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Hussain, I, Barimah, EK, Iqbal, Y et al. (3 more authors) (2021) Mechanical and Optical Properties of ZrO_2 Doped Silicate Glass Ceramics. Silicon, 13 (3). pp. 877-883. ISSN 1876-990X

https://doi.org/10.1007/s12633-020-00516-z

Mechanical and Optical properties of ZrO_2 Doped Silicate Glass Ceramics

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Abstract

In the present study, we report the physical and optical properties of low-cost glass (soda-lime silicate glass) fabricated from local minerals, obtained from Hazara division Khyber Pakhtunkhwa, Pakistan. Zirconium dioxide (1-3 %) was added as a nucleating agent to investigate its effect on phase, density, hardness, and optical properties of soda-lime silicate glass. In the obtained glass-ceramic materials, the major crystalline phase was cristobalite. It was found that an increase in ZrO_2 content and heat treatment of the samples, resulted in an increase in bulk crystallization of the samples. The mechanical properties were found to be improved with ZrO_2 addition. The bandgap of the sample was in the range 3.78 – 4.09 eV.

Keywords: Silica sand; Zirconium oxide; Soda-lime silicate glass

1 Introduction

The physical and optical properties of a glass make it a technologically attractive material for engineers. Different types of glasses are available in market, amongst these; silicate glass is widely used in commercial applications. Glass is one of the most brittle materials known so far. These materials are very sensitive to flaws or cracks. The adverse mechanical failure of a glass is often attributed to its high degree of brittleness. By converting the glass into glass-ceramics, the resistance against crack propagation usually increases, but still these materials remain sensitive to flaws. The sensitivity of these flaws can be controlled by embedding crystals in the glassy matrix.

The glass ceramics formations in the soda-lime-silica [1-4] have been widely studied because of a) the relative cheaper raw materials required and b) volume crystal nucleation rate is high enough up to 97 % in these systems. Conventionally, a nucleating agent is added to the glass composition for nucleation of crystals within the bulk material, resulting in a large number of micro- or nano-sized crystals [5-7]. The conversion of glass to glass ceramics usually occurs in two steps [8]. In the first step, nucleating agent is precipitated and in the second step, the precipitated seed crystals are grown up to the desirable size. In silicate glasses, nucleating agents such as TiO_2, ZrO_2, or a mixture of both are known to lead to bulk nucleation [9, 10]. It has also been studied that by the addition of samarium ions in silicate glasses greatly improves transparency, resistivity and chemical inertness [11] and as a result, high-strength glass-ceramics were produced [12]. Several researchers [13-15] investigated the effect of various nucleating agents (TiO_2, CaF_2, P_2O_5, ZrO_2) on the properties of several glass systems and reported remarkable effects of nucleating agents on the mechanical, magnetic and optical properties of the resulting glass ceramics.

The goal of the work described in this article was to study the effect of ZrO_2 on the crystallization behavior, hardness and optical properties of sodium-silicate (Na_2O, CaO, and SiO_2) glass ceramics, using X-ray diffraction (XRD), Vicker's indenter and UV/Vis/NIR Spectrophotometer.

2 Experimental

Sodium silicate glasses were synthesized using silica sand obtained from Hazara division in Pakistan. The silica sand (source of SiO_2) powder was initially examined using X-ray fluorescence (XRF) to determine the percentage composition of each constituent element (Table 1). According to XRF results, the samples were divided into four batches with different concentration of ZrO_2 dopant (Table 2). 30 g batch of each composition was weighed and mixed thoroughly. The well-mixed powders were melted in Pt. crucible for 3 h in the temperature range of 1450-1550 °C. The molten glass was then poured into steel mold and properly annealed in a pre-heated furnace at 450 °C to remove internal stresses.

Table 1 XRF results of the used raw materials

Silica Sand		Limestone		Soda ash	
Elements	Wt. %	Elements	Wt. %	Elements	Wt. %
SiO_2	93.3472	CaO	93.9293	Na_2O	91.0133
Al_2O_3	5.4606	MgO	1.8082	SiO_2	4.7213
		SiO_2	1.7208	Al_2O_3	1.8344
		Na_2O	1.1214	Cl	1.4868
Others	<1	Others	<1	Others	<1

