Original Paper

Influence of aluminium and neodymium additions on the structural relaxation of silica glasses – Raman investigations

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Raman spectra of silica glasses obtained from melted rock crystal without additions and of glasses doped with aluminium and neodymium were examined. The relative intensity of the 606 cm^{-1} band in Raman spectra was evaluated. The occurrence of this band is due to the presence of defects in the glass structure. The time required by the 606 cm^{-1} band to attain the equilibrium intensity at 1000 °C has been defined as the relaxation time of the silica glass structure under the given conditions of heat treatment. It has been found that additions in silica glass in the form of Al^{3+} and Nd^{3+} ions do not affect the value of the equilibrium intensity of the 606 cm^{-1} band and thus, they do not affect the equilibrium concentration of the defects which give rise to this band. However, the additions have a distinct effect on the length of the relaxation time of the glass structure. Neodymium, when occurring as a single addition of silica glass, reduces the relaxation time, whereas aluminium clearly makes the structure relaxation difficult. Glass doped both with aluminium and neodymium ($Al_2O_3/Nd_2O_3 = 4$) behaves similarly as glass doped with aluminium only. The role of additions in the structure of silica glass was discussed on the basis of the investigation results.

Einfluß von Aluminium- und Neodymzusätzen auf die Strukturrelaxation von Kieselglas – Raman-Untersuchungen

Aus Bergkristall wurden Kieselgläser erschmolzen, die z. T. mit Aluminium und/oder Neodym dotiert wurden. Die Proben wurden Raman-spektroskopisch untersucht, wobei die relative Intensität der Raman-Bande bei 606 cm^{-1} ausgewertet wurde. Das Auftreten dieser Bande weist auf Defekte in der Glasstruktur hin. Die Zeit, bis die 606-cm^{-1}-Bande bei einer Temperatur von 1000 °C ihre Gleichgewichtsintensität erreicht hat, wurde als Relaxationszeit der Kieselglasstruktur bei der gegebenen Wärmebehandlung definiert. Es zeigte sich, daß ins Kieselglas eingebrachte Dotierungen in Form von Al^{3+}- und Nd^{3+}-Ionen nicht die Gleichgewichtsintensität der 606-cm^{-1}-Bande beeinflussen und damit auch nicht die Gleichgewichtskonzentration der Defekte, die diese Bande verursachen. Die Beimengungen haben jedoch eine deutliche Wirkung auf die Relaxationszeit der Glasstruktur. Neodym reduziert diese Zeit, wenn es allein vorhanden ist, während Aluminium die Relaxation deutlich erschwert. Glas, das sowohl mit Aluminium als auch mit Neodym dotiert ist ($Al_2O_3/Nd_2O_3 = 4$), verhält sich ähnlich wie Glas, das nur Aluminium enthält. Auf der Grundlage der erhaltenen Meßergebnisse wird die Rolle der Dotierungen in der Kieselglasstruktur diskutiert.

1. Introduction

The development of modern technology has brought about a growing interest in silica glass doped with transition metals and rare earth elements. The incorporation of these elements into the structure of silica glasses is facilitated by aluminium which is introduced in the form of various chemical compounds, in amounts usually not exceeding 1 to 2 wt% Al_2O_3. An accurate determination of the structural positions taken by the additions in silica glass is a difficult problem and it is subject of current investigations. None of the investigation methods has supplied so far any direct information about the coordination number of the rare earth elements; the problem of coordinating the aluminium ions is also open for discussion. In the light of to-date investigations it is also difficult to give a definite answer whether the additions in the silica glass create fragments of their own crystalline structures typical of the given element or whether they enter into the structure of silica glass by forming substitutive and interstitial solid solutions. In case of transition metals and rare earth elements valuable information concerning the structure is obtained through the examinations of optical spectra [1 to 3], and in case of aluminium the examinations of electron paramagnetic resonance [4 and 5].

