

EVALUATION OF THERMAL AND MECHANICAL PROPERTIES OF $\text{ZnSO}_4\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Ho}_2\text{O}_3$ GLASS-CERAMICSAreej S. Alqarni^{a,*} and Ibrahim Bulus^b^aDepartment of Physics, College of Science, Princess Nourah Bint Abdulrahman University, P.O. Box 84428, 11671 Riyadh, Saudi Arabia^bDepartment of Physics, Kaduna State College of Education Gidan waya, P.O. Box 1024, Kafanchan, Nigeria

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In this study, a novel glass-ceramic (GC) obtained from $\text{ZnSO}_4\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Ho}_2\text{O}_3$ composition, coded as H0.0, H0.5 and H0.8, was synthesized via molten-solidified approach. The effect of varying content of Ho_2O_3 from 0.5 to 0.8 mol% on thermal and mechanical properties of the prepared GC were experimentally and theoretically scrutinized. The attained results showed that inclusion of Ho_2O_3 content amplified crystallite size from 42.3 to 50.5 nm. Besides, the values of elastic moduli (Young's, bulk, shear and longitudinal) computed via Makishima-Mackenzie's (MM) model were slightly augmented. Finally, the decent value of thermal stability ($> 150^\circ\text{C}$) and high fracture toughness of $> 20000\text{ MPa mm}^{1/2}$ achieved for the newly fabricated GC may be applicable in protective covers of portable electronics.

Keywords: $\text{ZnSO}_4\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Ho}_2\text{O}_3$ glass-ceramic; holmium ion effect; thermal properties; mechanical properties.

INTRODUCTION

Glass-ceramics (GC) with high hardness, reasonable Young's modulus, boosted fracture toughness and coupled with a suitable thermal stability are of great significance in modern optical displays systems.¹⁻³ Categorically, these materials by virtue of their strong resistance to scratching and sharp contact damage find manifold applications in the protective layer of various portable electronics like smartphones, laptops, tablets, wearable devices, and radiation shielding applications.^{4,5} Although, glass-ceramics depend on multiple factors namely, chemical composition, crystallinity, thermal history, kinetics, phase composition, and additives.⁶ The mechanical evolution of brittle materials depends on internal micromechanical stresses, which occur upon cooling due to the elastic and thermal mismatch between the constituent phases.⁷

Over the past decades, several competing glass-ceramics have been developed and reported by renowned scholars for diverse practical usage wherein lithium disilicates (LDs) remains the topmost and commercially available glass-ceramics for dental implants and bone regeneration.^{8,9} Besides, synthesis and characterization of iron phosphate-based glass-ceramic for potential utilization in nuclear waste immobilization was performed and testified by Wang *et al.*¹⁰ Thereafter, microstructure and phase composition dependent microwave dielectric properties of borophosphate GC has been examined by Jiang *et al.*¹¹ These GC's were commendable for low temperature co-fired ceramics (LTCC) application. However, the status of crystalline phases, thermal, magnetic, and density of $\text{ZnO-SrO-B}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-P}_2\text{O}_5$ glass-ceramics due to SrO and ZnO substitutions was analyzed.¹² In 2021, the structural analysis of multicomponent borophosphate glass ceramic was accomplished by Haily *et al.*¹² Further, Węgrzyk *et al.*¹³ had achieved and publicized high mechanical strength ZABS ($\text{ZnO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$) glass ceramics system routed with transition metal ions. Besides, a comprehensive analysis on structural, mechanical, gamma, and neutron attenuation characteristics of $\text{B}_2\text{O}_3\text{-PbO-TeO}_2\text{-CeO}_2\text{-WO}_3$

glasses was conducted by Solak *et al.*¹⁴ Very recently, Acikgoz *et al.*¹⁵ examined the influence of praseodymium oxide on the structural, mechanical and photon, charged particles, and neutron shielding properties of alumina borate glass.

Above and beyond, it has been well established that the thermo-mechanical evolution of GC materials can be promoted by introducing rare earth ions (REI's) impurities. This assertion is attributed to the strengthening and toughening potential of REI's as well as the purifying effect on the interface between grains and the effective solution.¹⁶ Ho_2O_3 , among the 17 rare earth ions, are famous for their light emitting characteristic owing to its several high excited energy levels over the visible spectral region responsible for the intense visible emissions.¹⁷ On this claim, Ho was chosen in this study, aiming at achieving cheap, tiny, efficient and safe glass-ceramic host. As reported in Gupta *et al.*,¹⁸ Ho_2O_3 is commonly used as additive and supporting mediator in structural glass-ceramics. Specifically, it is more significant that the ions has profound impact on the dielectric, optical, thermal and mechanical properties of glass ceramics. In fact, small amount of these ions can significantly affect the microstructural morphology as well as thermo-mechanical properties of glass-ceramics. Moreover, incorporation of Ho_2O_3 greatly enriched durability, glass transformation temperatures (T_g), low electrical conductivity and thermal expansion coefficients in borophosphate glass ceramics.¹⁹

