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Structural relaxation of scintillating Ce-doped $NaGd(PO_3)_4$ glass

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Abstract Structural relaxation of scintillating Ce-doped Na–Gd phosphate glass with a nominal composition of $Ce:NaGd(PO_3)_4$ was experimentally studied using non-isothermal thermo-mechanical analysis, and the relaxation process was described by the Tool–Narayanaswamy–Mazurin model. The distribution of relaxation times was expressed by the empirical Kohlrausch–Williams–Watts relaxation function with relaxation time directly proportional to dynamic viscosity. The model parameters and material constants were obtained by the nonlinear regression analysis of thermo-mechanical data. It has been concluded that the model used of structural relaxation correctly describes relaxation processes in studied Ce-doped $NaGd(PO_3)_4$ glass.

Keywords Structural relaxation · Tool–Narayanaswamy–Mazurin model · Thermo-mechanical analysis · $Ce:NaGd(PO_3)_4$ glass · Dynamic viscosity

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Introduction

Glasses prepared by quenching of the melt do not reach any equilibrium state but they seek to attain it. The process the glass undergoes to reach this state is called structural relaxation and it is connected with time-dependent changes in its structure [1, 2]. The fundamental information that is inevitable for the evaluation of the relaxation process is obtained from experiments performed by thermal analysis methods such as DSC and TMA. In the glass transformation range, the relaxation kinetics is well described by the Tool–Narayanaswamy–Moynihan model with application of Tool's fictive temperature, T_f, and the distribution of relaxation times expressed by the empirical Kohlrausch–Williams–Watts function (KWW) [3]. However, if structural relaxation and viscous flow proceed simultaneously, the Tool–Narayanaswamy–Mazurin (TNMa) model was proposed for the description of thermo-mechanical curves [4].

This article deals with the structural relaxation of Ce-doped Na–Gd phosphate glass with nominal composition of $NaGd(PO_3)_4$ and its aim is to describe structural relaxation of this glass by the Tool–Narayanaswamy–Mazurin (TNMa) model. In order to determine material constants and the model parameters, the nonlinear regression analysis of experimental data obtained by TMA and thermodilatometry is used. The reason for this study is that the Ce^{3+}-doped glass is a promising material for the detection of γ- and X-rays for medical and technical applications due to its low cost and high intensity of radioluminescence [5, 6].

Theory

The TNMa model [2, 4] of structural relaxation is based on a detailed experimental examination of the temperature

dependence of dynamic viscosity of glass in isostructural state (T_f = const.) and that of undercooled melt under a metastable equilibrium ($T = T_f$). The principal idea for the application of this model is the relation between the relaxation time τ and the dynamic viscosity η:

$$\tau = \frac{\eta}{K}, \tag{1}$$

where the shear modulus K is the material constant.

The temperature dependences of dynamic viscosity of the metastable equilibrium melt can be well described either by the Vogel–Fulcher–Tammann (VFT) equation in the form:

$$\log\ \eta = A + \frac{B}{T - T_0} \tag{2}$$

or, in a limited temperature range, by means of the Andrade (AND) equation:

$$\log \eta = A' + \frac{B'}{T}, \tag{3}$$

where T is the thermodynamic temperature, A, A', B, B' and T_0 are adjustable constants. On the other hand, the temperature dependence of isostructural glass viscosity is well described by the AND equation [7].

In agreement with Mazurin [4], the temperature dependence of dynamic viscosity expressed by the VFT is used for the melt under metastable equilibrium, while for that of isostructural glass, Andrade's equation (AND) is applied. By combination of above equations, the following dependence of dynamic viscosity on temperature was obtained:

$$\log \eta(T, T_f) = \left(A + \frac{B}{T_f - T_0}\right)\frac{T_f}{T} + \left(1 - \frac{T_f}{T}\right)\log \eta_0, \tag{4}$$

where T_0 is set to zero when the AND equation is used for undercooled equilibrium melt viscosity, T_f is the fictive temperature and η_0 stands for the common (i.e. T_f independent) high temperature limiting viscosity value of the AND equation isostructural viscosity.

The empirical KWW function [3] is expressed by:

$$M(\xi) = \exp\left[-(\xi)^b\right], \tag{5}$$

where the parameter b ($0 < b \leq 1$) determines the width of the relaxation time distribution and ξ is the dimensionless relaxation time given by:

$$\xi = \int_0^t \frac{\mathrm{d}t}{\tau[T(t), T_f(t)]}, \tag{6}$$

where t is the time.

The time and temperature dependences of the sample length l and their changes determined from thermomechanical measurements depend on both the thermodynamic and the fictive temperatures according to the relation:

$$\mathrm{d}l = l_0\left(\alpha_g \mathrm{d}T + \Delta\alpha \mathrm{d}T_f\right), \tag{7}$$

where l_0 is the starting length of the sample, α_g and α_m are the thermal expansion coefficients (considered as temperature independent) of isostructural glass and metastable equilibrium melt, respectively, and $\Delta\alpha = \alpha_m - \alpha_g$.