In the present study Raman spectroscopy has been applied for this purpose. A characteristic feature of the Raman spectrum of silica glass is the presence of two bands associated with the noncrystalline structure, namely the presence of a wide band within the range of the wavenumbers 450 to 500 cm^{-1} with the sharp maximum at 495 cm^{-1} and a single band with the maximum at 606 cm^{-1}. The 495 and 606 cm^{-1} bands are referred to in literature as the "defect" ones, and ascribed to the vibration of certain defected fragments of the glass structure, however, opinions concerning the nature of this defects differ [6 to 9]. The to-date assumption is that these defects are associated with deformation of the silicon–oxygen bonds [8 and 9].

From the investigations carried out so far it follows that the intensity of the defect bands varies

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and it depends on a number of factors, among others, on the thermal history of the glass [10], neutron irradiation [11], and the presence of impurities in the form of OH^- and F^- anions [7 and 10]. It has been found that at a definite temperature with increasing time of heating the intensity of the 495 and 606 cm^{-1} bands decreases until a certain equilibrium intensity is attained which is characteristic for the given temperature and which does not change any more. This temperature at which the glass has attained the state of apparent equilibrium and from which it has been rapidly cooled to ambient temperature is referred to as the fictive temperature. The increase of the fictive temperature leads to an increase in the intensity of the 495 and 606 cm^{-1} bands in the Raman spectrum of silica glass. This same effect can also be obtained through neutron irradiation. On the other hand, the presence of the OH^- and F^- anions in the glass does not affect the equilibrium intensity of the 495 and 606 cm^{-1} bands, but it considerably reduces the time required to attain the state of apparent equilibrium at the given temperature.

In the light of these facts it was to be expected that the silica glass additions in the form of ions of alien elements (aluminium, rare earths) might also bring about a change in the relaxation time of the structure of silica glass, which in case of Raman investigations should be signified by the length of time necessary for the defect bands to attain the equilibrium intensity.

2. Experimental

Raman examinations have been carried out for the following glasses:

a) pure silica glass;

b) silica glass doped with an amount of aluminium equal to 0.1 to 1.0 mol% Al_2O_3;

c) silica glass doped with neodymium to the amount of 0.05 mol% Nd_2O_3;

d) silica glass doped with aluminium and neodymium to the amount (in mol%) of 0.2 Al_2O_3 + 0.05 Nd_2O_3.

The glasses were melted from rock crystal with a total amount of impurities equal to 47 ppm. Aluminium was introduced in the form of hydrated aluminium chloride $AlCl_3 \cdot 6\,H_2O$, neodymium in the form of the oxide Nd_2O_3. The melting process took place in a vacuum electric furnace in graphite crucibles. At the same time, in order to eliminate the effect of the possible presence of the OH^- groups in the examined glasses on the character of Raman spectra, all the glasses were examined in infrared within the range 3 200 to 3 600 cm^{-1}. The number of the OH^- groups in the glasses was similar, of the order of a few parts per million. Thus, in practice, the examined glasses might be regarded as "anhydrous".

Raman spectra of the glasses were obtained using a Cary 82 (Varian (GB)) spectrophotometer. The source of electromagnetic monochromatic radiation was an Ar 514.5 nm laser. The glass samples selected for examinations had the shape of plane-parallel polished plates of identical size. Raman spectra were

Table 1. Results of Raman investigations of aluminium-doped silica glasses after heating at 1000 °C (fictive temperature T_f = 1300 °C)

Al_2O_3 content in mol%	annealing time in h	intensity ratio I_{606}/I_{800}	relaxation time in h
0	0	0.368 ± 0.005	16
	2	0.321 ± 0.003	
	4	0.313 ± 0.003	
	6	0.277 ± 0.007	
	8	0.232 ± 0.007	
0.1	0	0.368 ± 0.003	22
	2	0.360 ± 0.005	
	4	0.320 ± 0.007	
	6	0.295 ± 0.003	
	8	0.258 ± 0.004	
0.2	0	0.370 ± 0.002	28
	2	0.338 ± 0.007	
	4	0.321 ± 0.003	
	6	0.304 ± 0.003	
	8	0.277 ± 0.005	
0.5	0	0.370 ± 0.002	24
	2	0.368 ± 0.002	
	4	0.321 ± 0.003	
	6	0.318 ± 0.004	
	8	0.265 ± 0.002	
1.0	0	0.368 ± 0.002	18
	2	0.332 ± 0.004	
	4	0.313 ± 0.003	
	6	0.282 ± 0.004	
	8	0.242 ± 0.006	