Table 2 Glass composition (wt. %) of the prepared glasses

Glass batch	Compositions							Additive
	SiO_2	Na_2O	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	ZrO_2
Z0	70.04	13.04	10.73	4.83	0.11	0.27	0.40	00
Z1	70.04	13.04	10.73	4.83	0.11	0.27	0.40	01
Z2	70.04	13.04	10.73	4.83	0.11	0.27	0.40	02
Z3	70.04	13.04	10.73	4.83	0.11	0.27	0.40	03

The densities of all samples were determined by Archimedes principle. The micro hardness of the investigated glasses was measured using a Vicker's micro hardness indenter (Wilson Tukon 1202 Knoop/ Vicker's tester, USA). The samples were cut using a slow speed diamond saw, then ground and polished using various grades diamond pastes to get the smooth and flat surface before indentation. The phase identification of quenched and heat-treated samples was performed by X-ray diffraction analysis (XRD) using a Phillips X'pert diffractometer (USA). UV/Vis/NIR Spectrophotometer (LAMBDA 950 PerkinElmer, USA) was used to measure the optical properties of the investigated samples.

3 Results and discussion

3.1 Phase analysis

The XRD patterns of as-quenched glass samples are shown in Fig.1. XRD pattern of sample Z0 comprised of a broad band peaked around 2θ = 23°, which demonstrated that this sample was amorphous. Furthermore, XRD patterns of samples Z1, Z2 and Z3 exhibit much small broad band as compared to sample Zo, which represent that these samples were mixtures of amorphous and nano-crystalline phases. The transformation of these glasses into glass ceramics could be ascribed to the incorporation of cristobalite nanocrystals in the glasses. Fig. 2 (a and b) shows the XRD patterns of glass ceramics heated at 850 and 950 °C for 3 h, respectively. Sample Z0 was only surface crystallized and the major crystalline phase was cristobalite. While in samples Z1, Z2 and Z3, the formation of zirconium oxide and zirconium silicate phases was also observed along with the cristobalite as a major phase. The XRD results indicate that these oxides have limited solubility in the glass and promoted heterogeneous nucleation.

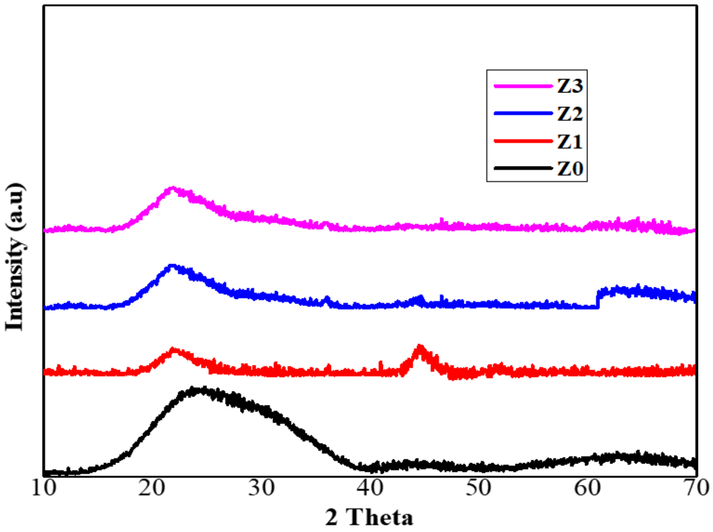

Fig. 1 XRD profiles of the glass samples showing the fully amorphous nature of Z0 sample and partially amorphous nature of Z1, Z2 and Z3 samples

