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Differential scanning calorimetry investigations on Eu-doped fluorozirconate-based glass ceramics

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Abstract

The properties of Eu-doped fluorochlorozirconate (FCZ) glass ceramics upon thermal processing and the influence of Eu-doping on the formation of BaCl₂ nanocrystals therein have been investigated. Differential scanning calorimetry indicates that higher Eu-doping shifts the crystallization peak of the nanocrystals in the glass to lower temperatures, while the glass transition temperature remains constant. The activation energy and the thermal stability parameters for the BaCl₂ crystallization are determined.

Keywords

crystallization; differential scanning calorimetry; glass ceramics; Eu-doping; glass transition; nanocrystals

1. Introduction

Fluorozirconate (FZ)-based glass ceramics are of great interest for applications such as image plates for medical diagnostics and up- or down-conversion layers for solar cells [1,2,3,4]. Their low phonon energy reduces the probability for non-radiative decay processes and thus make them attractive as a host material for fluorescent rare-earth (RE) ions such as Eu²⁺ [5]. Upon annealing the “as-poured” glass, BaCl₂ nanocrystals are formed in the glass matrix and some of the Eu²⁺ dopants are incorporated into the nanocrystals leading to enhanced fluorescence efficiencies of the material. The size, number, and structure of the BaCl₂ nanocrystals depends significantly on the annealing conditions and on glass composition. This paper discusses the effect of the Eu-doping on the crystallization properties of BaCl₂ nanoparticles in FZ glass ceramics. The crystallization behavior of the BaCl₂ nanocrystals is investigated extensively by differential scanning calorimetry (DSC).

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2. Materials and methods

The Eu-doped fluorochlorozirconate (FCZ) glasses investigated are based on the well-known ZBLAN composition [6]. The nominal compositions of the FCZ glasses are given in Table 1 (values in mol%). Note, that the actual composition is different. The fluorine/chlorine content is lower due to evaporation during the melting process [7]; there is also a small loss of zirconium. The EuF_2 is added at the expense of BaF_2 ; the Eu-doping level varies from 0 to 5 mol%. The constituent chemicals are melted in a glassy carbon crucible at 745°C in an inert atmosphere of nitrogen and then poured into a brass mold held at a temperature of 200°C , before being slowly cooled to room temperature.

The DSC is performed with a DSC 204 F1 Phoenix instrument (Netzsch). The sample is powdered by means of a mortar and pestle and then placed in an aluminum crucible; an empty crucible is used as a reference. The temperature is increased with heating rates of 5, 10, 15, 20, and 25 K/min while the differential temperature between the crucibles is measured.

3. Results and discussion

A typical DSC measurement with a heating rate of 10 K/min is shown in Figure 1. The glass transition temperature T_g is correlated with the melting temperature T_m by the “two-thirds rule” $T_g/T_m = 2/3$ which is typical for a large number of super-cooled liquids [8]. T_x identifies the onset of the first crystallization (which belongs to the crystallization of BaCl_2 according to previous work [9]) and T_p the temperature of the crystallization peak. The analysis of the DSC data results in a T_g of $225\text{--}226^\circ\text{C}$ for all Eu-doped FCZ glasses, which is the same within error and significantly smaller than the 262°C observed in pure ZBLAN [6]. In [9] a T_g of 205°C was found for a 1 mol% Eu-doped FCZ glass comprised of $52\text{ZrF}_4\text{--}10\text{BaF}_2\text{--}10\text{BaCl}_2\text{--}20\text{NaCl}\text{--}3.5\text{LaF}_3\text{--}3\text{AlF}_3\text{--}0.5\text{InF}_3\text{--}1\text{EuF}_2$ (values in mol%). We assume that the 4 mol% higher ZrF_4 content shifts T_g to lower temperatures since according to Table 2 the Eu-doping level does not affect T_g .

