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Crystallization behavior of rare-earth doped fluorochlorozirconate glasses

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Abstract

A series of fluorochlorozirconate (FCZ) glasses, each doped with a different rare-earth, was prepared and examined to determine thermal stability and activation energy, E_a , of the dopant dependent BaCl_2 crystallization. Non-isothermal differential scanning calorimetry (DSC) measurements were done to investigate the endothermic and exothermic reactions upon heat treatment of the glass samples. In comparison to the rare-earth free FCZ glass, significant changes in the Hruby constant, H_r , and E_a were found due to the addition of a rare-earth and also between the individual dopants.

Keywords

Crystallization; Differential scanning calorimetry; Glass ceramics; Rare-earth doping; Activation energy; Nanocrystals

1. Introduction

Rare-earth (RE)-doped fluorochlorozirconate (FCZ)-based glass ceramics are known for their scintillation (spontaneous emission upon irradiation) and storage phosphor (storage of electron-hole pairs until released with a laser) properties. The glasses are synthesized from a mixture of Zr, Ba, La, Al, and Na fluorides, known as ZBLAN [1]. Additional chlorine doping enables the growth of BaCl_2 nanocrystals in the glass matrix upon thermal processing [2,3].

Previous work on Eu^{2+} -doped FCZ glasses [2,3] has shown that Eu^{2+} is incorporated into these nanocrystals leading to an Eu^{2+} fluorescence. Note that Eu^{2+} does not fluoresce when embedded in the glass matrix. Fluorescence investigations on Nd^{3+} -doped FCZ glasses indicate that trivalent RE ions like Nd^{3+} ions can also be incorporated into the BaCl_2 nanocrystals [4].

RE doping has a significant influence on the BaCl_2 crystallization behavior: In Eu^{2+} -doped FCZ glasses, the BaCl_2 crystallization energy is about 260 kJ/mol [5], while preliminary differential scanning calorimetry (DSC) work on 5 mol% Nd^{3+} -doped FCZ glasses yielded a

crystallization energy of about 200 kJ/mol. In this work, a systematic study on the crystallization behavior of Eu^{3+} , Er^{3+} , Gd^{3+} , Nd^{3+} , and Tb^{3+} doped FCZ glasses is presented. The RE doping level was 1 mol% for all glasses. DSC experiments were performed to obtain thermal stability parameters and the activation energies of the dopant dependent BaCl_2 crystallization.

2. Materials and methods

2.1. Samples

All FCZ glasses investigated are based on the well-known ZBLAN composition [1]. The standard composition of the glasses consists of $52\text{ZrF}_4\text{-}20\text{BaCl}_2\text{-}20\text{NaF}\text{-}3.5\text{LaF}_3\text{-}3\text{AlF}_3\text{-}0.5\text{InF}_3\text{-}1\text{REF}_3$ ($\text{RE}=\text{Eu}^{3+}, \text{Er}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Nd}^{3+}$) (values in mole percent).

The constituent chemicals are melted in a platinum crucible at 750 °C in an inert atmosphere of argon and then poured into a brass mold that was at a temperature of 200 °C, i.e. below the glass transition temperature of 260 °C for a fluorozirconate (FZ)-based glass [1], before being cooled to room temperature linearly over 4 hours.

2.2. Setup

The thermal properties are investigated with a DSC 204 F1 Phoenix instrument (Netzsch). The samples are powdered by means of a mortar and pestle. The powder is placed in an aluminum crucible; a second empty crucible is used as a reference enabling the measurement of the differential temperature between them. To obtain thermal stability parameters and activation energies of the dopant dependent BaCl_2 crystallization, DSC signals are measured from room temperature to 450 °C with different heating rates of 5, 7.5, 10, 15, 20, 25, and 30 K/min.

3. Results and discussion

3.1. Thermal stability parameters

A typical DSC measurement for a 1 mol% Eu-doped FCZ glass is shown in Fig. 1. Four important points of interest are marked: The glass transition temperature, T_g , is associated with a sudden decrease of the glass viscosity and specific heat capacity. T_x is the onset of the first crystallization, which belongs to the crystallization of BaCl_2 [3], while T_p identifies the temperature of the crystallization peak. The highest crystallization peak at 320 °C is associated with crystallization of the glass matrix. For supercooled liquids, such as FCZ glasses, the melting temperature, T_m , is correlated with T_g by the “two-thirds rule” $T_m=2/3$ [6].

Fig. 2 shows the DSC data for all trivalent RE dopants at a heating rate of 10 K/min. The results are assembled in Table 1 and show that the dopants have only a small effect on T_g , i.e., Gd^{3+} -doped glass has the lowest value at 211 °C, while the glass transition temperatures for Er^{3+} - and Tb^{3+} -doped glasses are approximately the same as the rare-earth free glass at 213 °C. Nd^{3+} has a T_g of 214 °C, while Eu^{3+} has the highest value at 216 °C. However, the onset and peak of the BaCl_2 crystallization as well as the melting temperature of the glass itself show significant changes between the RE-free and the RE-doped FCZ glasses: No doping leads to a T_x of ≈ 234 °C, while the values for the glasses with dopants are generally ≈ 10 °C higher (244 °C for Er^{3+} and 249 °C for Nd^{3+} and Gd^{3+}). Similarly, the RE doping also leads to about a 10 °C shift of T_p from 239 °C to around 250 °C. In addition, the individual dopant affects the position of T_p , i.e., BaCl_2 crystallization starts at 249 °C in the Er^{3+} -doped glass, while for Nd^{3+} , the peak position is reached at 254 °C. In contrast, doping

results in a T_m of 435-436 °C, which is the same within error, and higher than the 419 °C observed in the RE-free sample.

