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Tetragonal to cubic transformation of SiO₂ stabilized ZrO₂ 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 (Dy^{3+}) is well established. To this aim, varied levels of Dy^{3+} additions in the $\text{ZrO}_2\text{-SiO}_2$ binary oxide system have been explored. The results indicate the effective role of Dy^{3+} in the formation of thermally and mechanically stable $c\text{-ZrO}_2$ (cubic zirconia) phase at higher temperatures. The presence of SiO_2 influenced the $t\text{-ZrO}_2$ stabilization whereas Dy^{3+} tends to occupy the ZrO_2 lattice sites to induce $c\text{-ZrO}_2$ transition. Magnetic and magnetic resonance imaging (MRI) tests displayed the commendable contrast ability of 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.¹¹⁻¹³ Among rare earth elements, Dysprosium (Dy^{3+}) exhibits visible luminescence by producing strong emission in both the blue (470-500 nm) and yellow (570-600 nm) region.¹⁴ Dy^{3+} possesses a high magnetic moment ($\mu=10.2 \mu\text{B}$) and an asymmetric electronic ground state ($6\text{H}_{15/2}$) 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.¹⁵ The high atomic number ($Z = 66$) and relatively high K-edge energy (53.8 keV) of Dy^{3+} also provides a higher X-ray attenuation coefficient at 100 keV ($3.36 \text{ cm}^2\cdot\text{g}^{-1}$) than the commercially available iodine based CT contrast agents.¹⁶ **These imaging contrast features of Dy^{3+} could support the monitoring of implant performance during its life span *in-vivo*.** Dy^{3+} additions could also play a major role in achieving a thermally stable ZrO_2 polymorph.¹¹

In view of the above potential advantages of Dy^{3+} as an addition to $\text{ZrO}_2\text{-SiO}_2$ binary oxides in terms of increased *t*- ZrO_2 stability and enhance MRI image contrast, we present a study of the influence of Dy^{3+} on the $\text{ZrO}_2\text{-SiO}_2$ 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^{3+} doped $\text{ZrO}_2\text{-SiO}_2$ (DZS) binary oxides was achieved through the sol-gel method. Analytical grade $\text{Dy}(\text{NO}_3)_3\cdot\text{H}_2\text{O}$, $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ and $(\text{C}_2\text{H}_5)_4\text{OSi}$ (TEOS), all procured from Sigma-Aldrich, India, were taken as precursors for the synthesis. The molar concentrations of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ and $(\text{C}_2\text{H}_5)_4\text{OSi}$ were maintained at a constant ratio of 1: 1 throughout the

synthesis whereas the $\text{Dy}(\text{NO}_3)_3$ additions were adjusted to obtain a wide range of compositions. Additionally, a pure $\text{ZrO}_2\text{-SiO}_2$ 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

Sample code	Molar concentrations of the precursors			% of added Dy^{3+} ions with respect to Zr^{4+}
	$\text{Dy}(\text{NO}_3)_3$	ZrOCl_2	TEOS	
ZS	-	0.5 M	0.5 M	-
DZS 5	0.025 M	0.5 M	0.5 M	5
DZS 10	0.050 M	0.5 M	0.5 M	10
DZS 15	0.075 M	0.5 M	0.5 M	15
DZS 20	0.100 M	0.5 M	0.5 M	20
DZS 25	0.125 M	0.5 M	0.5 M	25
DZS 30	0.150 M	0.5 M	0.5 M	30
DZS 50	0.250 M	0.5 M	0.5 M	50

The synthetic procedure is briefly explained as follows. Previously prepared $\text{Dy}(\text{NO}_3)_3$ 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 $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) 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*-ZrO₂, 01-078-1765 for *t*-ZrO₂, 01-071-4810 for *c*-ZrO₂, 01-083-1378 for ZrSiO₄ and 00-039-1425 for cristobalite (*c*-SiO₂). 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-Emission 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*-ZrO₂, *t*-ZrO₂, *c*-ZrO₂, ZrSiO₄ and *c*-SiO₂ were obtained from Smith *et.al.*,¹⁸ Howard *et.al.*,¹⁹ Wyckoff,²⁰ Hazen *et.al.*²¹ and Dera *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 14577²³ 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 T₂ Relaxivity measurement and *in vitro* MR imaging

T₂ relaxivity of DZS 50 samples was measured using a Siemens Magnetom Avanto 1.5 Tesla MRI scanner. An *in vitro* phantom containing DZS 50 at different Dy³⁺ 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 T₂ weighting. Using these images, the T₂ relaxation time is determined.

