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Tetragonal to cubic transformation of SiO$_2$ stabilized ZrO$_2$ polymorph through dysprosium substitutions

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Abstract

Partially stabilized tetragonal zirconia ($t$-$\text{ZrO}_2$) is of particular interest for hard tissue replacements. Ageing related failures of the ceramic associated with the gradual transformation from $t$-$\text{ZrO}_2$ to $m$-$\text{ZrO}_2$ (monoclinic zirconia) can lead to its premature removal from the implant site. In addition, monitoring the satisfactory performance of the implant throughout its life span without invasive techniques is a challenging task. The magnetic resonance imaging (MRI) contrast ability of dysprosium ($\text{Dy}^{3+}$) is well established. To this aim, varied levels of $\text{Dy}^{3+}$ additions in the $\text{ZrO}_2$-$\text{SiO}_2$ binary oxide system have been explored. The results indicate the effective role of $\text{Dy}^{3+}$ in the formation of thermally and mechanically stable $c$-$\text{ZrO}_2$ (cubic zirconia) phase at higher temperatures. The presence of $\text{SiO}_2$ influenced the $t$-$\text{ZrO}_2$ stabilization whereas $\text{Dy}^{3+}$ tends to occupy the $\text{ZrO}_2$ lattice sites to induce $c$-$\text{ZrO}_2$ transition. Magnetic and magnetic resonance imaging (MRI) tests displayed the commendable contrast ability of $\text{Dy}^{3+}$ stabilized $\text{ZrO}_2$-$\text{SiO}_2$ binary systems. Nanoindentation results demonstrate a remarkable enhancement on the mechanical properties.

Keywords: Silica; Zirconia; Dysprosium; Stabilization; Mechanical.
1. Introduction

The demand for bone implants is growing rapidly due to the increasing incidents of trauma and age related defects caused by osteoporosis. The development of synthetic biomaterials as an alternative to natural bone, with appropriate features of mechanical strength, biocompatibility and successful performance under in vivo conditions, is still under investigation. ZrO₂ and Al₂O₃ bio-inert ceramics have been well explored, owing to their superior mechanical properties but are restricted by their poor bioactivity.¹,² Calcium phosphate based bioactive ceramics [β-tricalcium phosphate (β-TCP, β-Ca₃PO₄), hydroxyapatite (HAP, Ca₁₀(PO₄)₆OH₂)] and SiO₂ based bioactive glasses have all been investigated as alternative materials but with limited success due to their poor mechanical properties.³,⁴ Attempts to develop ZrO₂/HAP and Al₂O₃/HAP composites have been unsuccessful due to their poor sintering behaviour and the formation of undesirable intermediate phases such as CaZrO₃, CaAl₂O₄, β-Ca₃PO₄, β-Ca₃PO₄ and m-ZrO₂.⁵,⁶

An earlier report explored ZrO₂-SiO₂ binary oxides as a ceramic-glass composite for hard tissue biomaterial applications.⁷ This system shows two important features: the preservation of a mechanically stable t-ZrO₂ phase coexisting with amorphous SiO₂⁸ and the presence of glassy SiO₂ in the range of 40-60 wt. %, which may enhance bone adaptation as proposed by Hench et al.⁹ It was shown that the presence of 50 wt. % SiO₂ is sufficient to preserve the t-ZrO₂ phase up to 1100° C. It was also found that the SiO₂ content hinders the low temperature degradation of t-ZrO₂ that is usually encountered by ZrO₂ based implants in vivo due to ageing phenomena.¹⁰ However, the SiO₂ stabilized t-ZrO₂ material showed lower values of Young’s modulus (E) and hardness (H) compared with yttria stabilized t-ZrO₂ systems (Y-TZP).
Rare earth additions to biomaterials have gained much attention in recent years due to their favourable features.\textsuperscript{11-13} Among rare earth elements, Dysprosium (Dy\textsuperscript{3+}) exhibits visible luminescence by producing strong emission in both the blue (470-500 nm) and yellow (570-600 nm) region.\textsuperscript{14} Dy\textsuperscript{3+} possesses a high magnetic moment ($\mu = 10.2$ $\mu$B) and an asymmetric electronic ground state (6H15/2) and therefore its presence in compounds will lead to a good transverse relaxivity at high magnetic fields, which makes them suitable for the design of negative (T2) magnetic resonance imaging (MRI) contrast agents.\textsuperscript{15} The high atomic number ($Z = 66$) and relatively high K-edge energy (53.8 keV) of Dy\textsuperscript{3+} also provides a higher X-ray attenuation coefficient at 100 keV (3.36 cm$^2$.g$^{-1}$) than the commercially available iodine based CT contrast agents.\textsuperscript{16} These imaging contrast features of Dy\textsuperscript{3+} could support the monitoring of implant performance during its life span in-vivo. Dy\textsuperscript{3+} additions could also play a major role in achieving a thermally stable ZrO$_2$ polymorph.\textsuperscript{11}

In view of the above potential advantages of Dy\textsuperscript{3+} as an addition to ZrO$_2$-SiO$_2$ binary oxides in terms of increased $r$-ZrO$_2$ stability and enhance MRI image contrast, we present a study of the influence of Dy\textsuperscript{3+} on the ZrO$_2$-SiO$_2$ binary oxide system through in-situ sol-gel synthesis, followed by a systematic analysis of the resulting phase composition and structure, mechanical strength and imaging contrast features.

