γ-IRRADIATION EFFECTS ON CRYSTALLIZATION KINETICS OF $Bi_{1.7}V_{0.3}Sr_2Ca_2Cu_3O_x$ GLASS-CERAMIC

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The effect of gamma irradiation on crystallization kinetics of $Bi_{1.7}V_{0.3}Sr_2Ca_2Cu_3O_x$ glass-ceramic was investigated using the differential scanning calorimetry (DSC) technique. The kinetic parameters of crystallization were calculated from the heating rate dependence of the glass transition temperature (T_g) and the crystallization peak temperature (T_p). As a result, gamma irradiation changes crystallization kinetics parameters of the glass-ceramic.

1. INTRODUCTION.

The effect of gamma irradiation on high-temperature superconductors (HTSC) is important for their practical applications. In particular, the effect of gamma-irradiation has special importance. Because, when HTSC is used in environment exposed to gamma rays, these rays can be penetrate through the protecting tubes and shielding and easily penetrate into superconducting devices [1]. The thermal behavior of the glass-ceramics plays an important role in determining the transport mechanism, thermal stability and practical applications. The thermal analysis techniques such as differential scanning calorimetry and thermogravimetry analysis (TG) methods have been widely used to determine thermal behavior of the solid materials [2-6]. Experimental data are usually analyzed by means of the nucleation and growth model proposed by Johnson et al [7]. The activation energy is the most important parameter for crystallization kinetics and it is associated with nucleation and growth process. Therefore, it is important to know. In previous study, we have investigated crystallization kinetics of $Bi_{1.7}V_{0.3}Sr_2Ca_2Cu_3O_x$ glass-ceramic [8]. In present study, we have investigated the effect of the gamma irradiation on crystallization kinetics of $Bi_{1.7}V_{0.3}Sr_2Ca_2Cu_3O_x$ glass-ceramic.

II. EXPERIMENTAL.

The classical melt-quenching technique was used to prepare the bulk glass. The starting materials are Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO and V_2O_5 powders which were used for production of the sample. These powders were mixed to obtain a homogeneous mixture for 1 h in dry atmosphere using a mortar. The mixture was put in an alumina crucible and then melted by placing the crucible for 90 min in a muffle furnace preheated to 1150 C. The obtained sample was rapidly quenched between two copper plates. The sample was produced as black glass sheet having 1 mm thickness [9]. The sample prepared was subjected to the gamma irradaition of 500 kGy. Differential scanning calorimetry measurements of non-irraditaed [8] and irradiated samples have been carried out on the bulk glasses using a TA Instrument DSC 2010 which is heat flux type differential scanning calorimeter and output are taken with a parallel connecting computer. DSC measurements were performed at heating rates of 5, 10, 15 and 20 K/min under nitrogen atmosphere using an aluminum crucible.

III. RESULTS AND DISCUSSION.

The activation energy for crystallization can be obtained from the heating rate dependence of the peak temperature of the crystallization. In order to determine the activation energy of the crystallization, the DSC measurements of the samples were performed at four different heating rate, as shown in Fig. 1.a [8] and b. Fig. 1.a shows the DSC curves of the sample at different heating rates. It is evaluated that when the sample studied is heated at a constant heating rate in a DSC experiment, it undergoes structural changes and eventually crystallizes. It is seen that the position of the glass transition peak depends on the heating rate. It is observed that there are two crystallization peaks (T_{p1} and T_{p2}), which may be due to the presence of distinct phase transformations. The maximum temperature of peak 1 (T_{p1}) increases from 759.15 to 775.4 K, while the maximum temperature of peak 2 (T_{p2}) increases from 803.61 to 825.67 K, when the heating rate is increased from 5 to 20 K/min. The peak temperature shifts to higher temperatures with increasing heating rate. As seen in Fig. 1 b, there are two crystallization peaks (T_{p1} and T_{p2}), which may be due to the presence of distinct phase transformations. The maximum temperature of the peak 1 (T_{p1}) increase from 759 to 776 K, while the maximum temperature of the peak 2 (T_{p2}) increase from 806 to 825 when heating rate increases from 5 to 20 K/min. The peak temperature shifts to higher temperatures with increasing heating rate. It is seen that the height of the crystallization peak increases with increasing heating rate and it is proportional to the concentration of nuclei in glass [10]. As seen in Fig. 1.b, the height of the first crystallization peak is greater than that of height of the second peak. The shift of peak temperature may be associated with particle size effects on heat transfer. Larger particles would have greater heat transfer resistance when it is considered a given heating rate. It takes longer for the center of particle to reach the furnace temperature. Thus, this process results in a higher crystallization.