3. Results

3.1 Phase behaviour

3.1.1 XRD analysis

The pure ZS system indicated the formation of *t*-ZrO₂ as a distinct phase at 1100 °C and beyond 1100 °C its degradation to *m*-ZrO₂ 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 Dy³⁺ additions to the ZrO₂-SiO₂ binary system after heat treatment at 1200 °C. It is evident from **Fig. 1** that lower concentrations of Dy³⁺ in the range of 5 - 15 wt.% resulted in the phase degradation to yield *m*-ZrO₂. However, Dy³⁺ concentrations in the higher range of 20 - 50 wt.% retained *c*-ZrO₂ as the sole phase to the resolution of the instrument. However, the mechanisms by which excess Dy³⁺ additions lead to a stabilisation of the *c*-ZrO₂ structure are not well understood from the present results.

Fig. 1 XRD patterns of Dy³⁺ added ZrO₂-SiO₂ binary oxides at 1200 °C.

At 1300 °C (**Fig. 2**), compositions containing higher concentrations of Dy³⁺ above 25 wt.% still indicated the presence of *c*-ZrO₂ as a sole phase. However, new crystalline phases namely *c*-SiO₂ and ZrSiO₄ in addition to *m*-ZrO₂ and *c*-ZrO₂ are observed with lower concentrations of Dy³⁺. At 1400 °C (**Fig. 3**) the formation of ZrSiO₄ and *c*-SiO₂ is evident at all compositions except DZS 50, which still displayed *c*-ZrO₂ as a distinct phase. Heat treatment beyond 1400 °C resulted in ZrSiO₄ formation for the all samples investigated, irrespective of Dy³⁺ additions (Figure not shown).

Fig. 2 XRD patterns of Dy^{3+} added ZrO_2 - SiO_2 binary systems at 1300 °C.

Fig. 3 XRD patterns of Dy^{3+} added ZrO_2 - SiO_2 binary systems at 1400 °C.

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 2θ 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*-ZrO₂. The bands determined at 154 and 268 cm^{-1} indicative of *t*-ZrO₂ and a band common to both *t*-ZrO₂ and *m*-ZrO₂ at 644 cm^{-1} are also witnessed in DZS 5.²⁵ The disappearance of *m*-ZrO₂ bands and an upsurge in the band intensity that corresponds to *t*-ZrO₂ is observed for the higher Dy³⁺ 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*-ZrO₂ is seen for DZS 20.²⁶ DZS 25, DZS 30 and DZS 50 compositions present the disappearance of bands respective of *t*-ZrO₂. Thus the simultaneous observation of the disappearance of the *t*-ZrO₂ bands and the formation of new bands pertaining to *c*-ZrO₂ indicates the *t*-ZrO₂ to *c*-ZrO₂ phase transformation.²⁷ At 1400 °C, the *c*-ZrO₂ phase is still preserved in DZS 50, whereas other compositions yielded the formation of ZrSiO₄ and *c*-SiO₂ as additional phases (spectra not shown). Thus the data from the Raman spectra are in good agreement with the XRD analysis.

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 °C 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.

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

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 $c\text{-ZrO}_2$. The amorphous nature of the SiO_2 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.