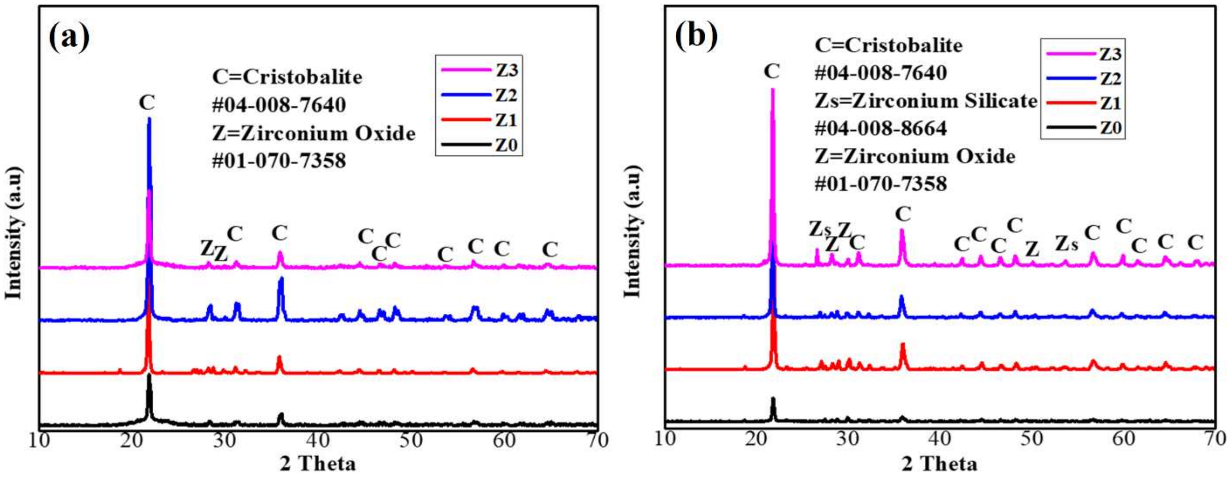

Figure 2. XRD profiles of the glass samples heat-treated at, a) 850 and b) 950 °C for 3h, showing the formation of the marked crystalline phases

3.2 Mechanical Properties

Density is an effective tool to explore the degree of structural compactness, modification of the geometrical configurations of the glass network, change in coordination and the variation of dimensions of the interstitial holes [16]. Vicker's hardness and the density of the zirconia doped silicate glasses as a function of the zirconia content before heat-treatment are shown in Fig. 3(a). Both the Vicker's hardness (Hv) and density (ρ) were found to increase with increasing ZrO_2 content [17]. The increase in hardness might be attributed to the formation of nanocrystals, evident from the broad XRD peaks. Fig. 3(b) shows the hardness and density of heat-treated zirconia doped silicate glasses. Hv was found to increase with heat treatment at higher temperature ($>T_g \sim 596$ °C); however, the dependence of hardness on the thermal history was more for the high zirconia contents. The thermal history has a positive impact on the hardness as appropriate heat treatment leads to the formation of crystalline phases in the parent glass samples [18]. As confirmed by XRD (Fig 2), cristobalite stable phase was formed as a result of heat treatment of the studied samples. Besides, the observed cristobalite phase formed in the zirconia doped glass samples, the observed increase in the hardness of the samples may be due to increasing zirconia content and heat treatment. It was also found from the fracture toughness data, that the toughness of the samples increased, and brittleness decreased with increasing ZrO_2 content. This might be due to the crystalline phase formation in the glass samples which oppose the crack propagation.

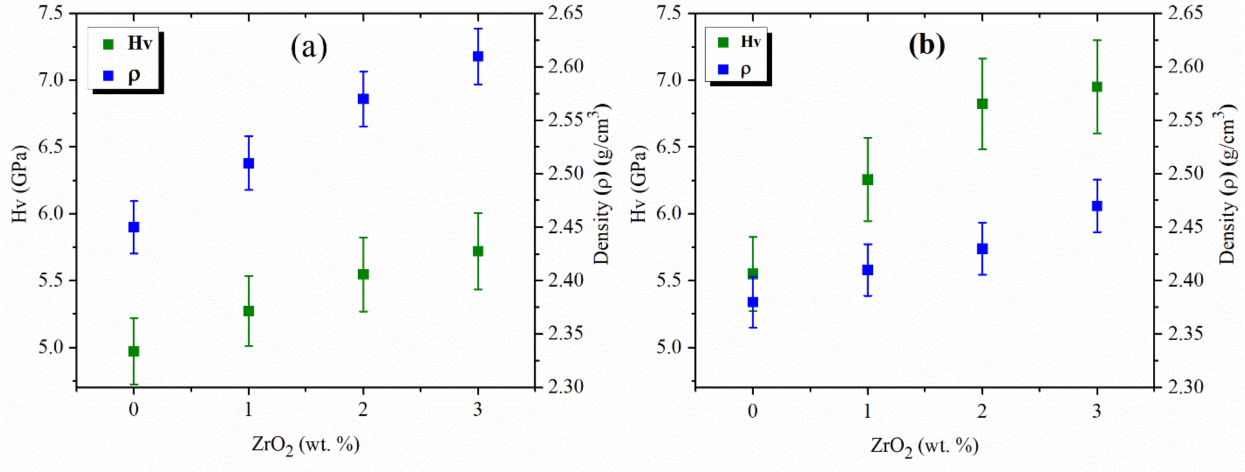

Fig. 3 Glass samples density (ρ) and hardness (Hv) as a function of ZrO_2 content a) before heat treatment and b) after heat treatment