The temperature at which the crystallization peak of BaCl_2 evolves does not change significantly with increasing Eu-doping. The large crystallization peak at 330°C is associated with crystallization of the glass matrix. This peak shifts diametrically: higher Eu-doping leads to a shift to higher temperatures. Table 2 shows important peak values and thermal stability parameters for all samples for a constant heating rate of 10 K/min. The parameters ΔT , H_r , and S are defined as

$$\Delta T = T_x - T_g \quad (1)$$

$$H_r = (T_x - T_g) / (T_m - T_x) \quad (2)$$

$$S = (T_x - T_g)(T_p - T_x) / T_g \quad (3)$$

where ΔT describes the devitrification tendency of the glass and H_r gives information on the nucleation rate of the crystals [10]. A wider $(T_x - T_g)$ gap results from a drop in the glass viscosity [11], while the denominator $(T_m - T_x)$ is influenced by the magnitude of the growth rate. If the gap decreases the crystal growth rate falls rapidly. The parameter S introduced by

Saad and Poulain [12] also takes into account the width of the devitrification peak. When the $(T_p - T_x)$ factor is high, the growth rate decreases. Table 2 shows that the Eu-doping has no significant influence on the thermal stability. The glass transition temperature T_g is not affected by the EuF_2 doping level, probably due to its similarity in size and chemistry to BaF_2 (fluorite crystal lattice structure).

Nonisothermal DSC measurements with different heating rates, α , enable the investigation of crystallization kinetics, namely the apparent activation energy E_a and the Avrami exponent n . The activation energy E_a can be determined by Kissinger's method (see Eqn. (15) in [13]):

$$\frac{d[\ln(\alpha/T_p^2)]}{d(1/T_p)} = -\frac{E_{a,\text{Kissinger}}}{R} \quad (4)$$

where R is the gas constant. The activation energy can also be determined by Ozawa's method (see Eqn. (10) in [14]) or by Flynn's method (see Eqn. (6) in [15]):

$$\frac{d(\log \alpha)}{d(1/T_p)} = -0.457 \frac{E_{a,\text{Ozawa/Flynn}}}{R} \quad (5)$$

The prefactor -0.457 is an average value for slopes between $20 \leq E_{a,\text{Ozawa/Flynn}}/(R \cdot T_p) \leq 60$ derived from the theoretically calculated slopes by Flynn (see Table I in [15]).

The Avrami exponent n_{Oz} is given by Ozawa's method (see Eqn. (23) in [17]) as:

$$\left. \frac{d\{\log[-\ln(1-x)]\}}{d(\log \alpha)} \right|_T = -n_{Oz} \quad (6)$$

where x is the crystallized volume fraction at a given temperature T . The crystallized volume fraction is given by (see Eqn. (1) in [18]):

$$x = \frac{\int_{T_0}^T (dH_c/dT') dT'}{\int_{T_0}^{T_\infty} (dH_c/dT') dT'} \quad (7)$$

where T_0 is the onset, T_∞ the end of crystallization temperature and dH_c/dT the heat flow into or out of the sample when it is heated or cooled to a temperature T . An illustration for different heating rates is given in Figure 2 for the 5 mol% Eu-doped FCZ glass. Shifts in peak maxima to higher temperatures upon increasing heating rates are observed from which E_a and n_{Oz} can be determined.

Also the intensity of the peak increases with higher α due to an enhanced heat flow dH_c/dT , i.e.,

$$dH_c/dT = m \cdot c_p \cdot \alpha \quad (8)$$

where m is the sample mass, c_p the sample specific heat capacity, and α the constant heating rate.

$E_{a, \text{ Kissinger}}$ and $E_{a, \text{ Ozawa/Flynn}}$ are obtained from the slopes of the linear fits by plotting $\ln(\alpha/T_p^2)$ vs. $1/T_p$ and $\log \alpha$ vs. $1/T_p$, respectively (Figure 3). Note, that the prefactor of -0.457 used in Eqn. 5 for the calculation of $E_{a, \text{ Ozawa/Flynn}}$ is only the initial value in an iteration process. In a first step, for the 5 mol% Eu-doped sample, for example, the following is obtained:

$$\frac{E_{a, \text{ Ozawa/Flynn}}}{R \cdot T_p} = \frac{-14.51 \cdot 10^3 \text{ K}}{-0.457 \cdot T_p} = 59.486 \quad (9)$$

with $T_p = 260.6^\circ\text{C}$, i.e. 533.75 K. Comparing this value with the values of Table I in [15] gives a corrected prefactor of -0.4489 , which is found in the “ $\Delta \log$ ” column. The calculation is repeated with the new prefactor until the prefactor remains constant. Two to three iterations are usually sufficient. For all samples, the corrected prefactors are between -0.4485 and -0.4510 .