Encouraged by the aforementioned facts, the aim of the present work is to synthesize Ho^{3+} -doped novel $\text{P}_2\text{O}_5\text{-B}_2\text{O}_3\text{-ZnSO}_4$ -based glass-ceramic by molten and solidified process. Borate (B_2O_3) and phosphate (P_2O_5) are chosen as exciting hosts because borate possess precious thermal strength, lower melting point, massive RE^{3+} solubility, and excellent transparency. Meanwhile, high gain, low dispersion, and comparatively higher refractive indices are the added advantages from phosphate which enables it to decolorize the borate flint units.²⁰ Besides, the existence of ZnSO_4 in $\text{P}_2\text{O}_5\text{-B}_2\text{O}_3$ glass-ceramic network enhance it physical, structural and optical performance.²¹ With this insight, herein, the effects of substituting P_2O_5 by Ho_2O_3 on the thermo-mechanical properties of the $\text{P}_2\text{O}_5\text{-B}_2\text{O}_3\text{-ZnSO}_4$ -based glass-ceramic was investigated. The overall outcomes of the present investigation established high

*e-mail: arsalqarni@pnu.edu.sa

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values of microhardness, Young's modulus, fracture toughness and good thermal stability. From the aforementioned achievement, the conceptual design and customization of present glass ceramics in developing protective covers for electronic displays on smartphones and wearable devices can be extended.

EXPERIMENTAL

Synthesis of glass-ceramic samples

The raw materials of high purity (99.999%) analytical grade reagents, ZnSO_4 , B_2O_3 , H_3PO_4 , and pure Ho_2O_3 (99.999%) were used in the fabrication of new glass ceramics (GC) with a well-defined stoichiometric compositions of $(40-x)\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3-30\text{ZnSO}_4-x\text{Ho}_2\text{O}_3$ (with $x = 0.0, 0.5$, and 0.8 mol%) coded as H0.0, H0.5 and H0.8. These GC with constituent's batch of 20 g each were made via melting-solidified approach. The resultant mixture of the compositions was gradually preheated at low temperature (300°C) for 30 min before being transferred to another furnace for complete melting at 1300°C for 90 min. Succeeding, the molten was poured on a warmed stainless-steel plate and solidified at 300°C for 2 h. To conclude, the obtained samples were kept in furnace and logically cool down to room temperature. Finally, samples were stored in a moisture free environment at room temperature. Some portions of the as-quenched samples were crushed into fine powder for structural and thermal analyses. Table 1 shows the sample compositions alongside the sample's codes. Additionally, the thermal history and photograph for the synthesized samples (with ~ 2 cm diameter) is presented in Figure 1.

Table 1. Glass-ceramics code and compositions

Sample code	Composition / mol%				Density / (g cm^{-3})
	ZnSO_4	B_2O_3	P_2O_5	Ho_2O_3	
H0.0	30	30	40	0.0	2.79
H0.5	30	30	39.5	0.5	2.85
H0.8	30	30	39.2	0.8	2.89

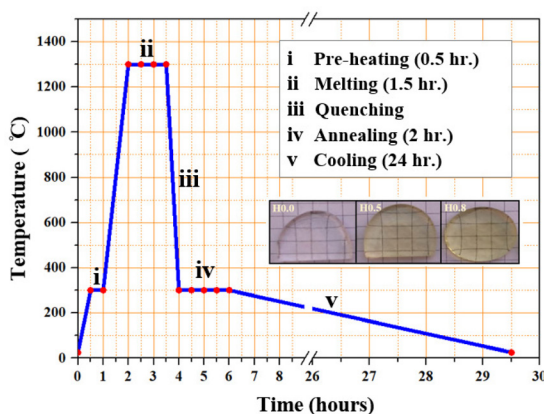


Figure 1. Thermal history and photograph for the synthesized samples

Characterisation of the synthesized glass-ceramics

By employing X-ray diffractometer (SmartLab Rigaku) equipped with $\text{Cu-K}\alpha$ (wavelength $\approx 1.5406 \text{ \AA}$) radiation, the microstructure status of our fabricated GC was exposed. This was conducted by logging the data in the angular range (2θ) from 10° to 80° with a step size of 0.02° . Additionally, the integrated EDX (energy-dispersive X-ray spectroscopy) in field-emission scanning

electron microscope (FE-SEM) was used for microstructure analysis. In addition, the thermal stability potency of GC was verified by differential thermogravimetry analysis (DTA). This was piloted by using thermal analyzer (HITACHI STA7200 model) at a heating rate of $10^\circ \text{ min}^{-1}$ within nitrogen atmosphere. Last but not the least, the microhardness measurement was carried out by using digital microhardness tester of Shimadzu HVM-2 model at room temperature. Particularly, 100 g load was applied for a peak-load time of 10 s, and the diagonals of indentation were measured with an accuracy of ± 0.11 m. Afterwards, the Vickers microhardness values was deduced as an average of 10 readings collected from different position of the sample surface.