To analyze the obtained results, we used the Kissinger method [11]

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_c}{RT_p} + const. \qquad (1)$$

where T_p is the temperature of the maximum DSC crystallization peak, β is the heating rate and R is the universal gas constant. The values of E_c were calculated from the slope of $\ln(\beta/T_p^2)$ v.s $1000/T$ plots (Fig. 2). The activation energy values for irradiated and non-irradiated [8] samples were found as 385.97 and 407.42 kJ/mol, respectively.

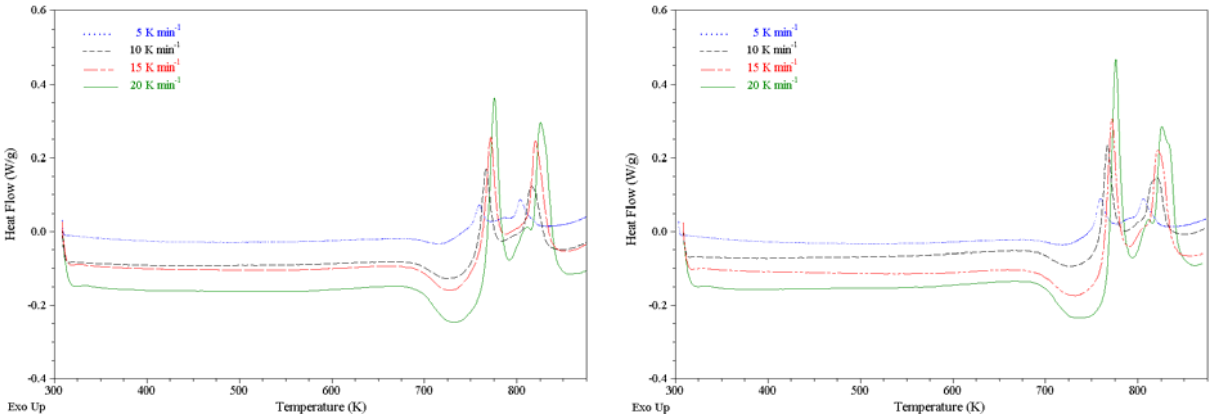

Fig. 1 The DSC curves of the samples at different heating rates **a)** non-irradiated sample **b)** irradiated sample

The crystal growth index (Avrami parameter) is another important kinetics parameter to evaluate crystallization capability of the sample. It is evaluated that if activation energy is lower, it is easier to crystallize for the sample. The crystallization activation energy values of the samples change with increasing heating rate. It is suggested that the higher heating rate is easier to crystallize of the sample. In order to obtain Avrami parameter *n*, the ln[-ln(1-*x*)] v.s ln(*β*) curves were plotted for first peak, as shown in Fig. 3. The following relation is used to obtain n,

$$n = -\frac{d[ln(-ln(1-x))]}{d[ln(\beta)]} \qquad (2)$$

From this relation, the Avrami parameter for non-irradiated and irradiated samples was found as about 2.19 and 2.51, respectively.