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 ZrO_2 particles throughout the SiO_2 matrix. The observation on the presence of Dy^{3+} and Zr^{4+} at same locations confirms that the added Dy^{3+} content occupies lattice sites in the ZrO_2 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*-ZrO₂ and *m*-ZrO₂ were determined for DZS 5, DZS 10 and DZS 15 compositions. The complete disappearance of *m*-ZrO₂ and an abrupt conversion of whole *t*-ZrO₂ to *c*-ZrO₂ are seen for DZS 20 sample, whereas *c*-ZrO₂ as a sole phase is detected for the higher Dy³⁺ contained compositions namely DZS 25, DZS 30 and DZS 50.

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*-ZrO₂ indicate a steady increase in the $a = b$ -axis values and a corresponding decrease in the c -axis values with respect to the increasing Dy³⁺ additions. In the case of the observed *t*-ZrO₂ to *c*-ZrO₂ transition in high Dy³⁺ contents, namely DZS 20, DZS 25, DZS 30 and DZS 50, a steady enhancement in the $a=b=c$ -axis values of the *c*-ZrO₂ phase is noted with increasing Dy³⁺ additions. This observation is reasonable and has been justified by comparing the structural parameters of standard *t*-ZrO₂ ($a = b = 3.5957$ Å and $c = 5.1844$ Å for ICDD card No. 01-079-1765) and standard *c*-ZrO₂ ($a = b = c = 5.100$ Å for ICDD card No. 01-071-4810). It is noted that the $a = b$ -axis values of standard *t*-ZrO₂ is lower than the $a = b$ -axis values of standard *c*-ZrO₂ whereas the c -axis values of standard *t*-ZrO₂ is higher than the c -axis values of standard *c*-ZrO₂. Hence, the observation of an increase in the $a = b$ -axis values and reduction in the c -axis values of *t*-ZrO₂ may indicate that Dy³⁺ additions play a crucial role in controlling the *t*-ZrO₂ to *c*-ZrO₂ phase transition through its presence on the lattice sites of Zr⁴⁺. This phenomenon is justified by the Dy³⁺ occupancy in the direction along $a = b$ -axis of *t*-ZrO₂ leading to lattice expansion along the $a = b$ -axis and simultaneous contraction along the c -axis

that leads to the $t\text{-ZrO}_2$ to $c\text{-ZrO}_2$ 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 $t\text{-ZrO}_2$ to complete the required phase transition from $t\text{-ZrO}_2$ to $c\text{-ZrO}_2$.

The refined data at 1300 °C confirms the phase degradation that yields $c\text{-SiO}_2$, ZrSiO_4 and $m\text{-ZrO}_2$ along with the dominant $t\text{-ZrO}_2$ for lower Dy^{3+} compositions. However, DZS 30 and DZS 50 still showed the presence of $c\text{-ZrO}_2$ as a sole phase at 1300 °C. A number of trends can be seen, such as loss in the phase fraction of $t\text{-ZrO}_2$, reductions in the phase fractions of $c\text{-SiO}_2$ and ZrSiO_4 towards higher Dy^{3+} doped samples and a complete absence of impurity phases in the $c\text{-ZrO}_2$ stabilized compositions, indicating that the presence of $c\text{-ZrO}_2$ in a $\text{ZrO}_2\text{-SiO}_2$ binary oxide system prevents either $c\text{-SiO}_2$ crystallization or reaction of amorphous SiO_2 with ZrO_2 to yield ZrSiO_4 . The lattice data of $t\text{-ZrO}_2$ and $c\text{-ZrO}_2$ 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 $t\text{-ZrO}_2$ content, enhancement in ZrSiO_4 content and no significant change in $c\text{-SiO}_2$. This implies that $t\text{-ZrO}_2$ prefers to react with amorphous SiO_2 to yield ZrSiO_4 rather than crystallized $c\text{-SiO}_2$. The observation that ZrSiO_4 forms even in $c\text{-ZrO}_2$ stabilized compositions, such as DZS 25 and DZS 30, shows that $c\text{-ZrO}_2$ 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 $c\text{-ZrO}_2$ with amorphous SiO_2 during heat treatment at higher temperatures.

Table 2 Refinement structural parameters of DZS compositions at different heat treatment temperatures.