RESULTS AND DISCUSSION

Structural properties

The XRD (X-ray diffraction) pattern of the as-produced H0.8 sample is epitomized in Figure 2. The obvious wide diffraction halo around $20-40^\circ$ endorse the amorphous nature of the present samples. In addition, a little diffraction peak noted at 27.84° was due to the reflection from the (310) lattice plane of B_2O_3 (based on ICDD card number 000060297), confirming the formation of the glass-ceramic phase. This peak was further analyzed and well fitted by using Gaussian function for all samples. The consequential fits are presented in Figures 3a, 3b and 3c, respectively. Evident from the said Figures together with Figure 3d affirmed that the crystallite size amplified from 40.30 to 50.00 nm and congruently strain decreased from 0.036 to 0.030 with increasing content of Ho^{3+} ions. The augmentation in the FWHM (full width at half maximum) and crystallinity stature of our GC originated from the quantum size effect. This remark is indeed consistent with the similar findings reported in Alqarni *et al.*⁴ and Gao *et al.*²² The enhanced crystallite size revealed an enhancement in the arrangement of atoms in the GC matrix with the replacement of phosphorus by holmium. This also indicated the formation of more bridging oxygens in the GC network.

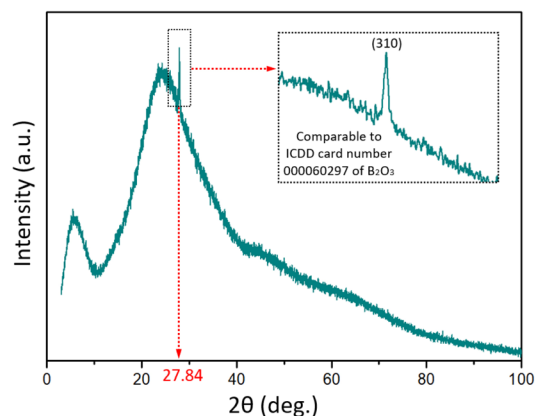


Figure 2. XRD patterns of the synthesised samples

To validate the structural and elemental analysis of our produced glass-ceramics, the typical EDX plot of all samples is shown in Figure 4. An inset unveiled the corresponding EDX images. The EDX scrutiny attests that the elemental constituents harmonized with the initial stoichiometry during the fabrication process. Figure 5 shows the EDX oxygen spectra for H0.0, H0.5 and H0.8 samples. The intensity of the oxygen spectra decreased with the increase of Ho^{3+} which implied lack of non-bridging oxygen participation due to the formation of more bridging oxygen. This finding is in good agreement with the enhanced crystallite size revealed by XRD.