Using the dimensions of the radial cracks, K_{IC} values were then calculated using the relationship given by Evans and Charles [19]

$$K_{IC} = 0.16 \times H_V \times \sqrt{a}\left(\frac{c}{a}\right)^{-3/2} \text{------(1)}$$

In the above equation *c* and *a* are the characteristic crack length and Vickers indentation diagonal length, respectively and Hv is the Vickers hardness. This has been shown to give results more consistent with conventional fracture toughness tests than other suggested relationships [20]. Brittleness values were calculated from the measured H_V and K_{Ic} values using

$$B = \frac{H_V}{K_{IC}} = \frac{22.505 C^{3/2}}{d^2} ------(2)$$

The calculated values of hardness, fracture toughness and brittleness of the samples before heat treatment and after heat treatment are given in Table 3.

Table 3 Fracture toughness and brittleness of ZrO_2 doped glasses (before heat treatment and after heat treatment) derived from Vicker's hardness data

Glasses (before heat treatment)				
Samples	Properties			
	Density (ρ) (g/cm^3) ± 0.01	Hardness (Hv) (GPa) ± 0.05	Fracture toughness (K_{Ic}) (MPam$^{1/2}$) ± 0.02	Brittleness (B) (μm$^{-1/2}$) ± 0.01
Z0	2.45	4.97	0.63	7.88
Z1	2.51	5.27	0.71	7.42
Z2	2.57	5.45	0.95	5.74
Z3	2.61	5.72	1.07	5.35
Glass-ceramics (after heat treatment)				
Samples	Properties			
	Density (ρ) (g/cm^3) ± 0.001	Hardness (Hv) (GPa) ± 0.05	Fracture toughness (K_{Ic}) (MPam$^{1/2}$) ± 0.02	Brittleness (B) (μm$^{-1/2}$) ± 0.01
Z0	2.38	5.55	0.69	7.99
Z1	2.41	6.26	1.02	6.13
Z2	2.43	6.82	1.46	4.66
Z3	2.57	6.95	1.71	4.05

Fig. 4 shows the micrographs of the indents made at 9.8 N loads on the heat treated zirconia doped sodium silicate glass samples. These indents show radial cracking along the diagonals, showing no shear banding or cracking .The fabricated sodium silicate glass had a brittleness of 5.35 ± 0.01 μm$^{-1/2}$ which decreased to 4.05 ± 0.01 μm$^{-1/2}$ after heat treatment. While the commercial soda-lime silica glass has a brittleness of 7.1 ± 0.1 μm$^{-1/2}$ and other commercial alkali-silicate systems glasses have brittleness in the range of 6-10 μm$^{-1/2}$. The properties of glasses and glass ceramics are summarized in Table 3.