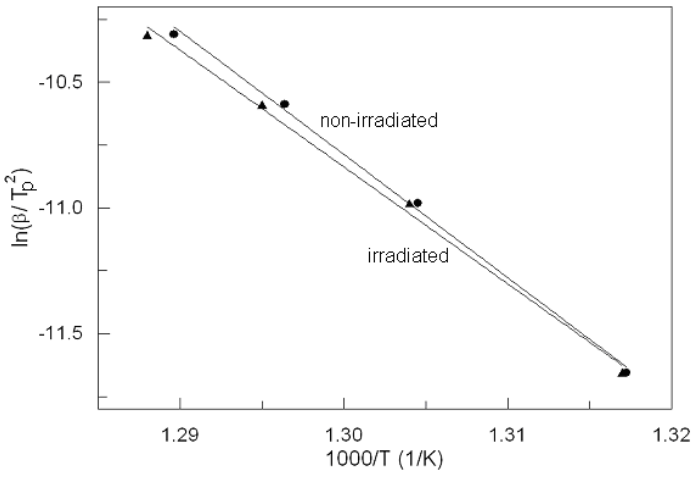

Fig. 2 The $\ln(\beta / T_p^2)$ v.s 1000/*T* plots of the samples

Avrami parameter of gamma irradiated sample was range from one-dimensional nucleation and its growth (n= 2.19) to two-dimensional growth (n=2.51) and increased with the effect of gamma irradiation. The higher the Avrami parameter is, the easier the crystallization is. The *n* parameter obtained suggest that the crystallization takes place easily in structure and crystallization mechanism is bulk crystallization mechanism, in which nucleation occurs in the bulk of the sample. It is evaluated that the gamma irradiation a few changes the Avrami parameter of the sample.

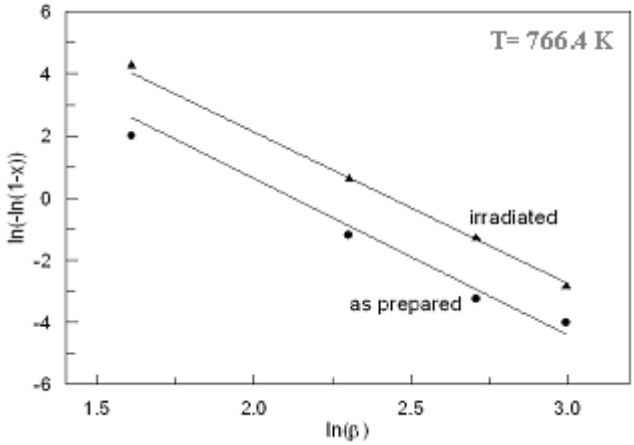

Fig. 3 The ln(-ln(1-*x*)) v.s ln(*β*) plots for the samples at different heating rates

As seen in Fig.1.b, the first one corresponds to the glass transition temperature T_g which appears as an endothermic peak. The glass transition temperature is a thermodynamic characteristic temperature for the sample. This calorimetric glass transition is generally considered to be due to changes in the amorphous structure, which approaches a thermodynamic equilibrium state as the temperature of the system is increased [12–14]. It is seen that the position of the glass transition peak depends on the heating rate. On the other hand, the glass transition activation energy, E_g, is the amount of energy absorbed by a group of atoms in the glassy region. This activation energy for glass transition provides molecular motion and rearrangement of atoms around the glass transition temperature and helps to a jump from one metastable state to another. The activation energies for glass transition were determined from the slope of $\ln(\beta / T_p^2)$ v.s 1000/*T* using glass transition peak temperatures and were found as 350.9 kJ/mol for non-irradiated [8] and 344.51 kJ/mol for irradiated sample. It is evaluated that the glass

transition activation energy decreases with applied irradiation. This suggests that the activation energy for glass transition can be reduced by applying irradiation to sample studied. The glass transition temperature dependence of heating rate can be expressed by relation [15],

$$T_g = A + B\ln(\beta) \quad (3)$$

where A and B are constants. The T_g v.s $\ln\beta$ plots for the sample were plotted. These plots confirmed the validity of the relation and A and B constants were found as 1.601 and 688.3 K for non irradiated [8] and 4.855 and 681.6 K for irradiated sample.

IV. CONCLUSION.

We have investigated the effect of gamma irradiation on crystallization kinetics of $Bi_{1.7}V_{0.3}Sr_2Ca_2Cu_3O_x$ glass-ceramic. It is found that gamma irradiation changes crystallization kinetics parameters (E_c, n) of the glass-ceramic.

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