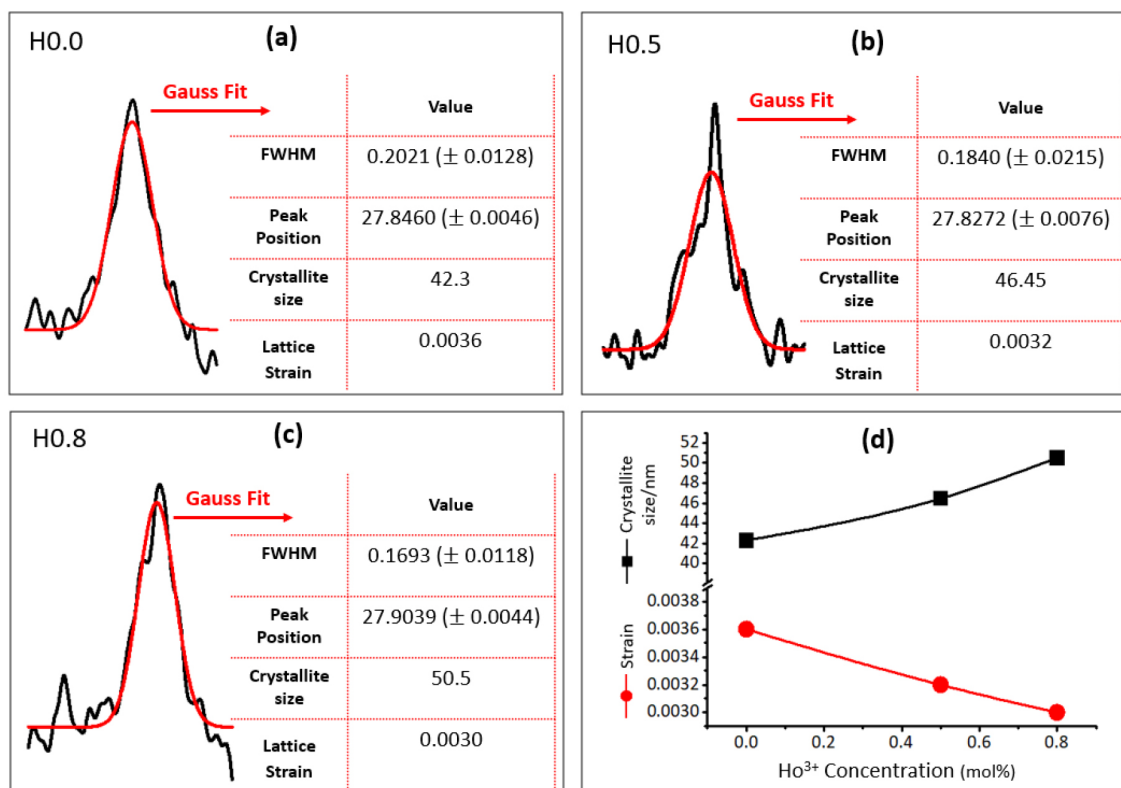


Figure 3. (a-c) XRD peak analysis; (d) crystallite size and lattice strain of the prepared glass-ceramics

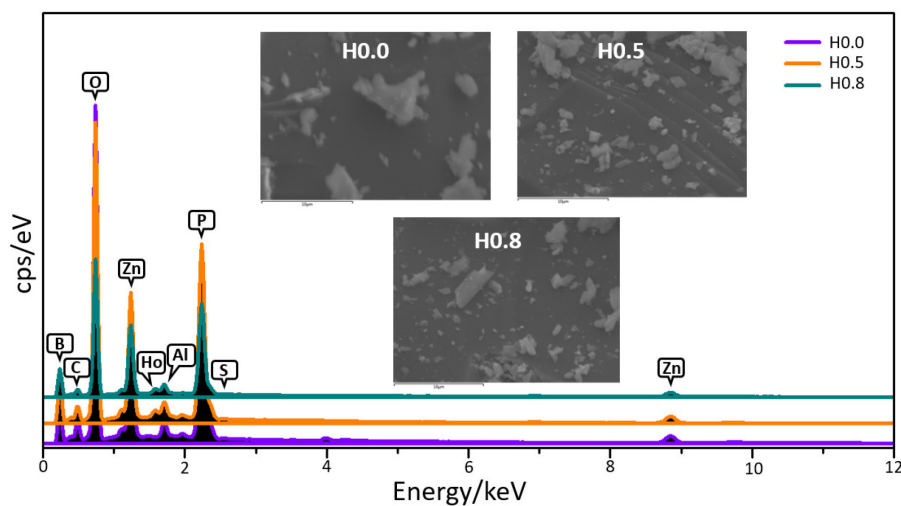


Figure 4. EDX spectra of the synthesised glass-ceramics. Insets are EDX images

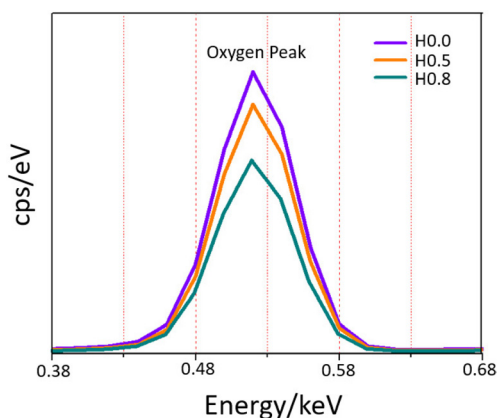


Figure 5. EDX oxygen spectra of the studied glass-ceramics

Thermal scrutiny of as-synthesized GC

Typically, DTA or DSC results exposed both melting and recrystallization peaks of materials.²³ Therefore, the thermal entities of present glass-ceramics were acquired by DTA thermograms and the attained results are presented in Figure 6. Evidently, the Figure 6 revealed relatively dip curve above 600 °C terming crystallization temperature (T_c). The onset crystallization temperature is denoted by T_x and transition temperature is marked as T_g (T_{g1} and T_{g2}). The melting temperatures (T_m) of the glass-ceramics was also ascertained from the DTA plot. Instantaneously, these parameters (T_{g1} , T_{g2} , T_x , T_m) together with thermal stability (S) evaluated by using the given the following expressions previously employed elsewhere²⁴ and the attained data are tabulated in Table 2. Standard deviation was ± 1 °C for all data.

