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The effects of gamma irradiation on non-isothermal crystallization kinetics and microhardness of the Li_2O–Al_2O_3–SiO_2 glass–ceramic

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Abstract The effects of gamma irradiation on crystallization kinetics and microhardness properties of the Li_2O–Al_2O_3–SiO_2 (LAS) glass–ceramic sample have been investigated. The glass–ceramic was irradiated to γ-source ^{60}Co of 0.7 MGy. The crystallization kinetics of the irradiated and non-irradiated samples were characterized using differential scanning calorimetry. The crystallization kinetics and microhardness properties of the glass–ceramic changed the gamma irradiation, and the high dose of gamma irradiation affects significantly the crystallization kinetics and microhardness properties of the Li_2O–Al_2O_3–SiO_2 glass–ceramic sample.

Keywords Glass–ceramics · Crystallization kinetics · γ-Irradiation effects · Microhardness

Introduction

Glass–ceramics are fine-grained materials, which are formed using standard glass manufacturing methods. They are polycrystalline materials with crystalline size about 1 μm and smaller than 1 μm [1–4]. Lithium alumina-silicate (LAS) is one of the most common glass–ceramics and has extensively been used in cook wares, cook top panels, heat-resistant windows and telescope mirror blanks owing to its excellent properties such as the low, zero or even negative thermal expansion coefficient, as well as thermal and chemical durability and mechanical advantages such as high strength, hardness and resistance to wear [5–17] and also these materials have high melting point and viscosity. The high melting point of glass–ceramic material is decreased with the addition of alkali oxides and earth-alkali oxides. These additives have been used in glass–ceramics for lower the melting temperatures for many years, such as Li_2O, Na_2O and K_2O [5, 6, 18]. The aim of present study is to investigate the effects of gamma irradiation on non-isothermal crystallization kinetics, density and microhardness of the LAS glass–ceramic sample.

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Experimental

Glass–ceramic sample was prepared with 77.5% SiO_2, 21.2% Li_2O and 1.3% Al_2O_3 (wt%) powder oxides whose purities are 99.5%. The powder mixture grinded for 3 hours was converted a pellet under 28.5 MPa pressure at 150 °C temperature. Then, this pellet has been melted in a platinum crucible in an electrical furnace for 2.5 h at 1300 °C temperature. The prepared glass–ceramic sample was irradiated to γ-source ^{60}Co of 0.7 MGy at a dose rate of 2.50 kGy/h (Ankara Nuclear Research and Training Centre, Turkey).

The calorimetric measurements were performed by a TA Instruments DSC 2010 calorimeter. The crystallization temperatures of the glass–ceramic sample were determined from DSC measurements performed under heating rates of 10, 15, 20 and 25 °C min^{-1}.

The measuring process of density for the non-irradiated and irradiated glass–ceramic materials was calculated by Archimedes's method.

Vickers microhardness values of the non-irradiated and irradiated glass–ceramics were measured on MHT-10 microhardness tester equipment. The glass–ceramic samples were coated with Bakelite for measuring their micro

hardness, and then surfaces of the samples were polished with emery papers in wet ground.

Results and discussion

DSC results of the non-irradiated and irradiated glass–ceramic samples are shown in Fig. 1. The crystallization kinetic parameters of the glass–ceramic sample were calculated with Avrami kinetics. The obtained parameters are given in Table 1. DSC curves of the sample give two peaks, as shown in Fig. 1 and as seen in Fig. 1, the second peaks of the glass–ceramic sample irradiated with gamma irradiation are the sharper and narrower than the peaks of the non-irradiated glass–ceramic sample.

The relation between reaction rate and crystallization peak temperature is defined by Arrhenius equation [19–21]

$$k = k_o \exp\left(-E_a/RT_p\right), \quad (1)$$

where k is the reaction rate, k_o is the frequency factor, E_a is the activation energy, R is the gas constant and T_p is the crystallization peak temperature. Also, relation between heating rate and activation energy is defined by Kissinger's equation [22, 23].

$$\ln\left(\alpha/T_p^2\right) = -\left(E_a/RT_p\right) + \text{constant}. \quad (2)$$

Using Eq. 2, the activation energies were calculated from the slope of $\ln(\alpha/T_p^2)$versus $1/T_p$ curves, as shown in Fig. 2. The activation energies for the first and second peaks were found to be 325.15 and 184.36 kJ mol^{-1}, before irradiation, and 383.81 and 213.19 kJ mol^{-1}, after irradiation, respectively.

