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Research Article

Effect of ZrO_2 on Physiochemical Properties of SiO_2-Al_2O_3-CaO-MgO-ZnO Glass-ceramic System

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Abstract: In present study, monoclinic-ZrO_2 (m-ZrO_2) was used as a nucleating agent with SiO_2-Al_2O_3-CaO-MgO system, to evaluate microstructural change, crystallization tendency, mechanical and chemical properties of glass ceramics as a function of zirconia addition. It was found that zirconia not only helps in crystallization of glass ceramic but also improves mechanical properties of glass ceramic. With increase in concentration of ZrO_2 in the system the chemical durability of against acid and alkali and Vickers's hardness increases, 1.64% ZrO_2 showed superior chemical durability and mechanical strength. Therefore, the experimental results provided strong evidence that this material had all the potential properties to be used as building material, or as an engine component.

Keywords: Glass-ceramic, crystallization, nucleating agent, diopside, zirconia

1. INTRODUCTION

Glass-ceramics are fine-grained polycrystalline solids normally obtained by controlled crystallization (devitrification) of amorphous solids [1-5]. The bulk chemical composition of the crystalline phases and microstructure resulting from the nucleation and growth sequence are the key factors that influence the properties of the final material. Glass-ceramics find applications in various fields of aerospace, medical and nuclear industry [1, 6].

Glass-ceramics in the SiO_2-Al_2O_3-CaO-MgO system have been widely investigated for its various useful properties like low cost, superior mechanical strength, good chemical durability and excellent wear resistance. Diopside CaO-MgO-$2SiO_2$ crystalline phase generally precipitates in SiO_2-Al_2O_3-CaO-MgO system which has desirable mechanical strength that may also be machined to some extent [6-8]. Diopside ($CaMgSi_2O_6$) glass-ceramics are well known for their mechanical and electrical properties, i.e., high mechanical strength, low dielectric constant, high quality factor and low temperature sinterability [9]. From previous studies it is well known that pure form of zirconia has three different crystallographic forms; monoclinic, tetragonal and cubic. The monoclinic zirconia remains stable up to 1150 ^{o}C when it transforms to tetragonal symmetry. At temperatures above 2300 ^{o}C the cubic form exists. The transformation tetragonal-to-monoclinic phase change is of technological importance as this stress-induced martensitc phase transformation at crack tip makes the material resistant to crack propagation, which is accompanied by a volume expansion of about 4% of material [10-12]. Therefore, glass-ceramics having secondary phase of tetragonal zirconia is supposed to improve strength of material as it is well known

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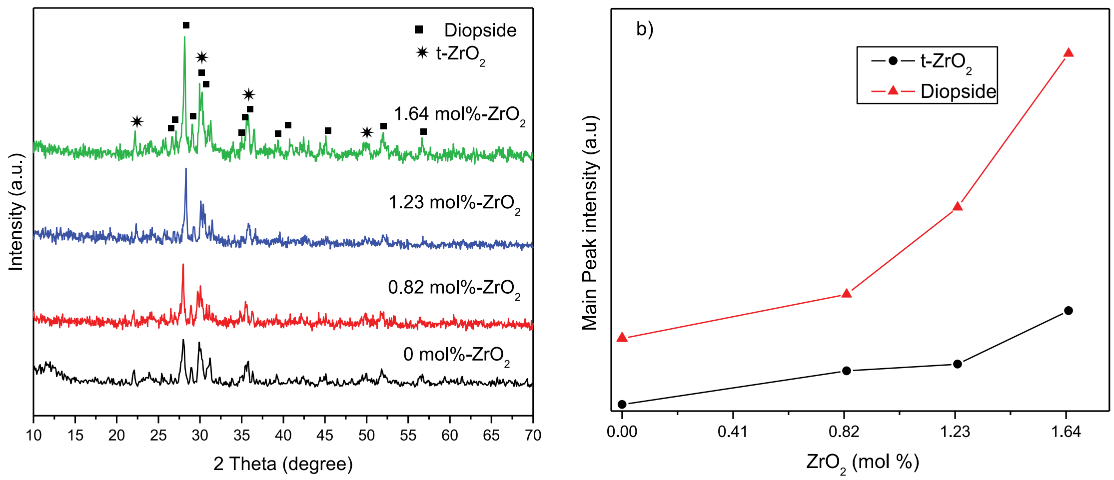

Fig. 1: (a) X-ray diffraction patterns of $CaMgSi_2O_6$ added with different amount of ZrO_2 after sintered at 1150 °C for 4 h; **(b)** Phase amount of $CaMgSi_2O_6$ and t-ZrO_2 in specimens at 1150 °C for 4 h.