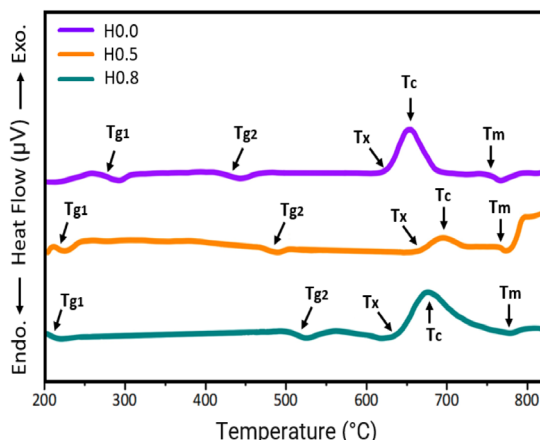


Figure 6. DTA thermograms of the synthesised glass-ceramics

$$\text{Thermal stability, } S = T_c - T_{g2} \quad (1)$$

The stability capability of the present glass-ceramics was further computed by employing the following thermal models:²⁹

$$\text{(I) Hruby's model, } H_R = \frac{T_x - T_{g2}}{T_m - T_x} \quad (2)$$

$$\text{(II) Weinberg model, } K_w = \frac{T_c - T_{g2}}{T_m} \quad (3)$$

$$\text{(III) Lu and Liu model, } K_{LL} = \frac{T_c}{(2T_x - T_{g2})^{T_m}} \quad (4)$$

$$\text{(IV) Du model, } \gamma_m = \frac{(2T_x - T_{g2})^{T_m}}{T_m} \quad (5)$$

An inclusive result attained herein were compiled in Table 2 and presented in Figure 7, and also validated through a suitable comparison with those obtained for other phosphate and borate-based glasses. The occurrence of two T_g 's in this study implied that the samples have two structural phases.³⁰ Assertively, T_{g2} value was in the range of the T_g for many phosphate glass systems,³¹⁻³³ while T_{g1} corresponds to the other phase present in the sample. It was found that the value of T_{g2} increased with the increase of Ho^{3+} in good agreement with other analysis in the manuscript. However, the T_{g1} values were relatively very low and reduced with the increase of Ho^{3+} . This revelation is common in many plastics, polymers (network structure

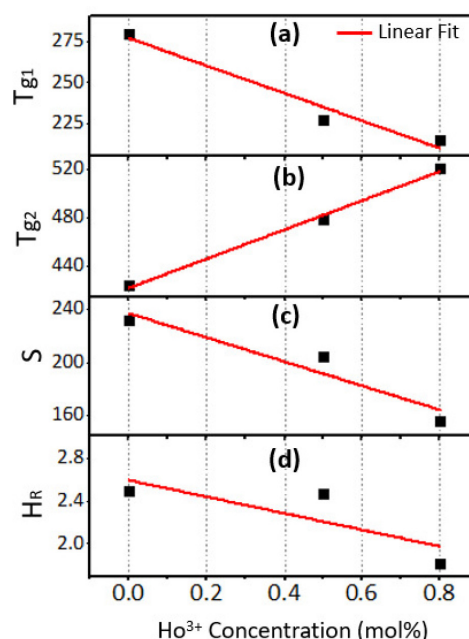


Figure 7. Correlation between selected thermal quantities (T_{g1} , T_{g2} , S , H_R) and various concentrations of Ho ions

like ceramic-glass) which are partially crystalline: they, therefore, have a glass transition temperature below which the amorphous phase freezes (somewhat lower due to partial crystallinity). Indeed, it is also an indication of enhancing the crystallinity of the crystalline areas inside the glass-ceramic network. The behavior of T_{g1} , and also hardness H_v result from a structural changes of the glass-ceramic network with probably the presence of small crystallites B_2O_3 .³⁴

In this study, a decline in T_{g1} value was observed with the consecutive addition of Ho^{3+} content. This may be attributed to the disparity in bond enthalpy values. Replacement of P–O having high bond enthalpy value with HO–O molecules possessing low bond enthalpy value reduced T_{g1} value. Meanwhile, both T_{g2} , T_c , T_m and T_x values increase simultaneously. However, according to the golden rule of calorimetry, the value of the thermal stability must be greater or equal to 100 °C.³⁵ Undeniably, our produced glass ceramics divulged better values of S ranging from 236 to 156 °C which is obviously > 100 °C. Besides, holmium ions free sample coded H0.0 disclosed higher value of S than the H0.5 and H0.8 samples. This implied that

Table 2. The comparison of the results obtained by DTA thermograms of the titled glass-ceramics (GC) with other reported system