As seen in Table 1, the crystallization peak temperature (T_p) and reaction rate (k) of the sample are dependent on the heating rate (α). The crystallization peak temperature (T_p) and reaction rate (k) of the sample increase linearly with the heating rate. The activation energy of the sample is increased with the gamma irradiation. The crystallization peak temperature, activation energy, reaction rate and frequency factor values of the sample increase with irradiation for the first peak. By way of exception, the crystallization peak temperature of the second peak of the glass–ceramic sample is decreased.

The Avrami exponents of the glass–ceramic materials can be computed by the modified Ozawa equation [24]

$$\ln[-\ln(1-x)]/\ln\alpha = -n, \quad (3)$$

where x is the volume fraction crystallized after any time t, n is the dimensionless exponent depended on the mechanism of transformation known as the Avrami exponent and α is the heating rate. Using Eq. 3, the Avrami exponents were calculated from the slope of the $\ln[-\ln(1-x)]$ versus $\ln\alpha$ curves, as shown in Fig. 3. The Avrami exponents of the non-irradiated and irradiated glass–ceramic samples were found to be 3.68, 2.18 and 1.97, 1.42, for the first and second DSC peaks, respectively. The Avrami exponent values of the glass–ceramic sample show that the crystallization mechanism changes from homogenous nucleation to two-dimension nucleation for the first peaks and changes from two-dimensional nucleation to surface nucleation for the second peaks, respectively [25–27]. It is obviously seen that the values of Avrami exponent (n) of the sample were decreased with gamma irradiation. This result indicates that the gamma irradiation decreases the crystallization mechanism of the glass–ceramic sample.

The densities of the non-irradiated and irradiated glass–ceramic materials can be calculated by Archimedes's method [28]

$$\rho = [a/(a-b)]\rho_l \quad (4)$$

where ρ is the density of the solid sample and ρ_l is the density of the immersion liquid. Water was used as immersion liquid and its density is 1 g cm^{-3}. Additionally, a and b are weights of the sample in air and liquid, respectively. The

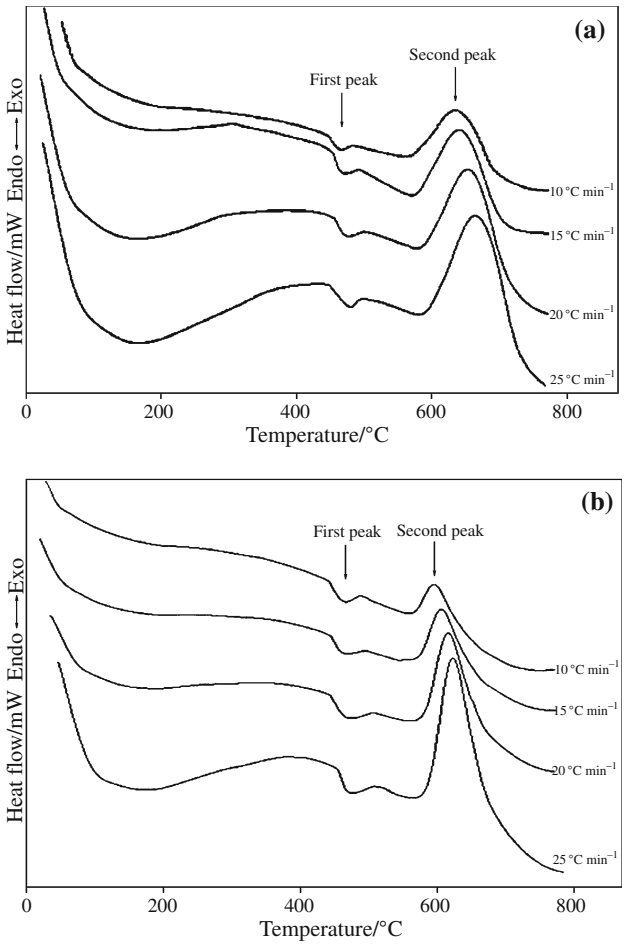

Fig. 1 DSC results of the glass–ceramic sample. **a** Before irradiation and **b** after irradiation