Table 2. Results of Raman investigations of doped silica glasses after heating at 1000 °C (fictive temperature T_f = 1300 °C)

kind of glass	annealing time in h	intensity ratio I_{606}/I_{800}	relaxation time in h
SiO_2	0	0.368 ± 0.005	16
	2	0.321 ± 0.003	
	4	0.313 ± 0.003	
	6	0.277 ± 0.007	
	8	0.232 ± 0.007	
SiO_2 + + 0.05 mol% Nd_2O_3	0	0.368 ± 0.003	12
	2	0.304 ± 0.005	
	4	0.277 ± 0.007	
	6	0.212 ± 0.003	
	8	0.192 ± 0.007	
SiO_2 + + 0.2 mol% Al_2O_3	0	0.370 ± 0.003	28
	2	0.338 ± 0.007	
	4	0.321 ± 0.003	
	6	0.304 ± 0.003	
	8	0.277 ± 0.005	
SiO_2 + 0.2 mol% Al_2O_3 + 0.05 mol% Nd_2O_3	0	0.370 ± 0.002	28
	2	0.338 ± 0.003	
	4	0.324 ± 0.002	
	6	0.288 ± 0.022	
	8	0.277 ± 0.005	

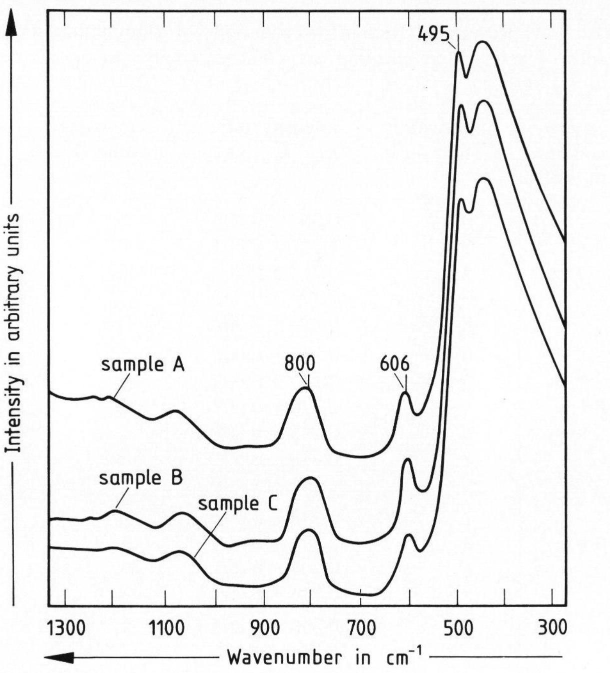

Figure 1. Raman spectra for various silica glasses after heating at 1000 °C for 8 h (fictive temperature T_f = 1300 °C). Sample A = SiO_2, sample B = SiO_2 + 0.2 mol% Al_2O_3, sample C = SiO_2 + 0.05 mol% Nd_2O_3.

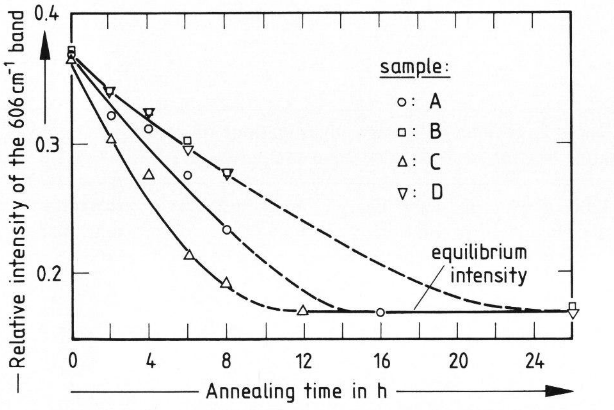

Figure 2. Relative intensity of the 606 cm^{-1} band versus annealing time for various silica glasses. Sample A = SiO_2, sample B = SiO_2 + 0.2 mol% Al_2O_3, sample C = SiO_2 + 0.05 mol% Nd_2O_3, sample D = SiO_2 + 0.2 mol% Al_2O_3 + 0.05 mol% Nd_2O_3.

measured in the 90° scattering configuration within the range of the wavenumbers from 100 to 1300 cm^{-1}.