Characteristics temperature (± 1 °C)	Our produced borophosphate GC			Reported data			
	H0.0	H0.5	H0.8	Phosphate-based		Borate-based	
				Ferrea <i>et al.</i> ²⁵	Goj <i>et al.</i> ²⁶	Subhashini <i>et al.</i> ²⁷	Shaan <i>et al.</i> ²⁸
T_{g1}	280	227	215	–	–	54	–
T_{g2}	424	478	521	577	763	421	401
T_x	621	651	636	760	–	487	–
T_c	656	683	677	721	853	–	455
T_m	749	766	763	893	1063	545	–
$T_m - T_c$	93	83	86	–	–	–	47
S	232	205	156	144	–	64	54
H_R	2.50	2.47	1.81	9.73	0.47	–	6.33
K_w	0.31	0.27	0.20	–	–	–	–
K_{LL}	0.56	0.55	0.53	–	–	–	–
γ_m	1.09	1.08	0.98	–	–	–	–

T_{g1} , T_{g2} : transition temperatures; T_x : onset crystallization temperature; T_c : crystallization temperature; T_m : melting temperature; S : thermal stability; H_R : Hruby's model stability capability; K_w : Weinberg model stability capability; K_{LL} : Lu and Liu model stability capability; γ_m : Du model stability capability.

H0.0 glass ceramic is more stable than its counterpart. The present findings harmonized with existing calorimetry parameters on other glass and glass-ceramics systems presented in Table 2. Apart from the S feature, the glass ceramic stability potential was further verified through Hruby's, Weinber, Liu and Liu as well as Du models and achieved data are listed in Table 2. Apparently, the thermal stability values evaluated via the aforementioned models are found to be less 3 which further assert good thermal stability of our investigated glass ceramics.

Mechanical properties

The microhardness of as-produced glass-ceramics was ascertained by using micro indentation hardness testing systems. Following the standard procedure earlier described in the Experimental section together with an in-depth protocol reported in the literature,^{36,37} the hardness value was deduced by employing the following classic equation of Vickers geometry:

$$H_V = \frac{1.8544P}{d^2} \quad (6)$$

where H_V is the Vickers hardness number in kg mm^{-2} , P is the normal load in kg, and d is the average diagonal length of the indentation in mm. Furthermore, other impressive mechanical derivatives including Young modulus (E), yield strength (Y), fracture toughness (K_{IC}) and brittleness index (BI) were also calculated as follows:

$$E = 81.9635H_V \quad (7)$$

$$Y = \frac{H_V}{3} \quad (8)$$

$$K_{IC} = 0.016 \sqrt{\frac{E}{H_V}} \left(\frac{P}{C^{3/2}} \right) \quad (9)$$

$$BI = \frac{H_V}{K_{IC}} \quad (10)$$

where E denotes elastic modulus, P is the load applied, and c is the crack length measured from the center of the indent.

Considering the above formulations, the microhardness (H_V), elastic modulus (E), yield strength (Y), indentation fracture toughness (K_{IC}) and brittleness index (BI) of the present glass-ceramics have been evaluated and are enlisted in Table 3. However, the typical image of the indentation impression of H0.5 glass-ceramic sample observed under optical microscope is presented in Figure 8. Evident from Table 3 unveiled that the value of microhardness decreases with Ho doping regime. This declaration is attributed to the impurity phases and irregular grain orientation distribution within the structure of present GC. Besides, E , Y , K_{IC} and BI values decrease meaningfully with increasing Ho doping. The reason behind this is because the aforementioned parameters are highly dependent on the hardness

values.³⁶ The matching result reported herein with those attained in similar systems; $\text{Bi}_{1.75}\text{Pb}_{0.25}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{-xSnxO}_{10+y}$ superconductor ceramics,³⁷ undoped and Ru doped BSCCO glass ceramic³⁸ and $\text{MgO/Al}_2\text{O}_3/\text{SiO}_2/\text{ZrO}_2$ glass-ceramics³⁹ is compiled in Table 3.

Theoretical evaluation of elastic moduli by using Makishima and Mackenzie's model

By invoking the ionic the values of packing density (PD) and dissociation energy G_i , the elastic moduli namely, Young (E), bulk (K), shear (G) and longitudinal (L) modulus as well as its derived parameters such as micro-hardness (H), Poisson ratio (μ), fractal bond connectivity (d) and Fugacity (f_e) of the current GC were theoretically computed by adopting Makishima and Mackenzie's (MM) model as follows:⁴¹

$$PD = \left(\frac{1}{V_m} \right) \sum V_i x_i \quad (11)$$

$$V_i = N_A \left(\frac{4\pi}{3} \right) (x R_A^3 + y R_O^3) \quad (12)$$

where R_A and R_O are the ionic radius of metal and oxygen, respectively.

