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DEVITRIFICATION OF Nd^{3+}-DOPED GLASSES IN THE AKERMANITE-GEHLENITE SYSTEM

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Abstract

The devitrification of glasses in the akermanite-gehlenite system [($C_2Al_{2-2y}Mg_ySi_{1+y}O_7$ ($0 \leq y \leq 1$)] doped with Nd^{3+} (2% mol) has been studied. DTA was used to determine the kinetics of the process. The Avrami law $\alpha = 1-\exp(-kt^n)$ with $n = 1$ was found to hold for doped gehlenite. For pure gehlenite, parameter n was determined to be 1.5. The activation energy of the devitrification process is independent of the presence of neodymium, and it is of the same order of magnitude as that for the viscous flow in molten silicates (ca. 650–750 kJ·mol^{-1}).

Keywords: akermanite-gehlenite system, DTA, kinetics

Introduction

The devitrification of glasses can lead to new materials called glass ceramics. In these materials, crystalline areas are embedded in a glass matrix. The chemical composition of the glass has to be selected in such a way that, during thermal treatment, a large number of crystal nuclei are formed and grown. The glass ceramics thus formed can have specific properties, for example a low thermal expansion. In numerous glass ceramics, the crystals dispersed in the glass matrix are so small and the refractive index of the crystals and residual glass are so close that they are transparent [1]. This has suggested the use of glass ceramics, doped for example with Cr^{3+} or rare earth cations, as luminescent materials for lasers, solar concentrators or phosphors [2]. Glass ceramics can have a high fluoroescence quantum efficiency, like crystals, and simultaneously they can easily formed as large rods or plates, like glass.

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The optical properties of neodymium-activated gehlenite-type materials have been widely studied in the literature. For example, single crystals of the gallium-containing compounds $Ca_{2-x}Nd_xGa_{2+x}Si_{1-x}O_7$ [3] and $SrGdGa_3O_7$:Nd [4] have been obtained, and laser action was observed in both cases.

Recently, we succeeded in growing single crystals of the aluminate $Ca_{2-x}Nd_xAl_{2+x}Si_{1-x}O_7$ by the Czochralski method [5, 6], and preliminary laser experiments under diode pumping were performed. This laser material appears promising, as it is well adapted to diode pumping and is expected to be tunable over more than 10 nm.

Glass ceramics formation needs a knowledge of the mechanism and kinetics of the nuclei formation and growth that takes place during the thermal treatment of the glass matrix. In addition to this, if glass ceramics are doped by optically active cations, an important point is the distribution of these cations between the crystals and glass matrix (this factor can determine the quantum efficiency of the glass ceramics material, which may decide its practical application). On the other hand, the presence in the glass matrix of additional dopants can strongly influence the kinetics and mechanism of devitrification with respect to non-doped glasses.

The system akermanite-gehlenite corresponds to the compositions $Ca_2Al_{2-2y}Mg_ySi_{1-y}O_7$, with y varying in the range $0 \leq y \leq 1$. The processes of devitrification in this system have been studied in detail, and the results have been presented in several papers [7–11]. The nucleation in this system has likewise been studied [12–15], including the influence of nucleating agents (TiO_2, CaF_2, Cr_2O_3, Fe_2O_3) on the crystallization phenomena in the considered system. Orsini and co-workers [7–11] studied rather the properties of this sytem without any dopants. In all the above-mentioned papers, the manners in which the glasses were obtained were almost the same. The starting materials (CaO or $CaCO_3$, MgO or $MgCO_3$, Al_2O_3, SiO_2) were mixed in appropriate proportions, melted in a platinum crucible in an electric furnace at ca 1500–1600°C, and then rapidly cooled. The devitrification of the samples has been investigated by differential thermal analysis (DTA) [7–11], thermodilatometric analysis [7], X-ray diffraction [7, 9–14] and scanning electron microscopy [7, 12–14].