Evaluation of the intensity of the defect bands was restricted to the 606 cm^{-1} band and it was carried out with respect to the band situated at 800 cm^{-1}, regarding it as an internal standard. The 800 cm^{-1} band is the most stable one and its origin is not associated with glass defects [12]. To evaluate the relative intensity of the 606 cm^{-1} band, the integral intensities of the 606 and 800 cm^{-1} bands after removing the background were measured using a

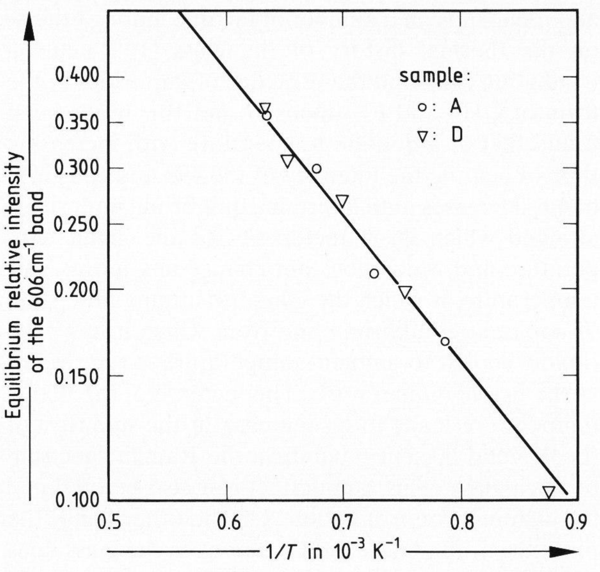

Figure 3. Temperature dependence of the equilibrium relative intensity of the 606 cm^{-1} band for various silica glasses. Sample A = SiO_2, sample D = SiO_2 + 0.2 mol% Al_2O_3 + 0.05 mol% Nd_2O_3.

planimeter and the ratio of intensities I_{606}/I_{800} calculated.

As the thermal history of glasses affects the intensity of the defect bands in Raman spectrum all the glasses were preheated at a temperature of 1300 °C. The heating was performed in an electric furnace in protective ampoules made of quartz glass. After a definite heating period the samples were removed from the furnace and cooled rapidly in water. The heating was carried out until the moment at which the relative intensity of the 606 cm^{-1} band did not change any further. For all the examined glasses this intensity was practically identical.

The glasses heated at 1300 °C to reach the equilibrium state were subsequently subjected to heat treatment at 1000 °C for different periods of time being treated in the same way as at 1300 °C. After successive heating periods the Raman spectra were recorded and the relative intensity of the 606 cm^{-1} band determined until the equilibrium intensity was reached. The time required to attain the equilibrium intensity has been defined as the relaxation time.

The results are listed in tables 1 and 2. The diagrams in figure 1 show the Raman spectra of silica glasses with a fictive temperature of 1300 °C after annealing at 1000 °C for 8 h; the diagrams in figure 2 show changes in the relative intensity of the 606 cm^{-1} band as a function of the annealing time for glasses containing characteristic amounts of additions.

In order to determine the temperature-dependent equilibrium intensity of the 606 cm^{-1} band the glasses were heated to the equilibrium state also at the temperatures 950, 1050, 1100, 1150, 1200, 1250 °C. It has been found that, similarly as at the temperatures 1000 and 1300 °C the values of the equilibrium intensity do not depend on the kind of the examined glass. The temperature dependence of equilibrium intensity of the 606 cm^{-1} band for silica glass without additions and for glass doped with aluminium and neodymium has been illustrated on the diagram in figure 3.

3. Results and discussion

The obtained experimental results indicate that, according to the expectations, the additions in the form of ions of alien elements in the structure of silica glass affect the time necessary to attain the equilibrium concentration of defects producing the 606 cm^{-1} band in Raman spectrum. A different effect was observed when the glass was doped only with aluminium from that observed when it was doped exclusively with neodymium. Glass doped both with aluminium and neodymium at the molar ratio $Al_2O_3/Nd_2O_3 = 4$ behaved in the same way as glass containing aluminium only.