The experimental data for all FCZ glasses and the resulting activation energies E_a for the BaCl_2 crystallization are summarized in Table 3. BaCl_2 has an almost even thermal stability since the apparent activation energies are identical within experimental error. The Avrami exponent n_{Oz} can be obtained from the slopes of the linear fits by plotting $\log[-\ln(1-x)]$ vs. $\log \alpha$ as shown in Figure 4. For the 5 mol% Eu-doped FCZ glass the values of n_{Oz} range from 1.6 to 2.5 and decrease with increasing temperature. For the initial crystallization process the higher Avrami exponent can be interpreted as dendritic (treelike) two dimensional with diffusion controlled growth of BaCl_2 nanocrystals inside the glass matrix and a constant nucleation rate. A decrease of n_{Oz} as temperature increases suggests a reduction of the nucleation rate.

Another approach to obtain the Avrami exponent is possible if a constant crystallization temperature and a random distribution of the nanocrystals can be assumed. The crystallized volume fraction x is then given by the Avrami equation (see Eqn. (20) in [19]):

$$x = 1 - \exp(-K_t t^{n_{Av}}) \quad (10)$$

where n_{Av} is the Avrami exponent, K_t is a temperature dependent rate constant reflecting nucleation and growth rates of the material (here BaCl_2), and x is the crystallized volume fraction at crystallization time t which is given by

$$t = \frac{T - T_0}{\alpha} \quad (11)$$

with the temperature T at crystallization time t , the onset of crystallization temperature is T_0 and the heating rate α .

To determine the parameters K_t and n_{Av} , Eqn. (10) is needed in double logarithmic form:

$$\log[-\ln(1-x)] = n_{Av} \log t + \log(K_t) \quad (12)$$

The relative crystallization x as a function of temperature at different heating rates is shown in Figure 5 for the 5 mol% Eu-doped sample. The reason for lower x values at higher heating rates at the same crystallization temperature is due to the fact that higher heating rate leads to shorter crystallization time.

The Avrami exponent n_{Av} and the temperature dependent rate constant K_t are obtained from the slopes and intercepts of the linear fits by plotting $\log[-\ln(1-x)]$ vs. $\log t$ (Figure 6).

Jeziorny modified the Avrami analysis by taking into account the effect of the heating rate (see Eqn. (3) in [20]). K_t is modified by the rate α :

$$\log(K_c) = \frac{\log(K_t)}{\alpha} \quad (13)$$

The rate constants and n_{Av} for a heating rate of 10 K/min are listed in Table 3. All samples show a K_c of approximately 1.1, i.e. nucleation and growth rate of the BaCl₂ nanocrystals are about the same size. The linear fits result in Avrami exponents n_{Av} of around 2.7 which are similar to the values received for the intermediate crystallization temperature by Ozawa's method. Note, that in Ozawa's calculations n_{Oz} depends on temperature, whereas n_{Av} is averaged over the temperature range of the complete crystallization. Figure 7 shows the BaCl₂ half-life of crystallization $t_{0.5}$, which is the time required for 50% of the BaCl₂ nanoparticles to crystallize. For all Eu-doping levels from 5 K/min (squares) to 25 K/min (diamonds) in steps of 5 K/min a higher heating rate always leads to shorter values of $t_{0.5}$ due to the enhanced heat flow and faster crystallization, respectively. By increasing the Eu-doping level an upward trend to longer crystallization time is identifiable only at a heating rate of 5 K/min. For all other rates the half-life remains almost constant with Eu-doping. The shorter timescale may be the reason for not allowing absolute crystallization further.

4. Conclusion

The results of the research show that the Eu-doping level has no influence on the BaCl₂ crystallization temperature, the glass transition temperature, or the thermal stability of the glasses. For all samples BaCl₂ crystallization activation energies and Avrami exponents are obtained from DSC measurements. Both E_a determination methods (Kissinger and Ozawa/Flynn) give values of about 260 kJ/mol within the same confidence interval, i.e. both can be used for the calculation. For the initial crystallization process the Avrami theory predicts a dentritic with diffusion controlled BaCl₂ crystallite growth mechanism if a constant nucleation rate is assumed during the crystal growth process but this still needs to be established from ongoing in situ transmission electron microscopy experiments.