Generally, it has been found that devitrification in this system proceeds in either one or two consecutive stages. At $y > 0.5$ (when the composition was closer to that of akermanite), the first stage of devitrification led to the formation of merwinite $Ca_3Mg(SiO_4)_2$. At higher temperatures, the crystalline phase with the same composition as the glass was observed and simultaneously the merwinite disappeared. When $y < 0.5$, only one stage was observed (crystallization of a phase with the same composition as the glass matrix). The temperature of devitrification increased with increasing x. It was found from DTA curves [7, 8] and X-ray diffraction spectra [9, 11] that the kinetics of devitrification follow the Johnson-Mehl equation (better known as the Avrami equation, which name will be used below) [3, 5]:

$$\alpha = 1 - \exp(-kt^{3/2}) \tag{1}$$

where α is the degree of devitrification and k is the rate constant.

In paper [3] on the basis of Eq. (1), an equation permitting determination of the activation energy from DTA peaks has been derived:

$$-\frac{E_\alpha}{2.30 \cdot RT_m} = \frac{3}{2}\lg(F) + \text{const} \tag{2}$$

where E_α is the activation energy, T_m is the temperature corresponding to the maximum of the peak in the DTA curve, and F is the linear heating rate [deg/min] in the DTA apparatus.

The activation energy for merwinite growth, was determined to be 165 kcal/mol (689.7 $kJ \cdot mol^{-1}$), a value of the same order as those found for viscous flow in molten silicates [16, 17]. This activation energy value for the first devitrification stage of the glass with $y<0.5$, within the limits of the hypothesis that the number of nuclei is constant at the growth temperature, represents mainly the activation energy for Al^{3+} ion diffusion.

It has also been found that the devitrification mechanism may be influenced by small traces of oxide impurities [3, 11]. The microstructure of devitrified glasses depends strongly on both glass composition and thermal treatment [11]. One of the most important results from the point of view of potential applications is given in [11]. The authors found that the appearance of microstructures which can give transparent but highly crystalline ceramics in the system $CaO-Al_2O_3-SiO_2$ is possible only in the presence of a fourth component (for example MgO or ZnO).

In the present paper, the kinetics of devitrification of glasses in the system akermanite-gehlenite doped with Nd^{3+} have been studied with the aim of the future preparation of new optical materials in this system. As far as we know, this system doped with either neodymium or other rare earth cations has never been studied before.

Experimental

Assuming that the formulas of gehlenite and akermanite doped with Nd^{3+} can be written as $Ca_{2-x}Nd_xAl_{2+x}Si_{1-x}O_7$ and $Ca_{2-x}Nd_xMgSi_{2-0.25x}O_7$, respectively, the five samples given in Table 1 correspond to the general formula:

$$Ca_{2-x}Nd_xAl_{(2+x)(1-y)}Mg_ySi_{1-x+y+0.75xy}O_7$$

where $x = 0.02$ and y is equal to 1, 0.8, 0.5, 0.2 or 0. They were prepared in the following way.

Starting materials: $CaCO_3$, MgO, Al_2O_3, SiO_2 and Nd_2O_3 (powders pure for analysis) were mixed in appropriate proportions, pressed in an isostatic press and sintered in an electric furnace at 1350°C for 72 h. After sintering, they were ground and sieved (grain size ≤ 80 μm). Powders obtained in this way were passed through a hydrogen-oxygen flame to melt them and the small molten droplets were quenched in cold water. As a result, samples (powders) of glasses composed of small balls with diameters ≤ 80 μm were obtained. X-ray analysis confirmed that samples 1–4 consisted of pure glassy phase. For sample 5, it was possible by X-ray diffraction to detect traces of crystalline gehlenite.

Table 1 Samples composition

Sample	Composition
1	$Ca_{1.980}Nd_{0.02}MgSi_{1.995}O_7$
2	$Ca_{1.980}Nd_{0.02}Al_{0.404}Mg_{0.8}Si_{1.792}O_7$
3	$Ca_{1.980}Nd_{0.02}Al_{1.01}Mg_{0.5}Si_{1.487}O_7$
4	$Ca_{1.980}Nd_{0.02}Al_{1.616}Mg_{0.2}Si_{1.183}O_7$
5	$Ca_{1.980}Nd_{0.02}Al_{2.02}Si_{0.98}O_7$

The neodymium content was chosen on the basis of the results of previous investigations concerning the optical properties of single crystals with compositions similar to those of the glasses studied in the present paper [5, 6].