$$\text{Young modulus, } E = 8.36 V_i G_i \quad (13)$$

$$\text{Bulk modulus, } K = 10 V_i^2 G_i \quad (14)$$

$$\text{Shear modulus, } G = \frac{30 V_i^2 G_i}{(10.2 V_i^2 - 1)} \quad (15)$$

$$\text{Longitudinal modulus, } L = K + \left(\frac{4}{3} \right) G \quad (16)$$

$$\text{Poisson ratio, } \mu = 0.5 - \frac{1}{7.2 V_i} \quad (17)$$

$$\text{Microhardness, } H = \frac{(1 - 2\mu)E}{6(1 + \mu)} \quad (18)$$

$$\text{Fractal bond connectivity, } d = 4 \left(\frac{G}{K} \right) \quad (19)$$

$$\text{Fugacity, } f_e = \frac{(1 - 2\mu)^2}{2(1 + \mu)} \quad (20)$$

By using the above-described formulations, the elastic moduli and its consequential entities were evaluated and enlisted in Table 4. Figure 9 typified the correlation between elastic moduli and Ho^{3+} contents in the present GC. Furthermore, a comparison between our findings with existing data on other borate and phosphate-based glass system has been established. Observably, the elastic moduli including E , G , K and L slightly increase with the increase in the H_2O_3 content.

Table 3. Evaluated Ho^{3+} doping dependent microhardness (H_V), fracture toughness (K_{IC}), brittleness index (BI), Young modulus (E) and yield strength (Y) of present glass-ceramics (GC) compared with other reported systems

Hardness parameter	Units	Present borophosphate GC			Reported data on other system			
		H0.0	H0.5	H0.8	Ozturk <i>et al.</i> ³⁷	Cook ³⁸	Seidel <i>et al.</i> ³⁹	Dittmer <i>et al.</i> ⁴⁰
H_V	GPa	3.89	3.83	3.85	2.04	2.94	8.80	0.89
K_{IC}	MPa $\text{mm}^{1/2}$	26640	30380	36960	18.56	308.04	1.90	1.12
BI	$\text{mm}^{-1/2}$	0.15	0.13	0.10				0.79
E	GPa	318.13	313.92	315.56	167.29	283.92	87.00	73.18
Y	GPa	1.30	1.28	1.28	0.68	1.56		0.29

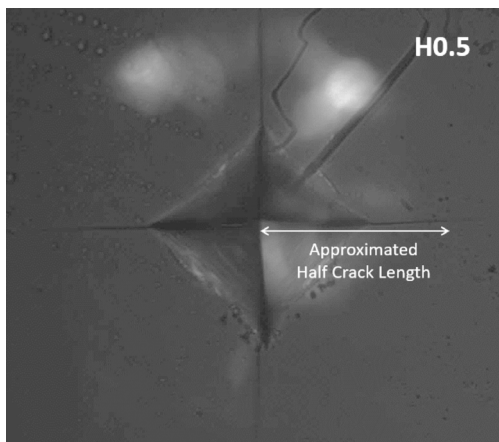


Figure 8. Typical image of the indentation impression of H0.5 glass-ceramic observed under optical microscope with 100 g applied load

The noted upsurge in these parameters is attributed to the growth in the median bonds *per* unit volume together with cross-link density.⁴⁵ Similarly, increment in Ho^{3+} content may augment the Coulomb factor of the lattice energy in the glass-ceramic system. However, large discrepancy between L and G moduli was observed which may be accredited to the volume effects. Rationally, resistance to penetration or indentation of any depends on its micro-hardness.⁴⁶ The unchanged behavior observed in micro-hardness values signified a constant rigidity and network connectivity in the present glass ceramic.

Basically, the variation of the Poisson's ratio (μ) in glass-ceramics reveal the dimensionality changes in its network. It has been established that the glass-ceramic network structure with 0.1 to

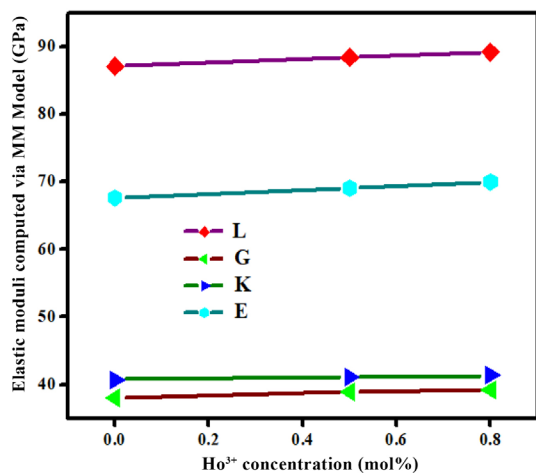


Figure 9. Theoretical elastic moduli dependent Ho^{3+} concentration (mol%) according to Makishima and Mackenzie's (MM) model