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Figure 1.
Plot of the DSC data for the 5 mol% Eu-doped FCZ glass. The heating rate was 10 K/min.

Figure 2.
Plot of the DSC data for the 5 mol% Eu-doped FCZ glass with different heating rates from 5 K/min to 25 K/min in steps of 5 K/min. The curves are vertically displaced for clarity.

Figure 3.

$\ln(\alpha/T_p^2)$ (full squares) and $\log \alpha$ (open squares) vs. $1/T_p$ for the 5 mol% Eu-doped FCZ glass. The slopes give the apparent activation energies E_a .

Figure 4. $\log[-\ln(1-x)]$ vs. $\log \alpha$ for the 5 mol% Eu-doped FCZ glass. The slopes give the Avrami exponents n_{Oz} by Ozawa's method.

Figure 5. Relative crystallization of the 5 mol% Eu-doped FCZ glass at different heating rates from 5 K/min to 25 K/min in steps of 5 K/min.

Figure 6.

$\log[-\ln(1-x)]$ vs. $\log[(T-T_0)/\alpha]$ for the 5 mol% Eu-doped FCZ glass and a heating rate of 10 K/min. The slope gives the Avrami exponent n_{Av} by Avramis method, while the rate constant K_t is obtained from the intercept of the linear fit.

Figure 7. Plot of the BaCl_2 half-life of crystallization vs. Eu-doping level of the Eu-doped FCZ glasses at different heating rates from 5 K/min (squares) to 25 K/min (diamonds) in steps of 5 K/min.

Table 1

Nominal composition of the Eu^{2+} -doped FCZ glasses investigated (values in mol%).

ZrF_4	BaF_2	BaCl_2	NaCl	LaF_3	AlF_3	InF_3	EuF_2
48	15	10	20	3.5	3	0.5	0
48	14	10	20	3.5	3	0.5	1
48	13	10	20	3.5	3	0.5	2
48	10	10	20	3.5	3	0.5	5

Table 2

Thermal stability parameters of Eu²⁺-doped FCZ glasses for a heating rate of 10 K/min. Note that T_g , T_x , T_p , and T_m are taken in Kelvin for the calculation of the thermal stability parameters.

Eu-doping (mol%)	T_g (°C)	T_x (°C)	T_p (°C)	T_m (°C)	T_g/T_m	ΔT (K)	H_r	S (K)
0	225.6 ± 0.5	258.8 ± 0.5	265.4 ± 0.5	434.8 ± 0.5	0.704 ± 0.001	33 ± 1	0.189 ± 0.007	0.44 ± 0.07
1	224.8 ± 0.5	254.8 ± 0.5	260.2 ± 0.5	431.7 ± 0.5	0.706 ± 0.001	30 ± 1	0.170 ± 0.007	0.33 ± 0.06
2	225.3 ± 0.5	256.8 ± 0.5	262.6 ± 0.5	430.7 ± 0.5	0.708 ± 0.001	32 ± 1	0.181 ± 0.007	0.37 ± 0.06
5	225.6 ± 0.5	254.3 ± 0.5	260.6 ± 0.5	427.3 ± 0.5	0.712 ± 0.001	29 ± 1	0.166 ± 0.007	0.36 ± 0.06

Table 3

Activation energies and Avrami exponents of Eu^{2+} -doped FCZ glasses for a heating rate of 10 K/min.

Eu-doping (mol%)	E_a , Kissinger (kJ/mol)	E_a , OzawaFlynn (kJ/mol)	n_{Oz} (262°C)	n_{Av}	K_t	K_c
0	262 ± 12	262 ± 12	2.4 ± 0.3	2.7 ± 0.1	1.92 ± 0.02	1.067 ± 0.001
1	273 ± 20	273 ± 19	2.7 ± 0.3	2.7 ± 0.1	3.08 ± 0.04	1.119 ± 0.001
2	267 ± 12	267 ± 12	2.8 ± 0.3	2.7 ± 0.1	3.11 ± 0.04	1.120 ± 0.001
5	269 ± 9	269 ± 8	2.2 ± 0.3	2.6 ± 0.1	3.39 ± 0.03	1.091 ± 0.001