The viscous flow is included in the model by:

$$\frac{1}{l}\left(\frac{\partial l}{\partial t}\right)_{T,T_f} = \frac{\sigma}{3\eta}, \tag{8}$$

where σ is the axial stress [8]. The relative sample length change ε can be expressed by:

$$\begin{aligned}\varepsilon = \frac{\Delta l}{l_0} \approx &\int_{T_1}^{T_2} \alpha_g \mathrm{d}T + \int_{T_{f,1}}^{T_{f,2}} \Delta\alpha \mathrm{d}T_f \\ &- \left(1 + \int_{T_1}^{T_2} \alpha_g \mathrm{d}T + \int_{T_{f,1}}^{T_{f,2}} \Delta\alpha \mathrm{d}T_f\right) \int_{t_1}^{t_2} \frac{\sigma}{3\eta(T, T_f)} \mathrm{d}t\end{aligned} \tag{9}$$

The full set of the unknown model parameters (and material constants) such as K, b, A (A'), B (B'), T_0, η_0, α_g and α_m will be determined using the nonlinear regression analysis [9–11] of the above equations.

Experimental

Glassy ingots of (10 × 10 × 50) mm^3 in magnitude with nominal composition of Ce:NaGd(PO$_3$)$_4$ were prepared by a direct synthesis of NaPO$_3$, GdPO$_4$ and P$_2$O$_5$ in stoichiometric relation and small amounts of CePO$_4$ as dopant. The mixture was heated up to 1,200 °C in a quartz crucible, cooled by pouring into a graphite mould, shortly tempered at 280 °C and then cooled down to room temperature [5, 6]. For the study of structural relaxation, the prismatic samples with the dimensions of (4 × 4 × 20) mm^3 were used.

Using a Netzsch TMA 402, three hysteresis loops were measured in the temperature range between approximately 570 and 750 K. The cooling and heating rates of the first loop were 10 K/min and those of other two loops were 5 K/min. The sample was loaded by a constant axial stress of 3.476 kPa.

The low temperature viscosity in the range between 10^8 and 10^{12} dPa s was determined from the deformation rate of a rectangular sample with an axial stress of 3.476 kPa.

Results and discussion

The thermal expansion coefficients of the glass, α_g, and the metastable melt, α_m, were calculated from the dilatometric cooling curve measured at the cooling rate of 5 K/min. The

values of $\alpha_g = (104 \pm 1)\cdot 10^7\ K^{-1}$ and $\alpha_m = (677 \pm 5)\cdot 10^7\ K^{-1}$ together with the glass transition temperature $T_g = (698 \pm 1)$ K were obtained by linear regression analysis of linear parts of the cooling curve (Fig. 1).

The measured values of dynamic viscosity of the undercooled melt are shown in Fig. 2 (points). The VFT and AND equations were used for the description of the measured equilibrium temperature dependence of viscosity. The nonlinear least squares method was used to find the parameters of both applied viscosity equations. The results are summarized in Table 1. As a better fit of the experimental data (i.e. higher F and significantly lower s_{apr}) was found for the VFT equation, only this equation was used in further calculations. The VFT fit of experimental data is presented in Fig. 2 (line).

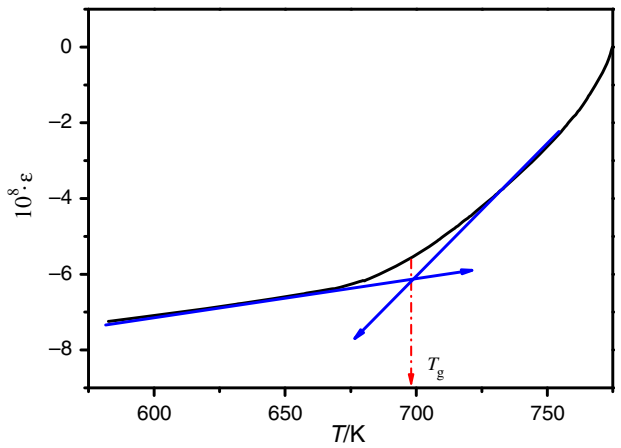

Fig. 1 Thermodilatometric cooling curve and determination of glass transition temperature

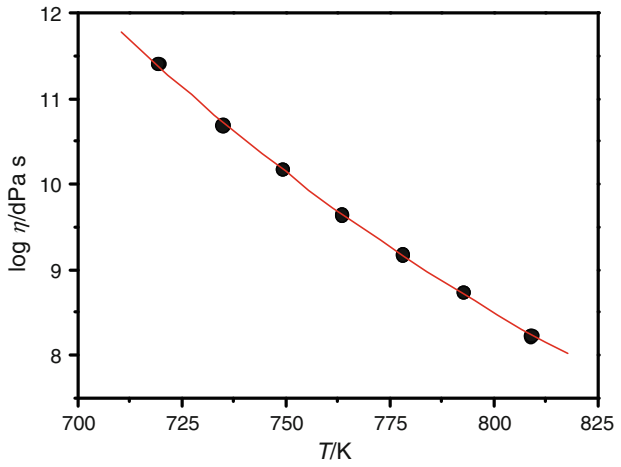

Fig. 2 Temperature dependence of equilibrium dynamic viscosity, points—experimental values, line—VFT fit