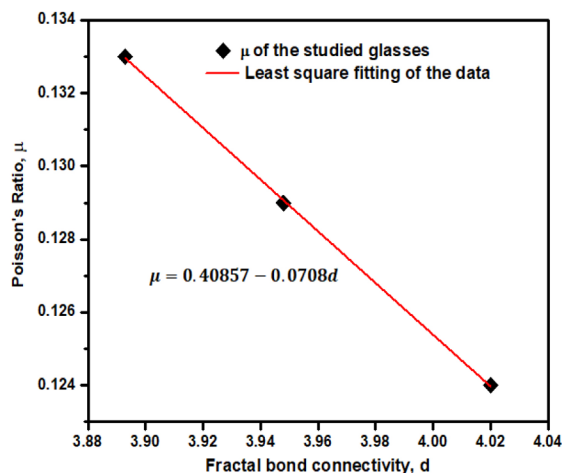


Figure 10. Variation of Poisson's ratio and fractal bond connectivity of the present GC

Table 4. Calculated elastic moduli and its derived quantities of the present GC compared with other reported systems

Elastic parameter	Units	Present borophosphate GC			Reported data			
		H0.0	H0.5	H0.8	Phosphate-based		Borate-based	
					Umar <i>et al.</i> ⁴²	Shaaban <i>et al.</i> ⁴³	Umar <i>et al.</i> ⁴²	Sidek <i>et al.</i> ⁴⁴
E	GPa	87.13	88.43	89.20	39.00	178.40	38.93	39.55
K	GPa	38.50	39.38	39.69	27.00	14.41	42.10	28.47
G	GPa	38.77	39.18	39.38	17.00	73.90	14.46	16.62
L	GPa	67.66	69.07	70.00	49.00	199.80	61.38	50.63
μ		0.12	0.13	0.13	—	0.21	0.34	0.27
H	GPa	0.11	0.11	0.11	—	—	1.49	3.07
d		4.02	3.94	3.89	2.63	—	—	2.34
f_e		0.26	0.25	0.26	—	—	—	—

0.2 value of μ implied high cross-link density in the network whereas those within 0.3 to 0.5 range of μ specified low cross-link density in their network. Evidently, our attained value of μ ranging from 0.12 to 0.13 affirmed high cross-link density in the studied glasses.⁴⁷ Besides, the evaluation of the effective dimension of certain materials for any disorderly mixture of fluid and solid backbone near the percolation limit as proposed by Bergman and Kantor⁴⁸ by using fractal bond connectivity (d) analysis classified network dimension as follows: for a 2-dimensional network, d value falls around 2.0 meanwhile the 1-dimensional glass network structure is symbolized by d value around 1.0 and for a 3-dimensional network, the d value is around 3.0 to 4.0. In the studied glasses, d -value for all glasses found to be ~ 4.0 which certifies their 3D network. However, careful assessment of μ and d trend (see Table 4) testified that the network dimensionality (d) of the present borophosphate based glass-ceramic network is decreasing while the Poisson's ratio is almost constant with increasing concentration of Ho^{3+} . This disclosure coincides with the proposed semi-empirical formulae $\mu = A - zd$,⁴⁹ which is well fitted to the curve epitomized in Figure 10 and yielded $\mu = 0.40857 - 0.0708d$. The achieved values for the two constants A and z further validate the earlier claim with $\sigma = 0.45 - 0.083D$ in oxyfluoro-zinc-tellurite.⁵⁰ Another vital quantity herein examined is the fugacity defined as the fluctuation of free volume of a system.⁵¹ This unit play a very crucial role molecular dynamics of liquids. It detects the degree of rigidity of the glass network. A mathematical model by great scientist called Williams-Landel-Ferry (WLF) was proposed to describe the viscosity of inorganic glasses and their structural properties.⁵² Therefore, careful examination of Table 4 revealed that the values of fugacity remain almost constant. This indeed reinforced the outcome from micro-hardness and the Poisson ratio.

CONCLUSIONS

In this study, some new kind glass-ceramic (GC) with stoichiometric composition of $\text{ZnSO}_4\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Ho}_2\text{O}_3$ were produced via melt-solidified method to ascertain the impact of Ho_2O_3 contents on thermal variables and mechanical properties. The overall findings unveiled high values of thermal stability ($> 150^\circ\text{C}$) and fracture toughness ($> 20000\text{ MPa mm}^{1/2}$). Furthermore, by sensibly replacing P_2O_5 with Ho_2O_3 , both crystallite size and elastic moduli values were remarkably enhanced. Thus, the obtained results suggest the possibility of using the current GC in protective covers of portable electronics.

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