For all the samples, detailed DTA analysis (Netzsch STA 409 apparatus connected online with a PC AT computer) were carried out at different heating rates (2, 5, 7.5, 10, 12.5 and 16 deg·min^{-1}). The sample mass was 65 ±1 mg in all experiments. The purpose was to determine both the activation energies and the kinetic equation relating to crystallization in the heated glasses. The results of these investigations are given below.

Results and discussion

a) Activation energy of the devitrification process

Figure 1 gives examples of DTA curves obtained at a heating rate of 10 deg·min^{-1}. The DTA curves obtained at other heating rates are similar, but with maxima shifted towards lower or higher temperatures, depending on the heating rate. As presented in [7–11] for samples with compositions closer to that of akermanite (samples 1–3), the devitrification passes through two overlapping stages. X-ray analysis of partially devitrified samples confirmed the

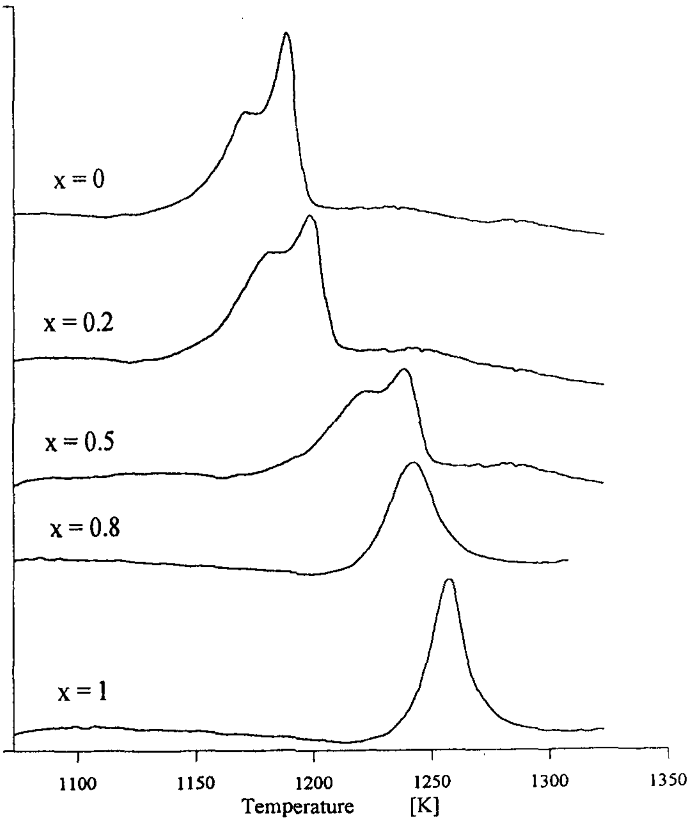

Fig. 1 DTA curves at heating rate 10 deg·min^{-1} (y=molar content of akermanite)

presence of merwinite which is in agreement with results in the papers mentioned above. Equation (2), derived in [3], was used to try to determine the activation energies by plotting the logarithm of the heating rate *vs*. the reciprocal of absolute temperature T_m. As an example, the results for sample 1 are given in Fig. 2(b). The activation energy values (indicated in Fig. 2(b) for sample 1), determined in the above way were higher than 1000 kJ·mol^{-1} for samples 1–5.