Table 1 Calculated parameters of the VFT and AND viscosity equations and statistical characteristics of the approximation

Model	Parameter	Value	Fisher's F	SD
VFT	A	-3.96 ± 0.49	2,861	0.019
	B/K	$5{,}350 \pm 382$		
	T_0/K	370 ± 14		
AND	A'	-16.98 ± 0.13	713	0.039

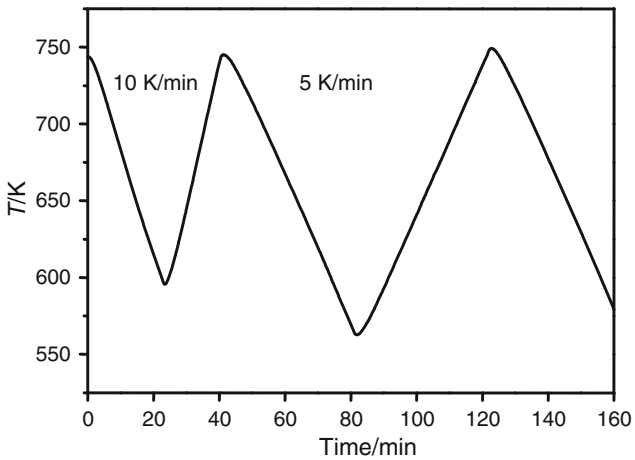

Fig. 3 The time–temperature regime of the TMA experiment, heating and cooling rates are 5 and 10 K/min, respectively

The time–temperature regime of the thermo-mechanical measurement is shown in Fig. 3. The parameters of the TNMa relaxation model (i.e. K, b, B, η_0, α_g and α_m) were determined by the nonlinear regression analysis of experimental data using the regression equation (9). With the aim of cross-checking of the model, the thermal expansion coefficients of glass and metastable melt as well as the B parameter of the VFT equation were also included in the set of "unknown" model parameters. As the starting estimates of both thermal expansion coefficients the values obtained from thermodilatometry were used. Similarly for the B parameter of the VFT equation, the starting value was taken from the viscosity analysis (Table 1). Temperature dependence of the sample relative deformation during the zig-zag thermal treatment is shown in Fig. 4. The calculated regression estimates of the parameters of TNMa relaxation model are summarized in Table 2. It is worth noting that estimates of thermal expansion coefficients as well as the estimate of the B parameter of the VFT equation are identical, within the tolerance limit, with the values obtained from thermodilatometry (thermal expansion coefficients) and temperature dependence of undercooled melt viscosity (B parameter of VFT equation). This confirms the validity of the relaxation model.

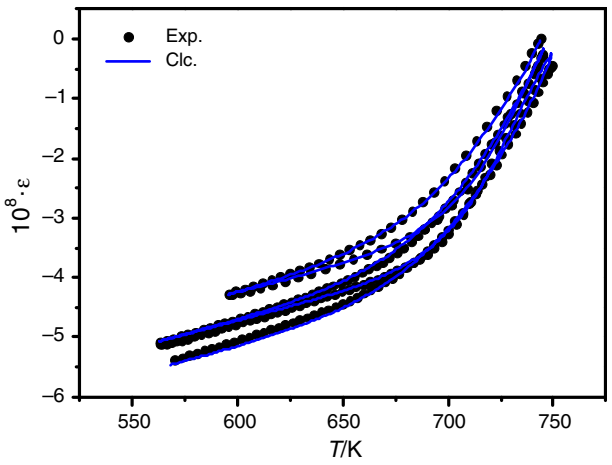

Fig. 4 Temperature dependence of sample relative deformation, points—experimental values, line—model, Eq. 9

Table 2 The values of the parameters of the TNMa model of structural relaxation and their standard deviations

Parameter	Value	SD
log K/dPa	9.52	0.03
b	0.491	0.011
B/K	5,286	1.4
10^7 α_g/K^{-1}	94	1.8
10^7 α_m/K^{-1}	647	5.8
log η_0/dPa s	−7.01	0.42
Fisher's F	4,523	
$10^6 \cdot s_{apr}$	55	

Conclusions

The structural relaxation of scintillating Ce-doped $NaGd(PO_3)_4$ glass was experimentally studied using non-isothermal thermo-mechanical analysis under different time–temperature regimes. The process was described by the TNMa relaxation model, and the VFT viscosity equation was used for the description of temperature dependence of viscosity, and the model parameters were determined by the nonlinear regression analysis of experimental data. The results of regression treatment show that TNMa realistically describes the structural relaxation of the glass studied. This is confirmed by low values of the standard deviation of approximation ($s_{apr} = 5.5 \cdot 10^{-5}$) that is on the level of experimental error as well as by the relatively high value of Fisher's statistics ($F = 4{,}523$). Another check is represented by good agreement of calculated and measured model parameters and material constants. It can be therefore concluded that the application of the TNMa model of structural relaxation correctly describes relaxation processes in studied scintillating Ce-doped $NaGd(PO_3)_4$ glass and that the method of gaining (evaluation) of model parameters is an extremely suitable and effective tool.

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