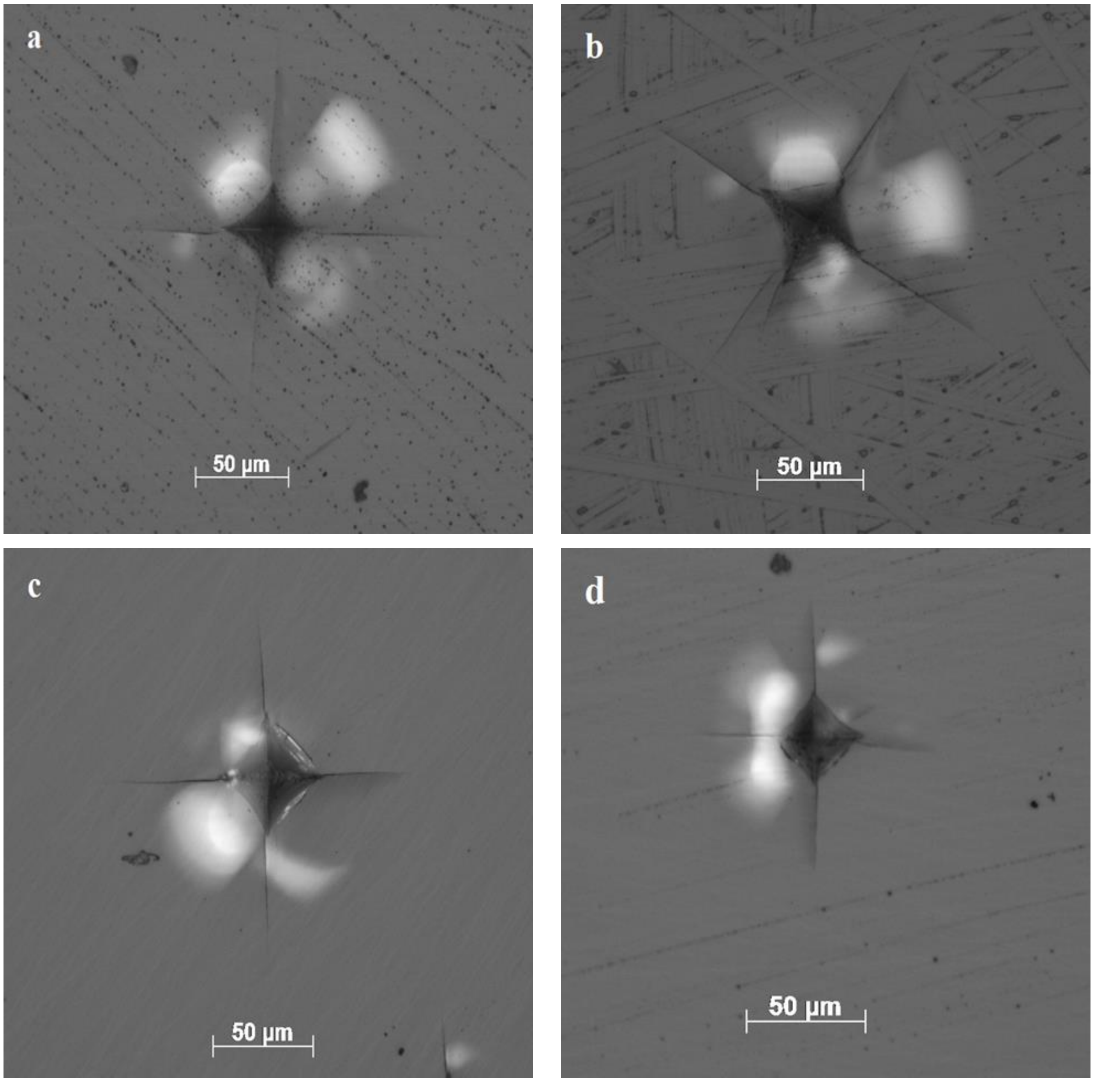

Fig. 4 Optical micrographs of micro hardness indentations of the samples, (a) Z0, (b) Z1, (c) Z2 and (d) Z3. These indents show radial cracking along its diagonals

3.3 Optical absorption and energy band gap (Eg)

The UV-Vis transmission spectra (in wavelength interval 250-1500 nm) of un-doped and ZrO_2 doped soda-lime silicate glasses before heat treatment are shown in Fig.5. The spectra show a good transmission around ~ 80 % for un-doped sample. As ZrO_2 was doped up to 1 to 3 wt. %, the transmission was observed to decrease slightly [21] as depicted in the Fig. 5.

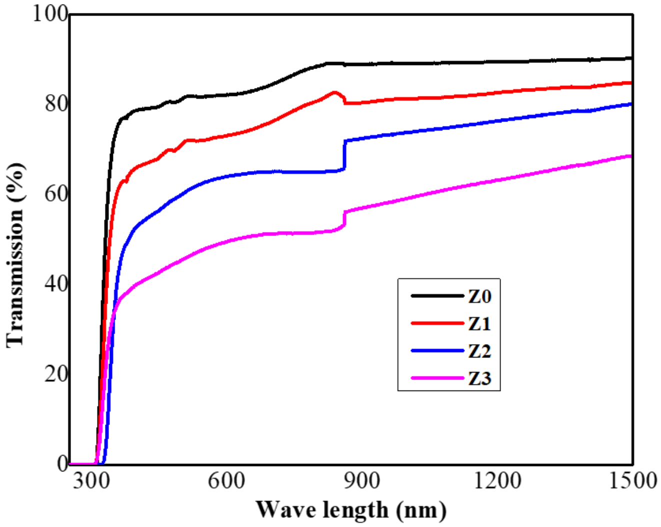

Fig. 5 UV-Vis spectra of the ZrO_2 doped glasses, a decrease in transmission with increasing ZrO_2 content.