These values are significantly different from that given in [3] (689.7 kJ·mol^{-1}); they seem to be too high as concerns any real process associated with devitrification. Accordingly, we tried to determine the activation energy by applying an equation commonly used in DTA curve analysis, the Kissinger equation [18]:

$$\ln \frac{F}{T_m^2} = -\frac{E_\alpha}{RT_m} \tag{3}$$

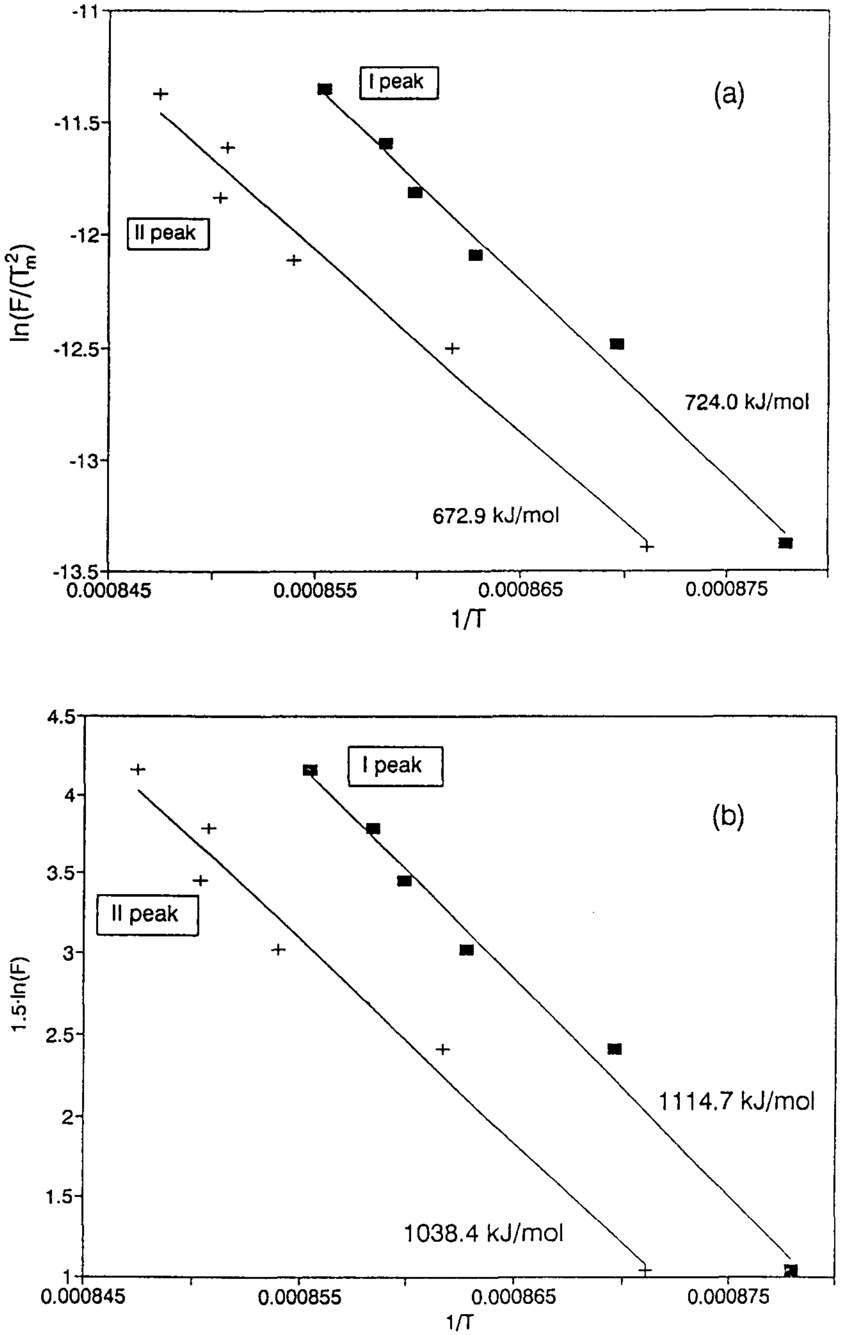

Fig. 2 Determination of activation energy from DTA peaks for akermanite (2% Nd) a) Kissingers's equation, b) Eq. (2)

The symbols have the same meanings as in Eq. (2).

Figure 2(a) shows the results of plotting the left-hand side of Eq. (3) *vs.* $1/T_m$ for sample 1. Table 2 gives the activation energies determined from the Kissinger equation for all studied samples.