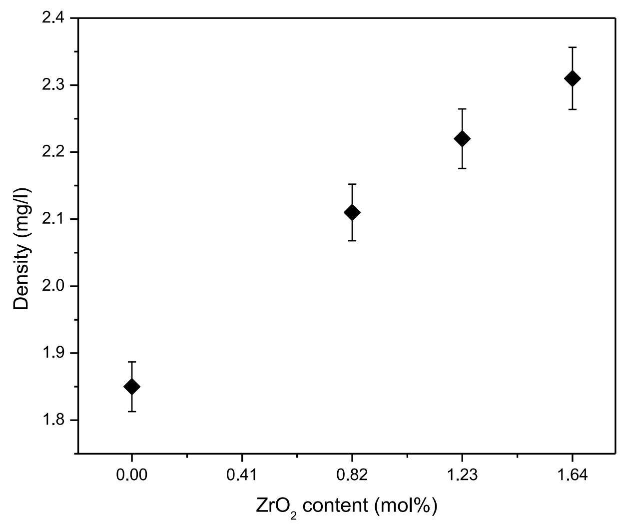

Fig. 2. The density of glass ceramic specimens sintered at 1150 °C for 2h as function of ZrO_2 concentration.

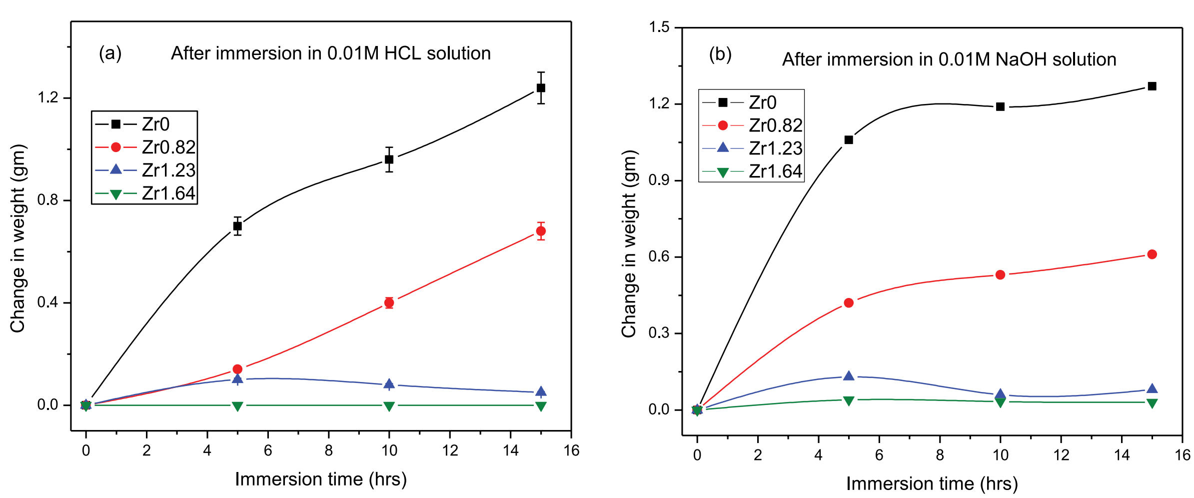

Fig. 3(a), 3(b): The chemical resistance against acid and alkali studied for various time intervals for all glass ceramic samples.

that addition of second strong phase can improve mechanical properties of material [7, 10, 13].

In present study, monoclinic-ZrO_2 was used with SiO_2-Al_2O_3-CaO-MgO system, to evaluate microstructural change, crystallization tendency, mechanical and chemical properties of glass ceramics as a function of zirconia addition.