1200 °C										
Sample code	χ^2	R_p (%)	R_{Bragg}	Phase fractions (%)					Lattice data for t -ZrO ₂ and *c -ZrO ₂	
				t -ZrO ₂	m -ZrO ₂			c -ZrO ₂	$a = b$ axis (Å) $^*a = b = c$ axis (Å)	c - axis (Å)
DZS 5	1.5	06.84	0.104	74.72	25.28			-	3.5987	5.1815
DZS 10	1.3	06.90	0.109	91.91	8.09			-	3.6126	5.1812
DZS 15	2.8	09.71	0.093	90.27	9.73			-	3.6202	5.1744
DZS 20	2.0	09.91	0.053	00.07	-			99.93	$^*5.1377$	
DZS 25	1.6	08.33	0.085	-	-			100	$^*5.1488$	
DZS 30	1.6	08.38	0.088	-	-			100	$^*5.1534$	
DZS 50	1.4	06.77	0.081	-	-			100	$^*5.1601$	
1300 °C										
Sample code	χ^2	R_p (%)	R_{Bragg}	Phase fractions (%)					Lattice data for t -ZrO ₂ and *c -ZrO ₂	
				t -ZrO ₂	m -ZrO ₂	c -SiO ₂	ZrSiO ₄	c -ZrO ₂	$a = b$ axis (Å) $^*a = b = c$ axis (Å)	c - axis (Å)
DZS 5	1.4	06.45	0.035	52.63	21.04	24.58	1.74	-	3.6031	5.1791
DZS 10	2.2	08.75	0.074	67.80	6.81	19.25	6.14	-	3.6119	5.1711
DZS 15	1.9	12.50	0.104	73.88	6.21	12.42	1.15	6.33	3.6302 $^*5.1016$	5.1601
DZS 20	1.7	09.72	0.082	-	-	8.35	-	91.65	$^*5.1109$	
DZS 25	1.1	08.81	0.120	-	-	-	2.60	97.40	$^*5.1494$	
DZS 30	1.9	09.10	0.103	-	-	-	-	100	$^*5.1541$	
DZS 50	1.6	09.64	0.093	-	-	-	-	100	$^*5.1603$	
1400 °C										
Sample code	χ^2	R_p (%)	R_{Bragg}	Phase fractions (%)					Lattice data for t -ZrO ₂ and *c -ZrO ₂	
				t -ZrO ₂	m -ZrO ₂	c -SiO ₂	ZrSiO ₄	c -ZrO ₂	$a = b$ axis (Å) $^*a = b = c$ axis (Å)	c - axis (Å)
DZS 5	1.8	06.89	0.0456	48.50	19.15	24.02	8.33	-	3.6028	5.1782
DZS 10	2.6	09.15	0.0678	52.99	7.26	20.29	19.51	-	3.6114	5.1701
DZS 15	3.7	10.82	0.1157	64.86	4.99	8.505	10.02	11.622	3.6335 $^*5.0955$	5.1658
DZS 20	2.7	10.36	0.1282	-	0.82	2.46	35.59	61.11	$^*5.1458$	
DZS 25	2.5	09.59	0.1075	-	-	10.61	40.63	48.76	$^*5.1498$	
DZS 30	1.9	09.55	0.0920	-	-	16.7	16.91	66.39	$^*5.1505$	
DZS 50	1.4	10.31	0.1429	-	-	-	2.37	97.63	$^*5.1583$	

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.

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)

Sample	Density (gm.cm ⁻³)	Hardness (GPa)	Elastic Modulus (GPa)
ZS	3.789 (0.03)	0.45 (0.50)	6.81 (1.00)
DZS 50	4.635 (0.04)	9.73 (0.75)	127.16 (2.76)

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 Dy³⁺ 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 $\text{ZrO}_2\text{-SiO}_2$ binary oxides measured at room temperature are shown in **Fig. 10**. The results indicate that saturation magnetization (M_s) increases as the Dy^{3+} addition increases. The presence of poor hysteresis loops indicates that added Dy^{3+} content in $\text{ZrO}_2\text{-SiO}_2$ binary oxides exhibits paramagnetic behaviour and these results are in accordance with the existing literature reports on Dy^{3+} doped materials.²⁸

Fig. 10 Hysteresis curves of **ZS** and Dy^{3+} doped $\text{ZrO}_2\text{-SiO}_2$ binary oxides measured at room temperature.