The activation energy for the first peak corresponds to the crystallization of merwinite. The second DTA peak corresponds to merwinite disappearance and the formation of crystals with the same composition as the glasses. The activation energies for samples 4 and 5 correspond to a process like that occurring at peak II for samples 1–3.

Comparison of the activation energies in Table 2 with those obtained from Eq. (2) shows that the values from the Kissinger equation in our case are significantly lower, and approximately the same as that given in [3].

Table 2 Activation energies for the devitrification process (Kissinger's equation)

Sample	Activation energy/kJ·mol^{-1}	
	I peak	II peak
1	724	673
2	704	545
3	529	720
4	615	
5	708	

In our opinion, activation energy values higher than 1000 kJ·mol^{-1} can not correspond to any real process taking place during devitrification. Thus, the straight line dependency observed for samples 1–5 in the case of Eq. (2) has numerical meaning only.

Nevertheless, the significant differences between the (let us say apparent) activation energy values obtained from Eq. (2) for our samples and those studied in [3] could show the influence of neodymium on the devitrification in the studied system. To confirm this, two additional samples, pure akermanite $Ca_2MgSi_2O_7$ and gehlenite $Ca_2Al_2SiO_7$, were prepared in the same way as described above. For these two samples, DTA measurements were performed under the same conditions as for samples 1–5 and activation energies were determined from Eq. (2) and (3). Equation (2) gave values of 1087 and 1028 kJ·mol^{-1} for the first and second stages of devitrification for akermanite; for gehlenite, the value was 1128 kJ·mol^{-1}. With the Kissinger equation, the values were 724, 673 kJ·mol^{-1} (akermanite) and 731 kJ·mol^{-1} (gehlenite). The values obtained were of the same order of magnitude as for samples doped with neodymium. Thus, the difference between the activation energy values obtained with the Kissinger equation and the values from [3] could not be explained by the presence of neodymium. In our case, for both pure and doped samples Eq. (2) is not valid.

On the other hand, there are numerous examples showing that activation energies obtained with the Kissinger equation do not correspond to those determined by direct methods using the temperature dependence of the rate constants derived from the kinetic equation describing the studied process.

b) Determination of the kinetic equation describing the devitrification process

In order to find a kinetic equation describing the process of devitrification, it was necessary to determine the degree of devitrification of the samples as a function of time. In our work, the theory of the DTA peak, known as the Borhardt-Daniels theory [19], has been successfully applied for this. In the scope of this theory, the degree to which the process (reaction) has proceeded after time t can be expressed as:

$$\alpha(t) = 1 - \frac{1}{F_o}\left(f - \frac{C_p}{K}\Delta T\right) \qquad (4)$$

where F_o is the total area under the DTA peak, f is the area under the DTA peak in the time region (t, ∞) (in practice in the region: time t to the time at which the DTA trace reaches the baseline), C_p is the heat capacity of the sample, and K is the ratio $\Delta H/F_o$ (ΔH is the enthalpy change) under the conditions of the experiment.

The C_p and K values and the areas F_o and f were determined by using standard reference substances and procedures (based on commonly known methods applied in DTA) included in the Netzch software [20]. Equation (4) was applied to the DTA peaks for sample 5 and for pure gehlenite at different heating rates, and the α values were determined as a function of time and the temperature of the sample. The above procedure could only be applied when there were no overlapping DTA peaks, which was true for these samples.

Assuming that the kinetics of devitrification can be described by the general Avrami equation:

$$\alpha = 1 - \exp(-kt^n) \qquad (5)$$

where k and n are constants, and with the degree of devitrification as a function of time (or temperature), it was possible to fit the experimental data to Eq. (5) in the following way. If rate constant k follows the Arrhenius law $k=k_o\exp(-E_\alpha/RT)$, Eq. (5) can be written as

$$\ln\ln\frac{1}{1-\alpha}+\frac{E_{\alpha}}{RT}=n\ln t+\ln k_{o} \tag{6}$$

Having the set of values $\alpha[T(t)]$ and using the least square method:

$$\sum_{i}\left(\ln\ln\frac{1}{1-\alpha_{i}}+\frac{E_{\alpha}}{RT_{i}}-n\ln t_{i}-\ln k_{o}\right)^{2}\rightarrow \min$$

we can find the values of n, k_o and E_α.