2. EXPERIMENTAL PROCEDURE

Three batch mixtures in SiO_2-Al_2O_3-CaO-MgO-ZrO_2 system with nominal composition mentioned in Table 1 was prepared from reagent grade chemicals. A small amount of ZnO was also added to system which is known to enhance chemical durability and to provide gloss to the glass-ceramic [9]. Raw materials were weighed and thoroughly mixed for one hour. Premixed batches were melted in Pt crucible, using preheated muffle furnace (Model 5132 Lindberg, USA) at temperature range 1450-1500 °C for 2hrs and then poured in cold water to obtain transparent glass frits, which was then dried and milled with agate mortar and pestle. The glasses were pulverized to particle size ≤40μm. Pellets (15mm in diameter) used for crystallization experiment and test pieces (3 × 4 × 40 mm) used for property measurements were formed by uniaxial pressing at 56 MPa.

Glass batches were converted into ceramic derivatives by controlled crystallization in order to achieve the desired crystalline structure at significant growth rate [15]. The pellets were sintered at 1150 °C for 2h for crystallization. The crystal phases grown in samples were determined by X-ray diffraction (XRD) (Model Bruker D8 Discover, Germany) using CuKα radiation in 2θ range from 10° to 70° and average crystallite size was measured by the Scherer's formula:

$$t = (K\lambda)/(B\cos\theta)$$

The bulk densities of glass-ceramics were measured by the Archimedes method using water as buoyant. The micro-hardness of glass-ceramics was measured via Vickers indentation (SHIMADZU, Japan) with indentation of 9.8N for 15 sec using diamond indenter; three valid indentations (no evident cracks or other defects) were considered to calculate a mean value.

The chemical durability of the glass-ceramics against acidic and alkaline conditions were examined, and especially in acidic condition because these materials are considered to have potential application as building material or as an engine component where it has to face serious threats of leaching and weight loss due to exposure to acid rains (occur in many countries) and chemical reactions inside engine, so all glass ceramics were examined for 0.01M HCL and 0.01M NaOH solutions at room temperature for various time intervals as a function of weight and density gradient.

The microstructure of glass-ceramic samples were observed by SEM-EDX (microscope FEI-QUANTA-200) operated in scanning electron emission mode.

3. RESULTS AND DISCUSSION

The investigation of the glass-ceramic materials Zr0.82, Zr1.23 and Zr1.64 by X-ray diffraction analysis (Fig. 1(a)) revealed that diopside ($CaMgSi_2O_6$) as primary phase developed in all

Table 1. Nominal composition of batches in mol %.

Sample No.	Oxide Composition (mol %)					
	SiO_2	Al_2O_3	CaO	MgO	ZnO	ZrO_2
Zr0	48.64	7.5	31.36	9.0	3.5	0
Zr0.82	47.82	7.5	31.36	9.0	3.5	0.82
Zr1.23	46.59	7.5	31.36	9.0	3.5	1.23
Zr1.64	46.18	7.5	31.36	9.0	3.5	1.64

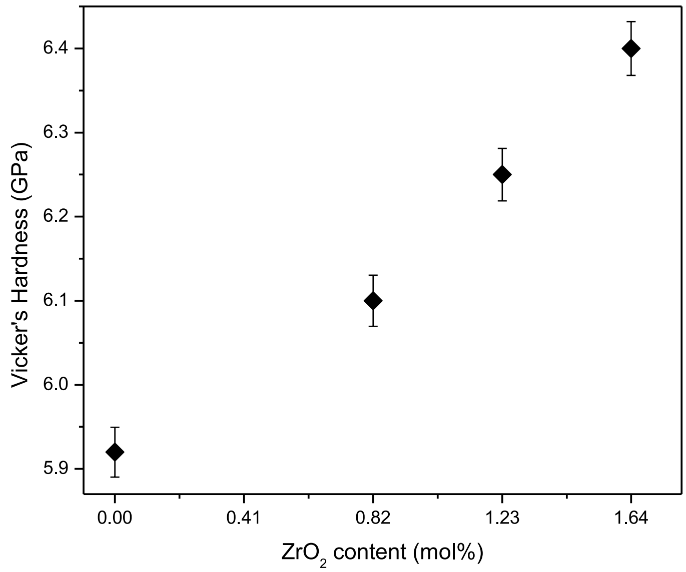

Fig. 4. Hardness of glass ceramic as function of zirconia content.