Fig. 11 MR Contrast enhancement images and MR relaxation time determined for different concentrations of DZS 50 sample.

The relaxation time ($1/T_2$) recorded with respect to different concentrations have been plotted in **Fig. 11** together with the r_2 map images. The images show that the brightness continues to increase as the concentration increases and the $1/T_2$ relaxation time indicates the same trend. This observation on increase in MR signal intensity and $1/T_2$ 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^{3+} content on the t - ZrO_2 to c - ZrO_2 phase transition. The compositions > 20 wt. % Dy^{3+} resulted in complete transformation to c - ZrO_2 without the formation of any impurity phases up to $1200^\circ C$. Further heat treatment triggered the crystallization of c - SiO_2 and $ZrSiO_4$ at a minor level in all the compositions except DZS 50 in which c - ZrO_2 is maintained till $1400^\circ C$. The homogenous dispersion of highly crystalline c - ZrO_2 particles throughout the amorphous SiO_2 matrix is confirmed by electron microscopy studies. The occupancy of Dy^{3+} at the cation lattice sites of ZrO_2 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^{4+} ions ($0.79 \text{ \AA}$) by larger Dy^{3+} ions ($0.91 \text{ \AA}$) at the cation lattice sites of c - ZrO_2 , as determined from refinement studies. The lattice substitution of Dy^{3+} occurred along the direction of $a = b$ -axis in the ZrO_2 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_2 . This hypothesis is further supported by comparison with the pure ZrO_2 - SiO_2 binary system in which t - ZrO_2

stabilization is accompanied by the formation of Si-O-Zr bonds between ZrO₂ particles and the SiO₂ matrix. Wang *et.al.*,²⁹ and Monte *et.al.*,³⁰ explored the presence of the a Si-O-Zr interfacial layer that causes the *t*-ZrO₂ stabilization in the ZrO₂-SiO₂ binary system through analytical techniques. In these studies heat treatment beyond 1100 °C affected *t-m* phase degradation, which is believed to be caused by the rupture of Si-O-Zr bonds in the pure ZrO₂-SiO₂ binary system. In the present study, DZS 50 with 50% Dy³⁺ addition, demonstrated the phase stability of *c*-ZrO₂ up to 1400 °C. HR-TEM studies (**Fig. 5d**) indicated the absence of any Si-O-Zr interfacial layer in DZS 50 and thus it is proposed that the *t* - *c* phase transition is purely caused by the occupancy of Dy³⁺ ions at the lattice sites of ZrO₂.