Figure 6 shows the typical absorption spectra and energy band gaps of the zirconia doped soda-lime silicate glasses. The absorption coefficient, $a(v)$, was determined near the absorption edge, at different photon energies for all the investigated glass samples. The quantity, $\alpha(n)$, can be displayed in several ways as described by the relation (3)

$$\alpha(v) = \frac{B\left(hv - E_g\right)^n}{hv} \text{-------} (3)$$

where B is a constant and Eg is the optical band gap energy. The index, n, can have any value between 0.5 and 3 depending on the nature of the inter-band electronic transitions [22]. It has been observed that for all amorphous materials, the measured absorption fits well to the above Eq. (3) for $n = 2$. Table 4 indicates that the optical energy band gap decreases with an increase in ZrO_2 from 1-3 wt. % in both types of samples i.e. before heat treatment and after heat treatment. The drop of E_g may be due to the variation of density as well as the variation in the number of non-bridging oxygen's (NBO).

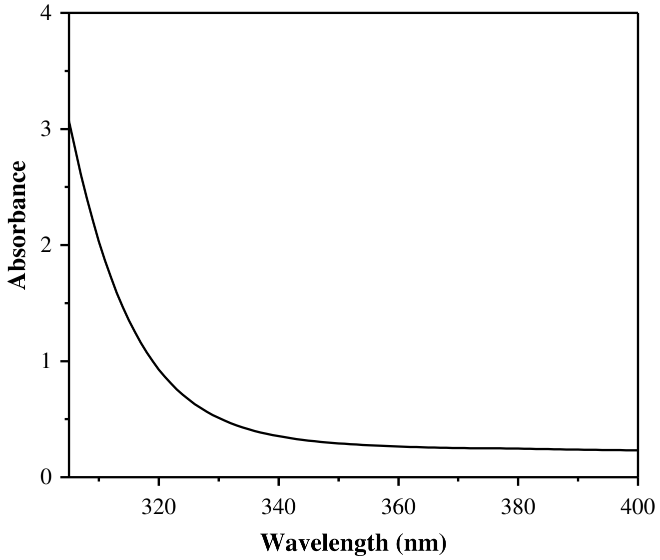

Fig. 6 Optical absorption spectra of ZrO_2 (3 %) doped sodium silicate glass

Refractive index of zirconia doped glasses was calculated using the relation (4)

$$\frac{n^2-1}{n^2+2}=1-\sqrt{E_g/20}\;------(4)$$

Refractive index (*n*) depends upon the composition of an optical material and on the polarizability of the material. In brief, the more polarizable the outer electrons are, the higher the refractive index. As given in Table 4, the refractive index increased with increasing concentration of ZrO_2 content. The addition of ZrO_2 content acts as a network modifier, which forms non-bridging oxygen (NBO) bonds. The NBO bonds have higher polarizability and as a result the refractive index increases [23]. The observed decrease in refractive index of heat-treated samples might be due to the formation of crystalline phases in the parent glass samples, which decreases polarizability [24].

Table 4 Density, optical energy band gap and refractive index of the zirconia doped samples before and after heat treatment

Samples	Samples (before heat treatment)		Samples after heat treatment		
	Energy band gap (E_g)	Refractive index (n)	Energy band gap (E_g)	Refractive index (n)	Density (ρ) (g/cm^3)
Z0	3.97	2.176	3.79	2.212	2.38
Z1	3.86	2.197	4.09	2.153	2.41
Z2	3.85	2.199	3.78	2.214	2.43
Z3	3.84	2.201	3.97	2.176	2.57

4 Conclusion

Different batches of low-cost soda-lime silicate glass were prepared using locally available raw materials. The base glass was modified by doping with various (1-3 wt. %) concentrations of the nucleating agent ZrO_2. The effect of nucleating agent and heat treatment on the crystallization and mechanical properties on the parent glass and its ceramics was investigated. XRD of the parent glass revealed the presence of cristobalite (SiO_2) as the main crystalline phase. The cristobalite, zirconium oxide and zirconium silicate phases were observed in heat treated glass samples doped with ZrO_2 as a nucleating agent. The peak intensities of the formed phases increased with heat treatment temperatures which demonstrated an increase in the crystallinity of the samples. Various analyses conducted on the as-quenched and heat treated samples revealed net increase in hardness. The refractive indices were also found to increase with the addition of nucleating agents. This study shows that the transmittance as well as the energy band gap of the samples decreased by converting the parent glasses into glass ceramics.

Acknowledgment

The author (Imtiaz Hussain) acknowledges the Higher Education Commission of Pakistan for the award of research fellowship under the International Research Support Initiative Program (IRSIP) at the University of Leeds, UK.

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