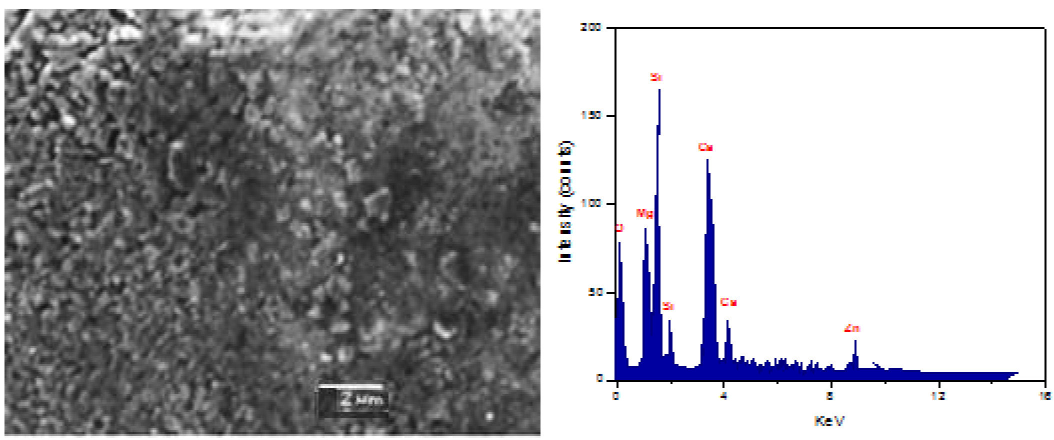

Fig. 5(a). SEM-EDX images of different magnification at Zr0.

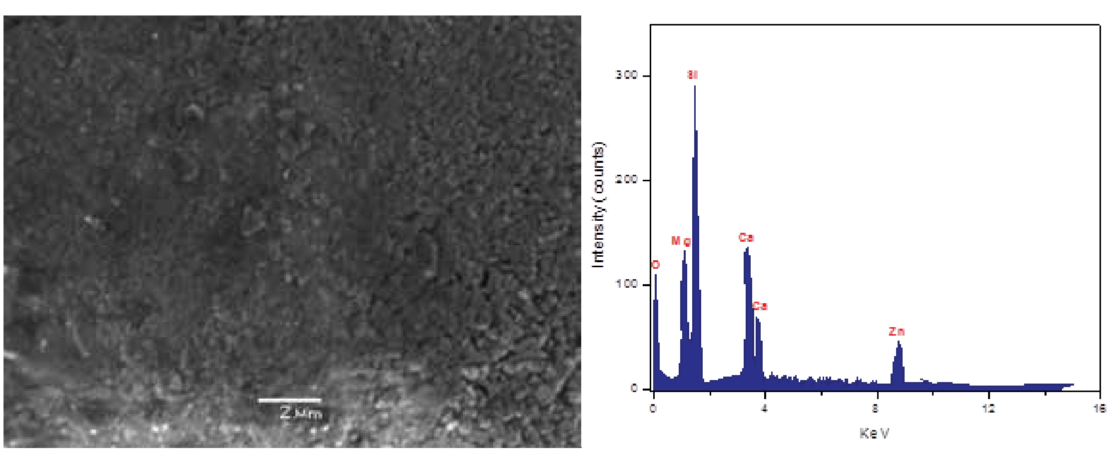

Fig. 5(b). SEM images of different magnification at Zr0.82.