Table 1 The crystallization kinetic values of the glass–ceramic sample for before and after gamma irradiation

α/C min^{-1}	Peak 1					Peak 2				
	T_p/°C	E_a/kJ mol^{-1}	k_o/s^{-1}	k/s^{-1}	n	T_p/°C	E_a/kJ mol^{-1}	k_o/s^{-1}	k/s^{-1}	n
Before irradiation										
10	465.22	325.15	7.07×10^{22}	0.705	3.68	638.82	184.36	1.08×10^{10}	0.298	2.18
15	470.79			1.048		645.33			0.354	
20	475.18			1.427		658.35			0.497	
25	477.83			1.716		669.80			0.663	
After irradiation										
10	467.49	383.81	1.00×10^{27}	0.857	1.97	598.64	213.19	2.03×10^{12}	0.342	1.42
15	471.65			1.214		608.93			0.483	
20	475.54			1.670		618.53			0.660	
25	478.29			2.099		624.59			0.801	

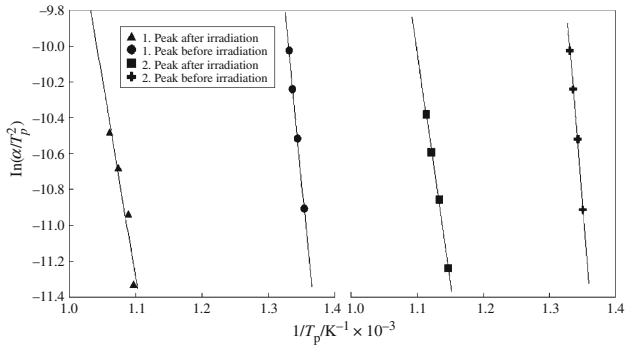

Fig. 2 The plots of $\ln\left(\alpha/T_p^2\right)$ versus $1/T_p$ of the glass–ceramic sample for before and after gamma irradiation

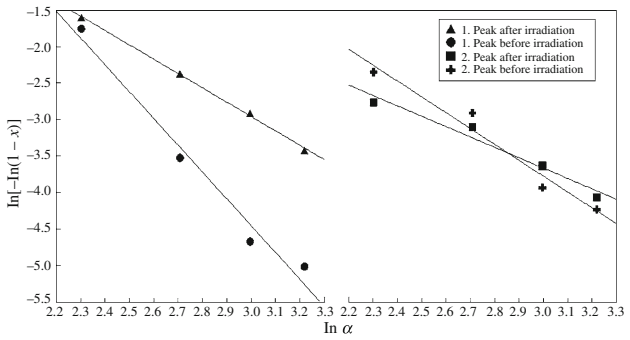

Fig. 3 The plots of $\ln[-\ln(1-x)]$ versus $\ln \alpha$ of the glass–ceramic sample for before and after gamma irradiation

molar volume V_m can be determined by the following relation

$$V_m = \text{Molecular mass}/\text{Density}. \quad (5)$$

The measured values of density, molar volume and microhardness of the glass–ceramic samples are given in Table 2. The density and molar volume values of the irradiated sample were virtually unchanged in comparison with the non-irradiated sample, as shown in Table 2. Additionally, the microhardness of the irradiated sample is increased due to the rising of internal energy [29].

Table 2 Values of density, molar volume and microhardness of the non-irradiated and irradiated glass–ceramic samples

Sample	ρ/kg m^{-3}	V_m/m^3 mol^{-1}	Microhardness/GPa
Non-irradiated	2323	23.33×10^6	8.297
Irradiated	2321	23.33×10^6	10.797

Conclusions

In this study, the gamma irradiation effects on crystallization kinetics of the LAS glass–ceramic samples have been investigated using non-isothermal kinetics. Once the glass–ceramic sample was irradiated with gamma irradiation, its crystallization kinetic parameters included Avrami exponent (n), reaction rate (k), activation energy (E_a) and frequency factor (k_o) were changed. The microhardness of the sample increases with gamma irradiation. The density and molar volume values of the irradiated sample do not change in comparison with the non-irradiated sample.

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