2. Materials and Methods

2.1 Powder synthesis

The synthesis of Dy\textsuperscript{3+} doped ZrO$_2$-SiO$_2$ (DZS) binary oxides was achieved through the sol-gel method. Analytical grade Dy(NO$_3$)$_3$.H$_2$O, ZrOCl$_2$·8H$_2$O and (C$_2$H$_5$)$_4$OSi (TEOS), all procured from Sigma-Aldrich, India, were taken as precursors for the synthesis. The molar concentrations of ZrOCl$_2$·8H$_2$O and (C$_2$H$_5$)$_4$OSi were maintained at a constant ratio of 1: 1 throughout the
synthesis whereas the Dy(NO$_3$)$_3$ additions were adjusted to obtain a wide range of compositions. Additionally, a pure ZrO$_2$-SiO$_2$ binary with 1:1 molar ratio was prepared for comparative purposes. The molar concentrations of the different precursors and the respective sample codes are reported in Table 1; the same codes will be used throughout the manuscript.

**Table 1** Molar concentrations of the precursors used for powder synthesis

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Molar concentrations of the precursors</th>
<th>% of added Dy$^{3+}$ ions with respect to Zr$^{4+}$</th>
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</thead>
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<td>ZS</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DZS 5</td>
<td>0.025 M</td>
<td>5</td>
</tr>
<tr>
<td>DZS 10</td>
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<td>DZS 15</td>
<td>0.075 M</td>
<td>15</td>
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<tr>
<td>DZS 20</td>
<td>0.100 M</td>
<td>20</td>
</tr>
<tr>
<td>DZS 25</td>
<td>0.125 M</td>
<td>25</td>
</tr>
<tr>
<td>DZS 30</td>
<td>0.150 M</td>
<td>30</td>
</tr>
<tr>
<td>DZS 50</td>
<td>0.250 M</td>
<td>50</td>
</tr>
</tbody>
</table>

The synthetic procedure is briefly explained as follows. Previously prepared Dy(NO$_3$)$_3$ stock solution as detailed in Table 1 was added to the ZrOCl$_2$ solution under vigorous stirring. The required amount of ethanol was added to this continuously stirred mixture at an operating temperature of 80 °C for 30 minutes. This was followed by the addition of 1 M TEOS to the solution under constant stirring conditions and finally 0.1 M of HNO$_3$ was added to this mixture as a catalyst. The homogeneous solution was slowly stirred to yield a precursor wet gel and this gel was dried at 120 °C overnight. The dried gel samples were ground to a fine powder using a mortar and pestle as preparation for further characterization.

### 2.2 Powder Characterization

Phase analysis of the ceramic powders was determined using a high resolution X-ray diffractometer (Rigaku, Ultima IV, JAPAN) with Cu Kα radiation (λ = 1.5406 Å) produced at 40 kV and 30 mA to scan the diffraction angles (2θ) between 10 and 70° with a 2θ step size of 0.02° per second. All the powder samples were heat treated at specific temperatures with a dwell
time of 4 hours in a high temperature muffle furnace. Phase determination was achieved using Standard ICDD (International Centre for Diffraction Data) Card Nos. 01-083-0944 for \( m \)-ZrO\(_2\), 01-078-1765 for \( t \)-ZrO\(_2\), 01-071-4810 for \( c \)-ZrO\(_2\), 01-083-1378 for ZrSiO\(_4\) and 00-039-1425 for cryostalbite (\( c \)-SiO\(_2\)). Raman spectra were obtained using a backscattering geometry in a Confocal Raman microscope (in Via Raman Microscope, Renishaw, UK). Magnetic Hysteresis measurements were carried out using a vibrating sample magnetometer (VSM 7404, Lake Shore Cryotronics, USA) under a maximum magnetic flux of 15 kGauss, at room temperature. For this purpose, the pure ZS and DZS powder samples were wrapped in Teflon tape and the applied magnetic field was varied from -10 kOe to 10 kOe. The microstructural features and selected area electron diffraction (SAED) patterns were studied by means of Transmission Electron microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) using a FEI Tecnai F30 (300 KV, Field-Emision Gun, FEG, FEI, Netherlands) equipped with a high angle annular dark field (HAADF) detector for STEM imaging and a silicon drift detector (SDD, Oxford Instruments, UK) for energy dispersive X-ray spectroscopy (EDX) analysis. Quantitative phase analysis of the powders was performed using the Rietveld method with the GSAS-EXPGUI software package.\(^{17}\) The standard Crystallographic Information Files (CIF) were obtained from the American Mineralogist crystal structure database. The standard crystallographic data for the refinement of \( m \)-ZrO\(_2\), \( t \)-ZrO\(_2\), \( c \)-ZrO\(_2\), ZrSiO\(_4\) and \( c \)-SiO\(_2\) were obtained from Smith \textit{et.al.},\(^{18}\) Howard \textit{et.al.},\(^{19}\) Wyckoff,\(^{20}\) Hazen \textit{et.al.},\(^{21}\) and Dera \textit{et al.},\(^{22}\) respectively. The procedure for structural refinement was carried out in accordance with the previous report by the authors.\(^{7}\)