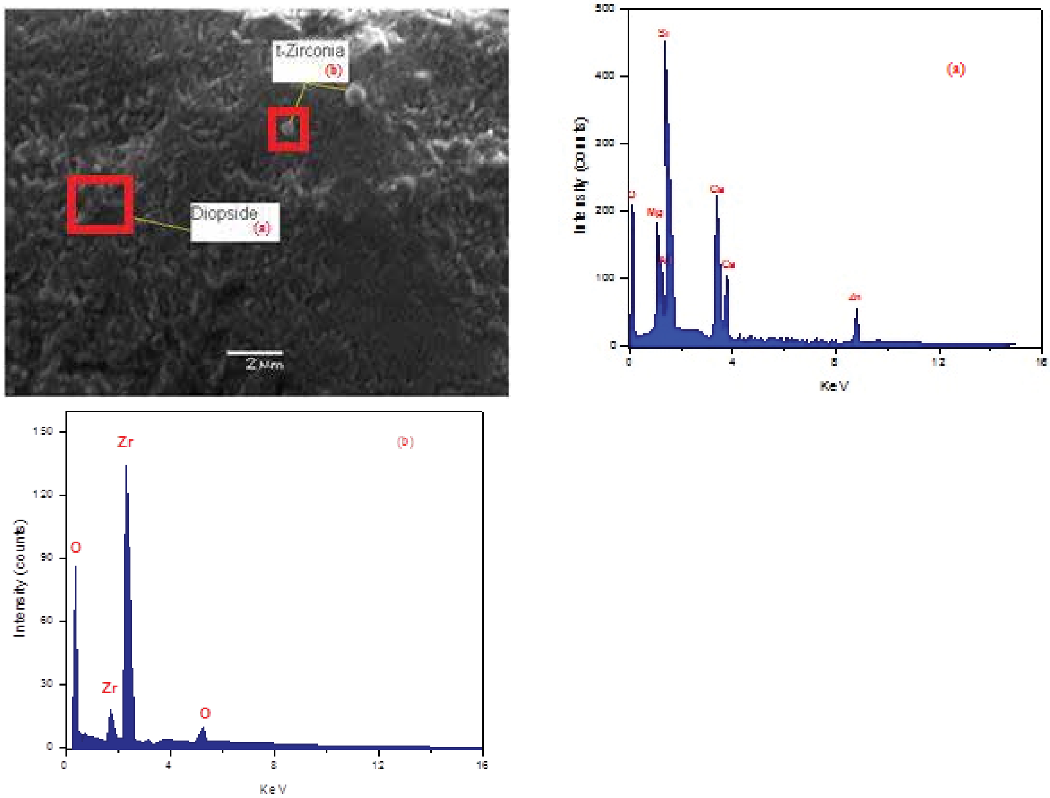

Fig. 5(c). SEM-EDX images of different magnification at Zr1.23.