The above procedure was used for DTA peaks obtained for sample 5 and pure gehlenite at different heating rates. Figures 3 and 4 give examples of the results obtained for DTA peaks at a linear heating rate of 2 deg·min^{-1} for both samples.

The values of the fitted parameters are indicated in the Figures. In the case of samples 5, the values of n and E_α obtained by mathematical treatment of DTA peaks corresponding to different heating rates varied in the regions $0.89\leq n\leq 1.09$ and $695\leq E_\alpha\leq 732$ kJ·mol^{-1}. Those for pure gehlenite were in the regions $1.40\leq n\leq 1.52$ and $707\leq E_\alpha\leq 741$ kJ·mol^{-1}.

Thus, it was finally found that the kinetics of devitrification for pure and Nd^{3+}-doped samples can be described by using the Avrami equation. The parameters n for pure and doped samples appeared significantly different. According to statistical analysis, it can be assumed that n is equal to 1.5 or 1.0 for pure and doped samples of gehlenite, respectively. This shows the strong influence of the presence of neodymium on the mechanism of devitrification, which is rather an unexpected result if we take into account the relatively low neodymium content.

Thus, the presence of neodymium seems to influence nucleus formation and growth. If we assume that the large and highly charged neodymium cation is a nucleating agent, then the presence of neodymium in the sample leads to a large number of nuclei at the beginning of the devitrification process. Under these conditions, a kinetic law describing crystallization with the assumption of a constant number of nuclei (compatible with $n=1$) seems to be likely [17].

On the other hand, the activation energy corresponding to the devitrification process does not seem to be affected by the presence of neodymium. Its magnitude shows good agreement with the values found from the Kissinger law. When our results are compared with those from [3], taking into account pure gehlenite only, it can be said that exactly the same Avrami equation with $n=1.5$ described the kinetics of devitrification in both cases. Nevertheless, there is still one difference: Eq. (2), derived in [3] on the assumption of the validity Avrami law, can not be applied to our data, because it gives too high activation energy values. In our opinion, one of the assumptions applied in [3] is doubtful. This con-

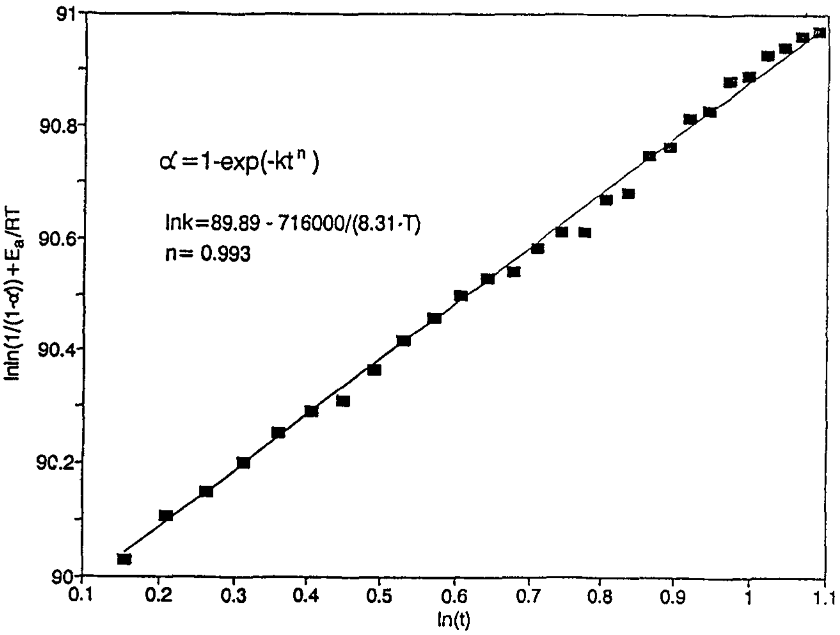

Fig. 3 Plot of $\ln\ln(1/(1-\alpha))+E_\alpha/RT$ vs. ln *t* for gehlenite (2% Nd)