2.3 Mechanical evaluation

Nanoindentation measurements of the ZS and DZS samples were carried out at room temperature using a Nanoindenter (Nanoindenter XP, Agilent, USA). For this purpose, as dried powders were initially heat treated at 700 °C to eliminate all the volatile impurities followed by
fine milling for 2 hours using planetary ball mill (Retsch, Germany). The milled powders were pressed into the form of pellets (13 mm diameter and 1 mm thickness) using a semi-automatic hydraulic press (Kimaya Engineers, India) under an applied load (10 kN) for 60 seconds. The pellets thus obtained were heat treated at specified temperatures for 4 hours, followed by polishing using a diamond paste and were subjected to mechanical tests. A triangular pyramid (Berkovich) diamond tip indenter with a radius of curvature of 50 nm was used with a maximum load of 100 mN. Nanoindentation experiments were carried out using the protocols of ISO 14577\textsuperscript{23} with 10 indentations for each pellet chosen at random locations. The surface morphological features of the pellets heat-treated at 1400 °C prior to diamond polishing were determined by FEG-SEM (Field Emission Gun Scanning Electron Microscopy, XL30, FEI, Eindhoven, Netherlands).

2.4 \textbf{T}_2 Relaxivity measurement and \textit{in vitro} MR imaging

\textit{T}_2 relaxivity of DZS 50 samples was measured using a Siemens Magnetom Avanto 1.5 Tesla MRI scanner. An \textit{in vitro} phantom containing DZS 50 at different Dy\textsuperscript{3+} concentrations were prepared to quantify the relaxivity values. All curve fitting procedures used to establish the relaxation rate maps were performed using Matlab, (The Mathworks Inc., MA, USA). A fast spin echo (FSE) sequence with an echo train length of 16 and a repetition time (TR) value of 3000 ms, matrix size of 512 × 512, slice thickness of 5 mm, and number of slices as 1 was used. The echo time (TE) was varied from 22 ms to 352 ms with a difference of 22 ms resulting in 16 images with varied \textit{T}_2 weighting. Using these images, the \textit{T}_2 relaxation time is determined.

3. \textbf{Results}

3.1 Phase behaviour

3.1.1 XRD analysis
The pure ZS system indicated the formation of \( t\)-ZrO\(_2\) as a distinct phase at 1100 °C and beyond 1100 °C its degradation to \( m\)-ZrO\(_2\) has been confirmed and these results are in accordance with the previous report by the authors.\(^7\) Fig. 1 displays the XRD patterns obtained from samples with a range of Dy\(^{3+}\) additions to the ZrO\(_2\)-SiO\(_2\) binary system after heat treatment at 1200 °C. It is evident from Fig. 1 that lower concentrations of Dy\(^{3+}\) in the range of 5 - 15 wt.% resulted in the phase degradation to yield \( m\)-ZrO\(_2\). However, Dy\(^{3+}\) concentrations in the higher range of 20 - 50 wt.% retained \( c\)-ZrO\(_2\) as the sole phase to the resolution of the instrument. However, the mechanisms by which excess Dy\(^{3+}\) additions lead to a stabilisation of the \( c\)-ZrO\(_2\) structure are not well understood from the present results.

**Fig. 1** XRD patterns of Dy\(^{3+}\) added ZrO\(_2\)-SiO\(_2\) binary oxides at 1200 °C.

At 1300 °C (Fig. 2), compositions containing higher concentrations of Dy\(^{3+}\) above 25 wt.% still indicated the presence of \( c\)-ZrO\(_2\) as a sole phase. However, new crystalline phases namely \( c\)-SiO\(_2\) and ZrSiO\(_4\) in addition to \( m\)-ZrO\(_2\) and \( c\)-ZrO\(_2\) are observed with lower concentrations of Dy\(^{3+}\). At 1400 °C (Fig. 3) the formation of ZrSiO\(_4\) and \( c\)-SiO\(_2\) is evident at all compositions except DZS 50, which still displayed \( c\)-ZrO\(_2\) as a distinct phase. Heat treatment beyond 1400 °C resulted in ZrSiO\(_4\) formation for the all samples investigated, irrespective of Dy\(^{3+}\) additions (Figure not shown).
Fig. 2 XRD patterns of Dy$^{3+}$ added ZrO$_2$-SiO$_2$ binary systems at 1300 ºC.

Fig. 3 XRD patterns of Dy$^{3+}$ added ZrO$_2$-SiO$_2$ binary systems at 1400 ºC.