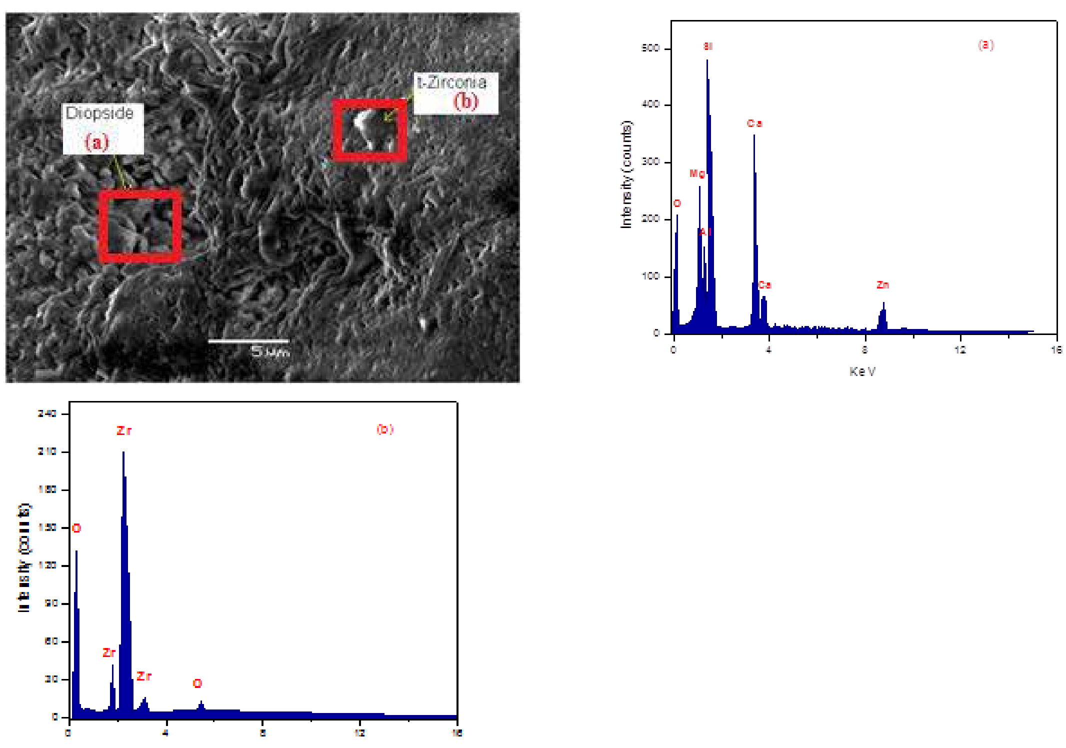

Fig. 5(d). SEM-EDX images of different magnification at Zr1.64.

glass ceramics and tetragonal-Zirconia (t-ZrO_2) was crystallized as secondary minor phase when glass was sintered at 1150 ^oC for 2 hours holding time. The phase intensity of diopside ($CaMgSi_2O_6$) increases by progressive increment of monoclinic-ZrO_2 (m-ZrO_2) concentration in the system therefore it was found that ZrO_2 stimulates crystallization. It may be understood as increasing ZrO_2 content in the system the peaks became sharper indicating more ordered crystalline structure of diopside phase. The amount of diopside phase increases illustrated by increase in peak intensity and amount of phase shown in (Fig. 1(b)), similar trend had been observed earlier by Feng et.al that Zirconia play a positive role in nucleating crystallization of diopside based glass ceramic [14]. The average crystallite size was ≈ 0.04117 µm (41.17 nm) measured by Scherer's formula.

The density of glass ceramics as a function of ZrO_2 concentration after sintering at 1150 ^oC was shown in (Fig. 2). However, a small change in densities of samples was observed which was therefore due to reduction in porosity during heat treatment process. It was also observed that reinforcement of t-ZrO_2 in diopside crystalline structure enhanced the densification of glass ceramics.

The chemical durability against 0.01M HCL and 0.01M NaOH solutions was found to improve with increase in concentration of ZrO_2 in the system illustrated by the change in weight of specimens after soaking in respective solutions shown in (Figure 3(a)), (Figure 3(b)) and Figure 3(c) respectively. This result indicated that addition of ZrO_2 to SiO_2-Al_2O_3-CaO-MgO system the provided it resistance against acidic and alkaline solution, as ZrO_2 is known to be good chemical stability [15].

The Vickers's hardness shown in (Fig. 4) was measured 5.92±1 GPa for Zr0, 6.1±2 GPa for Zr0.82, while Zr1.64 had 6.4±3 GPa, it show that secondary phase improved its mechanical properties. As it is well known that a small monoclinic-tetragonal (m-t) phase transformation would therefore play its role in enhancement of mechanical properties of glass ceramic [16].

Fig. 5(a), Fig. 5(b), Fig. 5(c) and Fig. 5(d) illustrate the SEM-EDX results of Zr0, Zr0.82, Zr1.23 and Zr1.64 ,respectively; it was found that with increase in the concentration of zirconia enhancement of crystal nucleation, grain growth in diopside phase and significantly reduction of porosity can clearly be identified in SEM images. The Zr1.64 glass ceramic can be seen more densified and grains of diopside also became enlarged. A few spherical shape grains of t-ZrO_2 were also visible in the SEM micrograph confirmed by the EDX spectra.

4. CONCLUSIONS

From our experimental results it was revealed that zirconia play stimulatory role in crystallization of glass ceramic in SiO_2-Al_2O_3-CaO-MgO-ZnO system. Zirconia not only enhanced densification process but also induced certain improved chemical and mechanical properties, which was therefore due to monoclinic to tetragonal (m-t) phase transformation of zirconia.

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