When the amount of aluminium from 0.1 to 1 mol% Al_2O_3 was incorporated into the glass structure a distinct increase of the relaxation time of the glass structure was observed; this time increasing at first along with increasing concentration of aluminium and decreasing afterwards. However, even at 1 mol% Al_2O_3 content the relaxation time is longer than that for pure silica glass (table 1). The prolongation of the relaxation time of the structure of silica glass due to the presence of aluminium is an indication that aluminium hinders the rearrangement of the structural units and attainment of a more advantageous state at the given temperature in thermodynamic terms. This fact is most probably associated with the denser packing of the glass structure. Aluminium probably does not cause the breaking-off of the bridging bonds nor the formation of active, non-bridging oxygen ions, as this would facilitate, similarly as in case when OH^- groups are present in the glass [10], the rearrangement of the structural units and reduction of the relaxation time. It appears that the results of Raman examinations favour the model proposed by Lacy [13 to 15] according to which in silica glass aluminium forms triple clusters composed of tetrahedra (AlO_4), having common oxygen. Moreover, to maintain electroneutrality, tree triple clusters require the presence of two aluminium ions in the octahedral voids. Such arrangements bring about as a result denser packing of the glass structure in relation to the silicon-oxygen network made up exclusively of tetrahedra (SiO_4) linked at corners.

When an amount of neodymium, equal to 0.05 mol% Nd_2O_3, is incorporated into the structure of silica glass the relaxation time is shortened with respect to silica glass without additions (table 2). Thus, the observed effect is similar to that which takes place in the presence of the OH^- groups in the glass [10], the substitution of oxygen by these groups implying the breaking-off of the bridging bonds in the silicon-oxygen network. Defects of this type facilitate the rearrangement of the structural units which enables quicker relaxation of the glass structure. By analogy it can be assumed that when silica glass is doped with neodymium oxide the addition of it results also in the breaking-off of the bridging bonds and in the formation of non-bridging oxygen ions which simultaneously compensate for the excess positive charge connected with the appearance of trivalent neodymium ions in the interstitial positions. This would suggest that the rare earth elements play the role of modifiers of the silicon-oxygen network.

When silica glass was doped simultaneously with aluminium and neodymium ($Al_2O_3/Nd_2O_3 = 4$) the relaxation time was prolonged similarly as in case of glass containing aluminium only (table 2). This indicates that the character of the structural changes in silica glass is determined by aluminium, while the neodymium ions become located in its vicinity. The neodymium ions will probably compensate for excess negative charge of the triple clusters made up of tetrahedra (AlO_4). Thus, they will play a similar role as the aluminium ions in the interstitial positions of glasses doped with aluminium only. This implies also that the presence of neodymium ions in interstitial positions does not require the breaking-off of the bridging bonds and the formation of non-bridging, active oxygen ions in order to retain electroneutrality. This accounts for a similar behaviour of glasses doped with aluminium only and those doped simultaneously with aluminium and neodymium – during the heat treatment.

From the obtained experimental data it follows that equilibrium intensities of the 606 cm^{-1} bands in the spectra of the examined glasses are very similar at the given temperature independently of the amount and kind of additions. The rectilinear dependence of the equilibrium intensity of the 606 cm^{-1} band on the inverse of fictive temperature (figure 3) indicates that this relation satisfies the Arrhenius equation:

$$I_e = C \exp(-\Delta E/k\,T) .$$

The "activation energy" calculated on this basis is equal to 0.45 eV. This result is in agreement with the results obtained by Mikkelsen and Galeener [10] for glasses with impurities in the form of OH^- and F^- anions (0.44 eV). This is evidence that additions in silica glass both in the form of cations and anions do not affect the equilibrium concentration of defects producing the 606 cm^{-1} band in Raman spectrum. The nature of these defects is thus not dependent on any type of additions in the silica glass. The additions affect only the duration of relaxation time of silica glass structure.

4. References

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