3.1.2 Raman Spectra

Raman spectroscopy is a more effective technique for distinguishing the $t$-ZrO$_2$ and $c$-ZrO$_2$ polymorphs than XRD analysis since both phases share similar 20 peak positions.$^{24}$ The Raman
spectra for all the investigated compositions after heat treatment at 1200 °C and the spectrum for DZS 50 after heat treatment at 1400 °C are presented in Fig. 4. DZS 5 displayed strong bands around 182, 193, 480 cm\(^{-1}\) and medium bands around 339, 352, 387, 624 cm\(^{-1}\) that indicate the presence of \(m\)-ZrO\(_2\). The bands determined at 154 and 268 cm\(^{-1}\) indicative of \(t\)-ZrO\(_2\) and a band common to both \(t\)-ZrO\(_2\) and \(m\)-ZrO\(_2\) at 644 cm\(^{-1}\) are also witnessed in DZS 5.\(^{25}\) The disappearance of \(m\)-ZrO\(_2\) bands and an upsurge in the band intensity that corresponds to \(t\)-ZrO\(_2\) is observed for the higher Dy\(^{3+}\) content compositions namely DZS 10, DZS 15 and DZS 20. In addition, the formation of a new band at 615 cm\(^{-1}\) that indicates the presence of \(c\)-ZrO\(_2\) is seen for DZS 20.\(^{26}\) DZS 25, DZS 30 and DZS 50 compositions present the disappearance of bands respective of \(t\)-ZrO\(_2\). Thus the simultaneous observation of the disappearance of the \(t\)-ZrO\(_2\) bands and the formation of new bands pertaining to \(c\)-ZrO\(_2\) indicates the \(t\)-ZrO\(_2\) to \(c\)-ZrO\(_2\) phase transformation.\(^{27}\) At 1400 °C, the \(c\)-ZrO\(_2\) phase is still preserved in DZS 50, whereas other compositions yielded the formation of ZrSiO\(_4\) and \(c\)-SiO\(_2\) as additional phases (spectra not shown). Thus the data from the Raman spectra are in good agreement with the XRD analysis.

![Raman spectra of DZS samples at 1200 °C and DZS 50 at 1400 °C.](image)

**Fig. 4** Raman spectra of DZS samples at 1200 °C and DZS 50 at 1400 °C.
3.2 Structural analysis

3.2.1 Transmission Electron Microscopy Studies

Transmission electron micrographs obtained from DZS 50 at 1400 ºC are illustrated in Fig. 5. Fig. 5a shows a homogeneous dispersion of dark spots respective of ZrO₂ grains throughout the SiO₂ matrix. However, the lack of uniformity in the size of ZrO₂ grains is clear in Fig. 5b. High resolution electron micrographs (Fig. 5c and 5d) for a single ZrO₂ grain embedded in the amorphous SiO₂ matrix clearly illustrate its spherical shape and crystalline nature.

![Transmission Electron micrographs](image)

**Fig. 5** Transmission Electron micrographs (a-d) and electron diffraction patterns (e & f) of DZS 50 sample heat treated at 1400 ºC.

Selected area electron diffraction patterns (Figs. 5e and 5f) also confirmed the presence of crystalline ZrO₂ grains embedded in the amorphous SiO₂ matrix. The spherical gains show high...
crystallinity and the diffraction pattern confirms the presence of c-ZrO₂. The amorphous nature of the SiO₂ matrix is revealed through Fig. 5f in which no diffraction spots are witnessed and these results are in consistent with the from XRD and Raman spectra.

![STEM-HAADF Image](image1)

![O](image2)

![Si](image3)

![Zr](image4)

![Dy](image5)

![Overall mapping](image6)

**Fig. 6** Elemental maps constructed from Scanning Transmission Electron Micrographs. (a – STEM-HAADF Image, b-e – mapping of individual elements, f- overall mapping)

Elemental mapping of Zr and Dy concentration recorded from the DZS 50 sample is presented in Fig. 6. The elemental map clearly demonstrates the wide distribution of ZrO₂ particles throughout the SiO₂ matrix. The observation on the presence of Dy³⁺ and Zr⁴⁺ at same locations confirms that the added Dy³⁺ content occupies lattice sites in the ZrO₂ phase.
3.2.2 Quantitative analysis

The Rietveld refinement results in the form of phase fractions and lattice parameters are presented in Table 2. The refined diffraction patterns of DZS 5 (1200 °C) and DZS 50 (1400 °C) are presented in Figs. 7a and 7b. The mixture of phases comprising $t$-ZrO$_2$ and $m$-ZrO$_2$ were determined for DZS 5, DZS 10 and DZS 15 compositions. The complete disappearance of $m$-ZrO$_2$ and an abrupt conversion of whole $t$-ZrO$_2$ to $c$-ZrO$_2$ are seen for DZS 20 sample, whereas $c$-ZrO$_2$ as a sole phase is detected for the higher Dy$^{3+}$ contained compositions namely DZS 25, DZS 30 and DZS 50.

![Refined powder diffraction patterns for DZS 5 at 1200 °C.](image)

Fig. 7a Refined powder diffraction patterns for DZS 5 at 1200 °C.
Fig. 7b  Refined powder diffraction patterns for DZS 50 at 1400 °C. (*Red dotted lines – observed, Solid green lines – calculated, and Pink shows the difference).