The factors that maintain the phase stability of *c*-ZrO₂ in DZS 50 to 1400 °C are dependent on the Dy³⁺ content and concomitant critical expansion in the lattice size of *c*-ZrO₂. This inference is supported by prior work on the effect of additions such as La³⁺, Gd³⁺, Fe³⁺ and the combination of Ca²⁺ and PO₄³⁻ on the ZrO₂-SiO₂ binary systems.^{31,27,32,10} In the case of the La³⁺ doped ZrO₂-SiO₂ binary oxides (LZS), the *t*-ZrO₂ to *c*-ZrO₂ phase transition is not observed even at higher levels of La³⁺ additions and the *t*-ZrO₂ phase is not retained beyond 1000 °C. In the case of Ca²⁺ and PO₄³⁻ doped ZrO₂-SiO₂ binary system (CPZS), Ca²⁺ and PO₄³⁻ dissolve in the SiO₂ matrix and the *t*-ZrO₂ phase is retained till 1100 °C. The Fe³⁺ doped ZrO₂-SiO₂ binary oxide system (FZS) results in a significant amount of ZrSiO₄ formation along with the presence of *t*-ZrO₂ even at 1100 °C and its subsequent heat treatment resulted in the complete transformation to ZrSiO₄. Gd³⁺ doped binary ZrO₂-SiO₂ (GZS) displayed a *t*-ZrO₂ to *c*-ZrO₂ phase transition at 1100 °C, however the phase stability of *c*-ZrO₂ was not preserved beyond 1100 °C. The La³⁺ and Ca²⁺ ions possess large ionic radii (La³⁺ = 1.06 Å and Ca²⁺ = 0.99 Å) in comparison with Zr⁴⁺ ions and due to these size differences, La³⁺ and Ca²⁺ are not preferred by the ZrO₂ lattice to affect phase transitions. This concept is also confirmed by the observed absence of any significant change in the lattice parameter of *t*-ZrO₂ 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+} ($0.94\text{\AA}$) 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 $t\text{-ZrO}_2$ and subsequent $t\text{-ZrO}_2$ to $c\text{-ZrO}_2$ phase transition in GZS system. However, $c\text{-ZrO}_2$ to $m\text{-ZrO}_2$ transition with Gd^{3+} additions above 25 wt.% suggests that $c\text{-ZrO}_2$ has reached its maximum lattice expansion and any further Gd^{3+} additions led to the $c\text{-ZrO}_2$ transforming to $m\text{-ZrO}_2$.

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 $c\text{-ZrO}_2$ in the GZS system is greater than the $a = b = c$ -axis parameter of the $c\text{-ZrO}_2$ 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 $1300\text{ }^\circ\text{C}$ for the $t\text{-ZrO}_2$ dominant DZS samples suggests that $t\text{-ZrO}_2$ is more prone to react with amorphous SiO_2 to form ZrSiO_4 than $c\text{-ZrO}_2$. 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 $1300\text{ }^\circ\text{C}$ whereas, in the absence of any stabilizers, the $\text{ZrO}_2\text{-SiO}_2$ mixture yielded ZrSiO_4 at $1200\text{ }^\circ\text{C}$. Thus, the observation of ZrSiO_4 formation at a minor level at $1300\text{ }^\circ\text{C}$ 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 $c\text{-ZrO}_2$ stabilized samples at $1400\text{ }^\circ\text{C}$ and the observation of complete transformation to ZrSiO_4 at $1500\text{ }^\circ\text{C}$ indicates that the phase stability of $c\text{-ZrO}_2$ 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 -ZrO₂ to c -ZrO₂ phase transition and the phase stability of c -ZrO₂.

The SEM studies showed a microstructure of an amorphous SiO₂ matrix reinforced by highly crystalline and dense c -ZrO₂ 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 form³⁴. However, as can be seen from the elemental mapping in Fig. 6, the added Dy³⁺ intends to occupy the lattice sites of ZrO₂ and hence its rapid leaching is avoided to thus reducing any toxic effects. The ability of the ZrO₂ - SiO₂ system to induce the formation of apatite, due to the presence of amorphous SiO₂, is documented in earlier reports^{10,35} and hence the proposed DZS system with inherent amorphous SiO₂ 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 -ZrO₂ to c -ZrO₂ phase transition in the ZrO₂-SiO₂ binary system is controlled by the insertion of Dy³⁺ into the lattice sites of ZrO₂. The phase stability of c -ZrO₂ has been preserved at temperatures up to 1400 °C for the maximum Dy³⁺ doped ZrO₂-SiO₂ binary oxides (DZS 50 and at this composition highly crystalline and dense ceramics form. The quantity of added Dy³⁺ and its associated positive change in lattice volume of c -ZrO₂ play a crucial role in delaying the formation of ZrSiO₄ 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 $\text{ZrO}_2\text{-SiO}_2$ systems resulted in its occupancy at ZrO_2 lattice to yield $c\text{-ZrO}_2$. Structural stability of $c\text{-ZrO}_2$ embedded in amorphous SiO_2 matrix remained till $1400\text{ }^\circ\text{C}$ that displays enhanced mechanical stability and imaging contrast features.