The thermal stability of glasses can be described by ΔT and the Hruby constant H_r , which are defined as

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

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

where ΔT gives information about the devitrification tendency of the glass; a wider gap results from a drop in the glass viscosity. H_r introduced by Hruby [7] also takes into account the gap between melting temperature and crystallization onset, which is influenced by the magnitude of the crystal growth rate. For smaller growth rates the gap decreases.

Fig. 3 shows H_r for the RE-doped FCZ glasses for different heating rates, α . For all heating rates, a significant gap is observed between the values of the RE-free and the RE-doped samples. In summary, Gd^{3+} has the highest H_r around 0.23, followed by Nd^{3+} , Tb^{3+} , Eu^{3+} , and lastly, Er^{3+} , with the lowest values between 0.16 and 0.18. The H_r mean value of 0.12 for the RE-free glass is even smaller and therefore an indication that RE doping leads to higher glass stability against crystallization on heating, which is in good agreement with the higher values for T_x and T_p for the RE-doped glasses.

3.2. Apparent activation energies

Upon increasing heating rates, shifts of the crystallization peak maxima to higher temperatures are observed from which the activation energy, E_a , of the $BaCl_2$ crystallization can be determined by Kissinger's method [8]:

$$\frac{d \left[\ln \left(\alpha / T_p^2 \right) \right]}{d \left(1/T_p \right)} = - \frac{E_a}{R} \quad (3)$$

where R is the gas constant. Thus, E_a is obtained from the slopes of the linear fits by plotting $\ln(\alpha/T_p^2)$ vs. $1/T_p$ as shown in Fig. 4. The results for all RE dopants are summarized in Fig. 5. Compared to the RE-free FCZ glass, the addition of a RE decreases the activation energy from 264 kJ/mol to 219 kJ/mol for Nd^{3+} doping. Between these values, Gd^{3+} has the second lowest value of 224 kJ/mol, followed by Tb^{3+} (235 kJ/mol) and Eu^{3+} (244 kJ/mol). Er^{3+} has the highest $BaCl_2$ crystallization activation energy of the dopants at a value of 252 kJ/mol.

Ionic radius in RE atoms decreases with atomic number and activation energy increases as the ionic radius decreases with the exception of europium. Covalent radius (the size of the atom that forms part of a covalent bond), also decreases with atomic number but in this case europium is the exception, having a larger covalent radius than the other dopants studied here, see Table 1 or [9]. A covalent bond needs a bond dissociation energy (BDE) to be broken by homolysis (high frequency light or in our case heat treatment). Generally, a larger covalent radius results in a lower BDE. Previous investigations on RE-doped FCZ glasses showed that Eu^{2+} and Nd^{3+} ions are partially incorporated into the $BaCl_2$ nanoparticles upon annealing, subsequent to pouring. In this step, a Ba ion is replaced by the RE ion, which was previously incorporated into the glass network or "free" in the glass. It was shown in [10] that trivalent Eu is incorporated in the fluorozirconate glass network but it is not clear that other RE ions behave in the same way. However, as Eu^{3+} -doped FCZ glasses yielded a much higher $BaCl_2$ crystallization activation energy, it is possible that the other REs studied

here are not bound to the glass network and therefore need less energy to diffuse and to act as a nucleation center.

4. Conclusion

Compared to RE-free FCZ glasses, RE doping results in an increased H_r parameter and decreased activation energy of the BaCl_2 crystallization. Er^{3+} has the highest E_a of 252 kJ/mol, while Nd^{3+} doping gives the lowest value at 219 kJ/mol. These differences could be attributed to the covalent radius between the dopants, since it decreases with atomic number. Note, that of the studied dopants, Eu^{3+} does not fit with the trend because of its large covalent radius of the studied dopants and its bond to the glass network. This work is a major step in determining the parameters for BaCl_2 crystallization and subsequently controlled nanocrystallite growth.

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

Fig. 2. Plot of the DSC data for FCZ glasses with different RE doping. The heating rate was 10 K/min. The curves are vertically displaced for clarity.

Fig. 3. Hruby constant for differently RE-doped FCZ glasses and different heating rate α .

Fig. 4.

$\ln(\alpha/T_p^2)$ vs. $1/T_p$ for the differently RE-doped FCZ glasses. The slopes give the apparent activation energies E_a .

Fig. 5. Activation energy E_a diagram for the BaCl_2 crystallization for differently RE-doped FCZ glasses.

Table 1

Thermal stability parameters of RE-doped FCZ glasses for a heating rate of 10 K/min. T_g , T_x , T_p , and T_m are taken in Kelvin for the calculation of the thermal stability parameters. Furthermore the covalent radii [9] of the different RE ions are listed.

Dopant	T_g (°C)	T_x (°C)	T_p (°C)	T_m (°C)	T_g/T_m	H_r	Covalent radius (Å)
None	212.7±0.5	234.3±0.5	239.2±0.5	418.5±0.5	0.703±0.001	0.117±0.006	-
Nd ³⁺	214.2±0.5	248.8±0.5	254.4±0.5	435.5±0.5	0.688±0.001	0.185±0.006	1.64
Eu ³⁺	215.6±0.5	245.0±0.5	250.7±0.5	435.0±0.5	0.690±0.001	0.157±0.006	1.85
Gd ³⁺	211.4±0.5	248.8±0.5	252.6±0.5	435.4±0.5	0.684±0.001	0.198±0.006	1.61
Tb ³⁺	212.2±0.5	246.7±0.5	251.4±0.5	435.6±0.5	0.685±0.001	0.183±0.006	1.59
Er ³⁺	212.5±0.5	244.0±0.5	248.8±0.5	435.4±0.5	0.685±0.001	0.164±0.006	1.57