The lattice parameters for \( t \)-ZrO\(_2\) indicate a steady increase in the \( a = b \)-axis values and a corresponding decrease in the \( c \)-axis values with respect to the increasing Dy\(^{3+}\) additions. In the case of the observed \( t \)-ZrO\(_2\) to \( c \)-ZrO\(_2\) transition in high Dy\(^{3+}\) contents, namely DZS 20, DZS 25, DZS 30 and DZS 50, a steady enhancement in the \( a=b=c \)-axis values of the \( c \)-ZrO\(_2\) phase is noted with increasing Dy\(^{3+}\) additions. This observation is reasonable and has been justified by comparing the structural parameters of standard \( t \)-ZrO\(_2\) \((a = b = 3.5957 \text{ Å and } c = 5.1844 \text{ Å for ICDD card No. 01-079-1765})\) and standard \( c \)-ZrO\(_2\) \((a = b = c = 5.100 \text{ Å for ICDD card No. 01-071-4810})\). It is noted that the \( a = b \)-axis values of standard \( t \)-ZrO\(_2\) is lower than the \( a = b \)-axis values of standard \( c \)-ZrO\(_2\) whereas the \( c \)-axis values of standard \( t \)-ZrO\(_2\) is higher than the \( c \)-axis values of standard \( c \)-ZrO\(_2\). Hence, the observation of an increase in the \( a = b \)-axis values and reduction in the \( c \)-axis values of \( t \)-ZrO\(_2\) may indicate that Dy\(^{3+}\) additions play a crucial role in controlling the \( t \)-ZrO\(_2\) to \( c \)-ZrO\(_2\) phase transition through its presence on the lattice sites of Zr\(^{4+}\). This phenomenon is justified by the Dy\(^{3+}\) occupancy in the direction along \( a = b \)-axis of \( t \)-ZrO\(_2\) leading to lattice expansion along the \( a = b \)-axis and simultaneous contraction along the \( c \)-axis.
that leads to the \( t \)-ZrO\(_2 \) to \( c \)-ZrO\(_2 \) phase transition. It is also noted that a critical measure of 20 wt. \% Dy\(^{3+}\) additions is required for sufficient lattice expansion along the \( a = b \)-axis of \( t \)-ZrO\(_2 \) to complete the required phase transition from \( t \)-ZrO\(_2 \) to \( c \)-ZrO\(_2 \).

The refined data at 1300 °C confirms the phase degradation that yields \( c \)-SiO\(_2 \), ZrSiO\(_4 \) and \( m \)-ZrO\(_2 \) along with the dominant \( t \)-ZrO\(_2 \) for lower Dy\(^{3+}\) compositions. However, DZS 30 and DZS 50 still showed the presence of \( c \)-ZrO\(_2 \) as a sole phase at 1300 °C. A number of trends can be seen, such as loss in the phase fraction of \( t \)-ZrO\(_2 \), reductions in the phase fractions of \( c \)-SiO\(_2 \) and ZrSiO\(_4 \) towards higher Dy\(^{3+}\) doped samples and a complete absence of impurity phases in the \( c \)-ZrO\(_2 \) stabilized compositions, indicating that the presence of \( c \)-ZrO\(_2 \) in a ZrO\(_2 \)-SiO\(_2 \) binary oxide system prevents either \( c \)-SiO\(_2 \) crystallization or reaction of amorphous SiO\(_2 \) with ZrO\(_2 \) to yield ZrSiO\(_4 \). The lattice data of \( t \)-ZrO\(_2 \) and \( c \)-ZrO\(_2 \) at 1300 °C replicates the same trend as observed at 1200 °C.

The refined data at 1400 °C indicates the following trends for the phase fractions in comparison with the data obtained at 1300 °C: a further reduction in \( t \)-ZrO\(_2 \) content, enhancement in ZrSiO\(_4 \) content and no significant change in \( c \)-SiO\(_2 \). This implies that \( t \)-ZrO\(_2 \) prefers to react with amorphous SiO\(_2 \) to yield ZrSiO\(_4 \) rather than crystallized \( c \)-SiO\(_2 \). The observation that ZrSiO\(_4 \) forms even in \( c \)-ZrO\(_2 \) stabilized compositions, such as DZS 25 and DZS 30, shows that \( c \)-ZrO\(_2 \) is also not stable and tends to react with amorphous SiO\(_2 \). However, restriction on ZrSiO\(_4 \) formation is sustained in the DZS 50 composition that led to the inference that Dy\(^{3+}\) plays an essential role in the resistance in reactivity of \( c \)-ZrO\(_2 \) with amorphous SiO\(_2 \) during heat treatment at higher temperatures.
Table 2  Refinement structural parameters of DZS compositions at different heat treatment temperatures.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$\chi^2$</th>
<th>$R_p$ (%)</th>
<th>$R_{Bragg}$</th>
<th>Phase fractions (%)</th>
<th>Lattice data for $t$-ZrO$_2$ and $^{*}$c-ZrO$_2$</th>
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<td></td>
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<td></td>
<td></td>
<td>$t$-ZrO$_2$</td>
<td>$m$-ZrO$_2$</td>
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<td></td>
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<td>09.10</td>
<td>0.103</td>
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<td>-</td>
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<tr>
<td>DZS 50</td>
<td>1.6</td>
<td>09.64</td>
<td>0.093</td>
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<td>-</td>
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<tr>
<td><strong>1400 °C</strong></td>
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<td>0.0456</td>
<td>48.50</td>
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<td>7.26</td>
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<td>-</td>
</tr>
<tr>
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<td>10.31</td>
<td>0.1429</td>
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<td>-</td>
</tr>
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</table>
3.3 Morphological studies