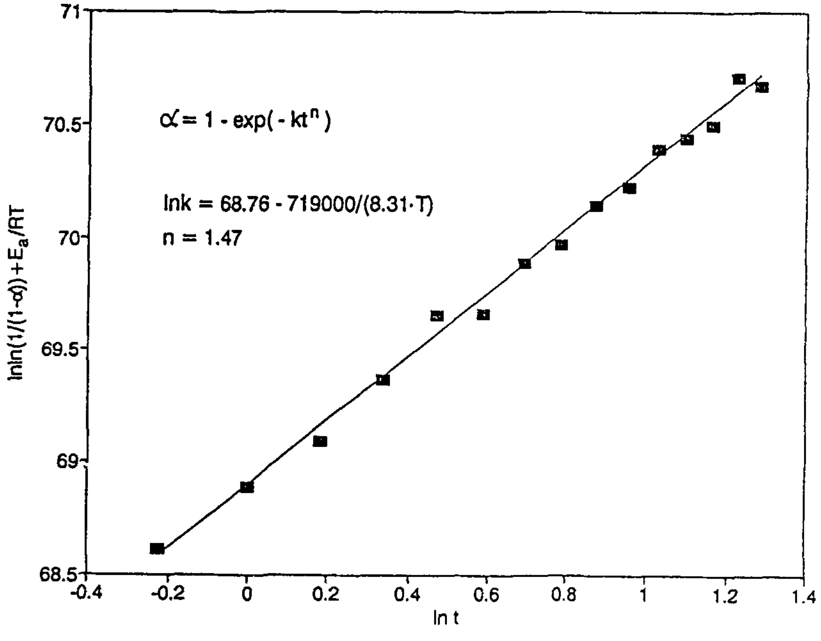

Fig. 4 Plot of $\ln\ln(1/(1-\alpha))+E_\alpha/RT$ vs. ln *t* for pure gehlenite

cerns the time of the transition of glass into crystals, which was assumed to be inversely proportional to the heating rate in the DTA apparatus, a fact which could not be confirmed in the scope of our results. However, exactly the same kinetic equation could be applied for pure gehlenittie glass samples in both studies, so that Eq. (2) should give approximately the same E_α values, even if these values have numerical meaning only. If not, it means that different shifts of the DTA peaks as a function of the heating rate were observed in each case. We have no explanation for this.

The detailed interpretation of the kinetics by using DTA peaks was performed for gehlenite samples only. The problem of the kinetic equation describing the devitrification of samples 1–4 with different compositions in the akermanite-gehlenite system remains open. In a future paper, we will show that, by interpretation of the emission spectra of Nd^{3+} in the studied glasses, it appears possible to determine the degree of crystallization for partially devitrified samples as a function of time. It will also be shown that the Avrami law with $n=1$ can be applied to describe the kinetics of devitrification for all Nd^{3+}-doped samples studied in the present work [18].

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Zusammenfassung — Es wurde die Entglasung von Gläsern in dem mit Nd^{3+} (2 mol%) versetzten Akermanit-Gehlenit-System [$C_2Al_{2-2y}Mg_ySi_{1+y}$ ($0\leq y \leq 1$)] untersucht. DTA wurde zur Bestimmung der Kinetik des Prozesses eingesetzt. Für versetztes Gehlenit fand man ein Zutreffen der Avrami'schen Regel $\alpha=1-\exp(-kt^n)$. Für reines Gehlenit erhielt man für den Parameter n einen Wert von 1,5. Die Aktivierungsenergie des Entglasungsprozesses ist unabhängig von der Gegenwart von Neodym und hat die gleiche Größenordnung wie für den viskosen Fluß in geschmolzenen Silikaten (ca. 650–750 kJ/mol).