\varphi H_2O$ in the solution.

On heating, a controlled reconstructive molecular decomposition occurs from the polymer gel of thin fibrils, resulting in a $Li^+$: $t$-$ZrO_2$ powder. A typical micrograph in Fig. 2(b) shows clusters of $Li^+$: $t$-$ZrO_2$ crystallites in derived shapes (100 - 500 nm dia) of precursor of thin fibrils. As can be seen by a close-up of the micrograph in Fig. 2(b), the sample has $Li^+$: $t$-$ZrO_2$ crystallites of rectangular bars (or prisms) of 15-25 nm average dia, which has been correlated to fwhm-values in the XRD peaks in the Debye-Scherer formula ($D$-20 nm) value. It demonstrates the sample consisting of mostly single crystallites. The final $Li^+$: $t$-$ZrO_2$ size and morphology vary sensitively depending on the $Li^+$ content and the final calcination temperature.

X-ray diffractogram in $Li^+$:$ZrO_2$ powder, after heating the polymer precursor at 500–600 °C in air, has a total of 19 peaks in the 20-100 ° range of the diffraction angle $2\theta$. A typical diffractogram for 3.0 mol per cent $Li^+$: $t$-$ZrO_2$ powder, heated at 600 °C for 2 h, is given in Fig. 3. As marked by the $(hkl)$ values, all the major peaks are indexed in terms of the lattice reflections from the $P4_{2/mnc}$ tetragonal crystal structure as in the monolithic $ZrO_2^{12}$. No diffraction peak is visible in independent $LiO$, confirming the fact that most of the $Li^+$ used in this reaction is consumed in forming $Li^+$–doped $t$-$ZrO_2$.

In Table 2, the observed values of the interplanar spacings $d_{hkl}$ are fairly reproduced, within a standard deviation of ± 0.0010 nm, assuming average lattice parameters $a = 0.3615$ nm and $c = 0.5201$ nm, with volume $V = 0.0680$ nm$^3$ and density $\rho = 6.01$ g/cm$^3$. In comparison to $\rho = 6.10$ g/cm$^3$ in monolithic $t$-$ZrO_2^{14}$, a smaller $\rho$-value observed in this example is according to smaller ionic size of $Li^+$ relative to the $Zr^{4+}$ value. As can be analysed by intensities in the diffraction peaks, as described earlier$^{10-12}$, the sample has a small impurity ~ 5 per cent due to incipient growth of $m$-$ZrO_2$.

The diffractogram of the precursor gel powder consists of three halos, as shown in the inset of Fig. 2, at wave vectors 18.7 nm$^{-1}$, 29.3 nm$^{-1}$ and
DIFFRACTION ANGLE $2\theta$ (degree)

Figure 3. (a) X-ray diffractogram in $Li^+\cdot t$-ZrO$_2$ nanopowder after 2 h of heating a precursor [of diffractogram in the inset (b)] at 600 °C in air.

38.3 nm$^{-1}$ in three prominent pair distribution functions in the Zr$^{4+}$ and O$^{2-}$ ions in an amorphous structure,

Table 2. Interplanar spacing ($d_{hkl}$) and relative peak intensities ($I_p$) in XRD peaks in 3.0 mol per cent $Li^+\cdot t$-ZrO$_2$ powder

<table>
<thead>
<tr>
<th>$d_{hkl}$ (nm)</th>
<th>Bulk</th>
<th>$I_p$</th>
<th>$h$</th>
<th>$k$</th>
<th>$l$</th>
</tr>
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<tr>
<td>0.3636*</td>
<td>0.3630</td>
<td>08</td>
<td>1</td>
<td>1</td>
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<tr>
<td>0.3160*</td>
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<td>18</td>
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<td>1</td>
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<tr>
<td>0.2956</td>
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<td>1</td>
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<tr>
<td>0.2843*</td>
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<td>1</td>
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<tr>
<td>0.2600</td>
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<td>0</td>
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<tr>
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<tr>
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<td>0.1481</td>
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<td>0.1305</td>
<td>0.1296</td>
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<tr>
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<td>0.1268</td>
<td>07</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
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<td>1</td>
<td>3</td>
</tr>
<tr>
<td>0.1168</td>
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<td>3</td>
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<tr>
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<td>0.1045</td>
<td>0.1041</td>
<td>10</td>
<td>3</td>
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<td>2</td>
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</table>

The bulk values, with $a = 0.3592$ nm and $c = 0.5168$ nm, are reported from literature$^{11}$. *m-ZrO$_2$.

which plays a crucial role in deriving $Li^+$–doped $t$-ZrO$_2$ in this experiment. Otherwise, the precipitate often decomposes to hydrated zirconia $ZrO_2\cdot yH_2O$, which hardly crystallises into $t$-ZrO$_2$.

4. CONCLUSION

A novel chemical method, using hydrolysis of dispersed $Zr^{4+}$ and $Li^+$ cations via polymer molecules of PVA and sucrose in cold water, is developed and explored to obtain $Li^+$–doped $t$-ZrO$_2$. Adding $NH_4OH$ hydrolysates $Zr^{4+}$ and $Li^+$ as a hydroxyl compound $LiZr_{1-x}O_{0.5-x}(OH)_{2.5-x}\cdot yH_2O$, which occurs in shapes of thin fibrils in support over the PVA-sucrose polymer molecules. A $Li^+$– $t$-ZrO$_2$ powder occurs on heating the precursor at temperature as low as 500 °C in air. The PVA-sucrose polymer molecules offer three important functions: (i) a solid dispersoid, (ii) a templateing agent, and (iii) a solid fuel. The sample, having 3-5 mol per cent $Li^+$, consists of as small crystallites as 10-25 nm, in shape of the tetraoids, unless heating above 600 °C. In comparison to traditional sol-gel process, this is a rather simple method for processing of shape-controlled ceramics such as ZrO$_2$ and its derivatives.

ACKNOWLEDGEMENTS

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14. McClume, W.F. Powder diffraction files JCPDS (Joint Committee on Powder Diffraction Standards). *In* International Centre for Diffraction Data, Swarthmore, PA. (a) 24-1164 (t-ZrO$_2$) and (b) 13-307 (t-ZrO$_2$).

Contributors

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