Micrographs of the DZS 50 sample are presented in Fig. 8. The micrographs indicate a homogeneous distribution of highly crystalline particles throughout the continuously aligned non-crystalline phase. The particles are in the sub-micron size range and have a range of sizes. The back scattered electron (BSE) image reveals the white, high contrast Dy\(^{3+}\) doped ZrO\(_2\) particles embedded in the grey SiO\(_2\) matrix. This is confirmed from the tabulated EDX spectrum gained through spot analysis from white coloured grains that possess higher Dy\(^{3+}\) and Zr\(^{4+}\) content. The close observation revealed that Dy\(^{3+}\) doped ZrO\(_2\) particles are highly crystalline single grains in an amorphous SiO\(_2\) matrix. These observations coincide with the structural features found with TEM analysis.

![Micrographs of DZS 50 sample](image1)

![Micrographs of DZS 50 sample](image2)

![EDX spectrum](image3)

<table>
<thead>
<tr>
<th>Element</th>
<th>Series</th>
<th>Content (wt.%)</th>
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</thead>
<tbody>
<tr>
<td>Dysprosium</td>
<td>L-series</td>
<td>29.22</td>
</tr>
<tr>
<td>Zirconium</td>
<td>L-series</td>
<td>52.73</td>
</tr>
<tr>
<td>Silicon</td>
<td>K-series</td>
<td>05.16</td>
</tr>
<tr>
<td>Oxygen</td>
<td>K-series</td>
<td>12.89</td>
</tr>
</tbody>
</table>

Fig. 8 FEG-Scanned Electron Micrographs of DZS 50 sample heat treated at 1400 °C and EDX spectra recorded by spot analysis for a large white grain.
3.4 Mechanical properties

Density and mechanical properties of pure ZS at 1100 °C and DZS 50 at 1400 °C are presented in Table 3. The mean value and standard deviation of density were determined from five different measurements and mechanical data was derived from ten different indents at random locations.

Table 3 Physical and Mechanical properties of ZS and DZS 50 samples. Mean values (standard deviation)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (gm.cm$^{-3}$)</th>
<th>Hardness (GPa)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZS</td>
<td>3.789 (0.03)</td>
<td>0.45 (0.50)</td>
<td>6.81 (1.00)</td>
</tr>
<tr>
<td>DZS 50</td>
<td>4.635 (0.04)</td>
<td>9.73 (0.75)</td>
<td>127.16 (2.76)</td>
</tr>
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</table>

Fig. 9 presents load versus depth profiles from the DZS 50 samples. These are highly uniform and consistent. This demonstrates the highly dense nature of the DZS 50 due to its higher thermal stability. The density and mechanical properties of DZS 50 sample (Table 3) are significantly greater than the ZS sample. This indicates that the Dy$^{3+}$ content plays an important role in generating better densification and consequent enhancement in mechanical properties.
Fig. 9 Load versus Depth profile determined for DZS 50 from indentation.

3.5 Imaging Characteristics

Magnetic hysteresis curves of ZS and Dy$^{3+}$ doped ZrO$_2$-SiO$_2$ binary oxides measured at room temperature are shown in Fig. 10. The results indicate that saturation magnetization (Ms) increases as the Dy$^{3+}$ addition increases. The presence of poor hysteresis loops indicates that added Dy$^{3+}$ content in ZrO$_2$-SiO$_2$ binary oxides exhibits paramagnetic behaviour and these results are in accordance with the existing literature reports on Dy$^{3+}$ doped materials.$^{28}$

![Magnetic hysteresis curves of ZS and Dy$^{3+}$ doped ZrO$_2$-SiO$_2$ binary oxides measured at room temperature.](image1)

Fig. 10 Hysteresis curves of ZS and Dy$^{3+}$ doped ZrO$_2$-SiO$_2$ binary oxides measured at room temperature.
MR Contrast enhancement images and MR relaxation time determined for different concentrations of DZS 50 sample.

The relaxation time (1/T<sub>2</sub>) recorded with respect to different concentrations have been plotted in Fig. 11 together with the r<sub>2</sub> map images. The images show that the brightness continues to increase as the concentration increases and the 1/T<sub>2</sub> relaxation time indicates the same trend. This observation on increase in MR signal intensity and 1/T<sub>2</sub> relaxation time clearly indicates that the investigated DZS 50 possess MRI contrast behaviour and hence can be utilized to monitor the implant performance in vivo.

4 Discussion

The XRD and Raman spectroscopy results confirmed the influence of Dy<sup>3+</sup> content on the t-ZrO<sub>2</sub> to c-ZrO<sub>2</sub> phase transition. The compositions > 20 wt. % Dy<sup>3+</sup> resulted in complete transformation to c-ZrO<sub>2</sub> without the formation of any impurity phases up to 1200 °C. Further heat treatment triggered the crystallization of c-SiO<sub>2</sub> and ZrSiO<sub>4</sub> at a minor level in all the compositions except DZS 50 in which c-ZrO<sub>2</sub> is maintained till 1400 °C. The homogenous dispersion of highly crystalline c-ZrO<sub>2</sub> particles throughout the amorphous SiO<sub>2</sub> matrix is confirmed by electron microscopy studies. The occupancy of Dy<sup>3+</sup> at the cation lattice sites of ZrO<sub>2</sub> is confirmed from the elemental mapping and EDX spectra recorded from TEM and SEM respectively.

The mechanism behind the t - c phase transition is believed to be the substitution of the relatively small Zr<sup>4+</sup> ions (0.79 Å) by larger Dy<sup>3+</sup> ions (0.91 Å) at the cation lattice sites of c-ZrO<sub>2</sub>, as determined from refinement studies. The lattice substitution of Dy<sup>3+</sup> occurred along the direction of a = b-axis in the ZrO<sub>2</sub> structure and this is manifested by the observed increase in a = b-axis dimensions and parallel reduction in the c-axis parameters of t-ZrO<sub>2</sub>. This hypothesis is further supported by comparison with the pure ZrO<sub>2</sub>-SiO<sub>2</sub> binary system in which t-ZrO<sub>2</sub>
stabilization is accompanied by the formation of Si-O-Zr bonds between ZrO<sub>2</sub> particles and the SiO<sub>2</sub> matrix. Wang <i>et al.</i>,<sup>29</sup> and Monte <i>et al.</i>,<sup>30</sup> explored the presence of the a Si-O-Zr interfacial layer that causes the <i>t</i>-ZrO<sub>2</sub> stabilization in the ZrO<sub>2</sub>-SiO<sub>2</sub> binary system through analytical techniques. In these studies heat treatment beyond 1100 °C affected <i>t-m</i> phase degradation, which is believed to be caused by the rupture of Si-O-Zr bonds in the pure ZrO<sub>2</sub>-SiO<sub>2</sub> binary system. In the present study, DZS 50 with 50% Dy<sup>3+</sup> addition, demonstrated the phase stability of <i>c</i>-ZrO<sub>2</sub> up to 1400 °C. HR-TEM studies (<b>Fig. 5d</b>) indicated the absence of any Si-O-Zr interfacial layer in DZS 50 and thus it is proposed that the <i>t - c</i> phase transition is purely caused by the occupancy of Dy<sup>3+</sup> ions at the lattice sites of ZrO<sub>2</sub>.

The factors that maintain the phase stability of <i>c</i>-ZrO<sub>2</sub> in DZS 50 to 1400 °C are dependent on the Dy<sup>3+</sup> content and concomitant critical expansion in the lattice size of <i>c</i>-ZrO<sub>2</sub>. This inference is supported by prior work on the effect of additions such as La<sup>3+</sup>, Gd<sup>3+</sup>, Fe<sup>3+</sup> and the combination of Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> on the ZrO<sub>2</sub>-SiO<sub>2</sub> binary systems.<sup>31,27,32,10</sup> In the case of the La<sup>3+</sup> doped ZrO<sub>2</sub>-SiO<sub>2</sub> binary oxides (LZS), the <i>t</i>-ZrO<sub>2</sub> to <i>c</i>-ZrO<sub>2</sub> phase transition is not observed even at higher levels of La<sup>3+</sup> additions and the <i>t</i>-ZrO<sub>2</sub> phase is not retained beyond 1000 °C. In the case of Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> doped ZrO<sub>2</sub>-SiO<sub>2</sub> binary system (CPZS), Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> dissolve in the SiO<sub>2</sub> matrix and the <i>t</i>-ZrO<sub>2</sub> phase is retained till 1100 °C. The Fe<sup>3+</sup> doped ZrO<sub>2</sub>-SiO<sub>2</sub> binary oxide system (FZS) results in a significant amount of ZrSiO<sub>4</sub> formation along with the presence of <i>t</i>-ZrO<sub>2</sub> even at 1100 °C and its subsequent heat treatment resulted in the complete transformation to ZrSiO<sub>4</sub>. Gd<sup>3+</sup> doped binary ZrO<sub>2</sub>-SiO<sub>2</sub> (GZS) displayed a <i>t</i>-ZrO<sub>2</sub> to <i>c</i>-ZrO<sub>2</sub> phase transition at 1100 °C, however the phase stability of <i>c</i>-ZrO<sub>2</sub> was not preserved beyond 1100 °C. The La<sup>3+</sup> and Ca<sup>2+</sup> ions possess large ionic radii (La<sup>3+</sup> = 1.06 Å and Ca<sup>2+</sup> = 0.99 Å) in comparison with Zr<sup>4+</sup> ions and due to these size differences, La<sup>3+</sup> and Ca<sup>2+</sup> are not preferred by the ZrO<sub>2</sub> lattice to affect phase transitions. This concept is also confirmed by the observed absence of any significant change in the lattice parameter of <i>t</i>-ZrO<sub>2</sub> in both the LZS and CPZS
systems. The smaller sized Fe$^{3+}$ ion tends to occupy the lattice sites of ZrO$_2$ and promotes the rapid crystallization of ZrSiO$_4$. The larger size of Gd$^{3+}$ (0.94Å) compared to Zr$^{4+}$ ion favours its occupancy in the ZrO$_2$ structure. This is justified by the observed steady enhancement in the lattice parameters of $t$-ZrO$_2$ and subsequent $t$-ZrO$_2$ to $c$-ZrO$_2$ phase transition in GZS system. However, $c$-ZrO$_2$ to $m$-ZrO$_2$ transition with Gd$^{3+}$ additions above 25 wt.% suggests that $c$-ZrO$_2$ has reached its maximum lattice expansion and any further Gd$^{3+}$ additions led to the $c$-ZrO$_2$ transforming to $m$-ZrO$_2$.

In the present DZS system, the size difference between Dy$^{3+}$ and Zr$^{4+}$ is smaller than the difference between Gd$^{3+}$ and Zr$^{4+}$ and this effect results in the accommodation of a larger quantity of Dy$^{3+}$ ions in the ZrO$_2$ lattice than is possible with Gd$^{3+}$ ions and hence any phase degradation is not witnessed till 50 wt.% of Dy$^{3+}$ additions. Note that the $a = b = c$-axis parameter of $c$-ZrO$_2$ in the GZS system is greater than the $a = b = c$-axis parameter of the $c$-ZrO$_2$ in the DZS system for equal doping concentrations of both Dy$^{3+}$ and Gd$^{3+}$.

The observation of minor levels of ZrSiO$_4$ formation at 1300 °C for the $t$-ZrO$_2$ dominant DZS samples suggests that $t$-ZrO$_2$ is more prone to react with amorphous SiO$_2$ to form ZrSiO$_4$ than $c$-ZrO$_2$. Kaiser et.al reported that the temperature of ZrSiO$_4$ formation is strongly dependent on the type of ZrO$_2$ powder.$^{33}$ In that particular work, Kaiser et.al witnessed that yttria stabilized ZrO$_2$ - SiO$_2$ systems delayed ZrSiO$_4$ formation till 1300 °C whereas, in the absence of any stabilizers, the ZrO$_2$-SiO$_2$ mixture yielded ZrSiO$_4$ at 1200 °C. Thus, the observation of ZrSiO$_4$ formation at a minor level at 1300 °C in the present study is consistent since ZrO$_2$ is stabilized by lattice substitution of Dy$^{3+}$ ions. The observation of a gradual formation of ZrSiO$_4$ even in $c$-ZrO$_2$ stabilized samples at 1400 °C and the observation of complete transformation to ZrSiO$_4$ at 1500 °C indicates that the phase stability of $c$-ZrO$_2$ cannot be preserved beyond a certain heat treatment limit. Hence, it could be inferred that the ionic radii of stabilizing agents, the amount
of dopant concentration and heat treatment temperature are the deciding factors in determining the $t$-ZrO$_2$ to $c$-ZrO$_2$ phase transition and the phase stability of $c$-ZrO$_2$.

The SEM studies showed a microstructure of an amorphous SiO$_2$ matrix reinforced by highly crystalline and dense $c$-ZrO$_2$ ceramics that resulted in the remarkable enhancement in mechanical properties. The mechanical properties of the DZS 50 sample are compatible with the properties of commercial Ti6Al4V alloys (Young’s modulus of 115 GPa for Ti6Al4V – ASTM data sheet).

It is well known that there is a risk of reduced biocompatibility if rare earth metals are present in their free ionic form$^{34}$. However, as can be seen from the elemental mapping in Fig. 6, the added Dy$^{3+}$ intends to occupy the lattice sites of ZrO$_2$ and hence its rapid leaching is avoided to thus reducing any toxic effects. The ability of the ZrO$_2$ - SiO$_2$ system to induce the formation of apatite, due to the presence of amorphous of SiO$_2$, is documented in earlier reports$^{10,35}$ and hence the proposed DZS system with inherent amorphous SiO$_2$ is anticipated to also promote the formation of apatite in vivo. Magnetic measurements reveal paramagnetic behaviour and MRI data displayed the commendable MRI contrast nature of the DZS 50 sample. Hence, DZS 50 could be recommended as a promising candidate for load bearing applications in medical implants.

**Conclusions**

The presence of the $t$-ZrO$_2$ to $c$-ZrO$_2$ phase transition in the ZrO$_2$-SiO$_2$ binary system is controlled by the insertion of Dy$^{3+}$ into the lattice sites of ZrO$_2$. The phase stability of $c$-ZrO$_2$ has been preserved at temperatures up to 1400 $^\circ$C for the maximum Dy$^{3+}$ doped ZrO$_2$-SiO$_2$ binary oxides (DZS 50 and at this composition highly crystalline and dense ceramics form. The quantity of added Dy$^{3+}$ and its associated positive change in lattice volume of $c$-ZrO$_2$ play a crucial role in delaying the formation of ZrSiO$_4$ during higher temperature heat treatments. The enhanced magnetic resonance contrast of DZS 50 has been verified. The mechanical strength of
DZS 50 matches the commercially available synthetic bone implants and hence it could be recommended for the utilization of load bearing bone replacement applications.

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Dy$^{3+}$ additions to ZrO$_2$–SiO$_2$ systems resulted in its occupancy at ZrO$_2$ lattice to yield $c$-ZrO$_2$. Structural stability of $c$-ZrO$_2$ embedded in amorphous SiO$_2$ matrix remained till 1400 °C that displays enhanced mechanical stability and imaging contrast features.