

IR and Raman study of calcium aluminosilicate glasses of the composition $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$

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Vibrational spectra are measured for calcium aluminosilicate glasses with the composition (in mol%) $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$. The OH bands show a systematic change with x in both MIR and NIR regions. The strongly asymmetric band at about 3550 cm^{-1} shifts to lower wave numbers with increasing x . In the same way the OH combination band at about 4500 cm^{-1} shifts to lower wave numbers. For the 3550 cm^{-1} band an extinction coefficient of about $60\text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ is suggested for all the samples with x from 15 to 32. For the 4500 cm^{-1} band the extinction coefficient decreases from 1.0 to $0.49\text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ with increasing x from 15 to 32. Systematic changes in the Raman and IR reflectance spectra reflect the substitution of Al^{3+} for Si^{4+} and a corresponding increase of Ca^{2+} in the network. Thus, the vibrational spectra can be related to a fully polymerized network without or with a small amount of nonbridging oxygens also for glasses with $x \geq 25$.

1. Introduction

Infrared and Raman spectroscopy have been used extensively to investigate structures of aluminosilicate glasses. Most of the work was carried out either to study hydroxyls and water in glasses or to study the network structure, although it is known that the structure of hydroxyls in glasses depends on the network structure. This work aims to study vibrational spectra of glasses with the composition (in mol%) $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ ($15 \leq x \leq 32$) and to analyse vibrational bands of both the OH groups and the network. In particular the OH structure for these glasses depends on the amount and on the role of both calcium and aluminium. Calcium may act as a network modifier breaking bridging oxygen bonds to form nonbridging oxygen or as a charge balancer for the Al^{3+} . The chosen compositional series of aluminosilicate glasses include high-silica glasses ($15 \leq x < 25$), anorthite glass ($x = 25$), and low-silica glasses ($25 < x \leq 32$). All the Ca^{2+} can act as charge balancer because the molar ratio $\text{CaO}/\text{Al}_2\text{O}_3$ is equal to 1.

Calcium aluminosilicate glasses with compositions along the "charge-balanced" $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ join were studied by Raman spectroscopy [1 to 4]. A number of samples with components SiO_2 , CaO and Al_2O_3 , including anorthite glass, were studied by infrared reflectance spectroscopy [5]. The general conclusions are that all of these glasses have structures

based on tetrahedral aluminosilicate networks and Al^{3+} is charge-balanced by Ca^{2+} so that the glass network is nominally fully polymerized with Ca^{2+} cations occupying sites within this network. These conclusions were confirmed by ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) spectroscopical investigations of calcium aluminosilicate glasses along the join with molar ratio $\text{CaO}/\text{Al}_2\text{O}_3 = 1$ up to $x = 25$ [6]. Aluminium and silicon were found in tetrahedral coordination of a three-dimensional network structure of only $\text{Q}^{4(1)}$ structural units. For low-silica glasses NMR results are opposite. So-called extra-network aluminium and a considerable amount of Q_3^3 units were found for low-silica glasses with x between 29.8 and 36.5 by Engelhardt et al. using ^{29}Si NMR and ^{27}Al NMR [6]. But for a glass with $x = 33.3$ a fully polymerized network, containing only Q^4 units, was inferred from ^{29}Si NMR and ^{27}Al NMR measurements [7].

This work presents OH vibration bands in the MIR and NIR regions, which are discussed in relation to a network structure, characterized by IR reflectance and Raman spectra of the calcium aluminosilicate glasses and compared with quartz glass spectra. For these glasses the hydrogen content was determined by nuclear reaction analysis (NRA), which allows one to calculate the extinction coefficients of the OH bands and to study

¹⁾ Q_m^n denotes SiO_4 tetrahedra with n bridging oxygens (BO) and m Si-O-Al bridges. $4 - n$ is the number of nonbridging oxygens (NBO).

Table 1. Studied samples of vitreous silica and of the calcium aluminosilicate glasses with the composition (in mol%) $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ ($15 \leq x \leq 32$); thickness d in mm

| glass no. | x in mol% | d in mm |
|-----------|-------------|-----------|
| 1 | 0 | 4.91 |
| 2 | 15 | 0.48 |
| 3 | 15 | 4.90 |
| 4 | 17 | 0.49 |
| 5 | 17 | 4.74 |
| 6 | 18 | 0.48 |
| 7 | 18 | 4.95 |
| 8 | 22 | 0.50 |
| 9 | 22 | 4.66 |
| 10 | 25 | 0.50 |
| 11 | 25 | 4.75 |
| 12 | 27 | 4.97 |
| 13 | 30 | 0.49 |
| 14 | 30 | 4.93 |
| 15 | 32 | 0.50 |
| 16 | 32 | 4.63 |

the behaviour of these extinction coefficients in dependence on glass composition.

2. Experimental

Calcium aluminosilicate glasses with the composition (in mol%) $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ (table 1) were prepared by melting dried calcium carbonate, aluminium oxide and quartz sand [6 and 8]. The glasses were molten in Pt/Rh crucibles in an induction furnace at 1600 °C and carefully cooled with a rate of 0.5 K min⁻¹ in the range between 900 and 400 °C. The commercial vitreous silica Vitrosil was included in the study for comparison.

The water content of the studied glasses was determined by NRA as described in a previous study [9]. The ¹⁵N technique, which relies on the resonant nuclear reaction ¹H(¹⁵N, α γ)¹²C, was employed. The hydrogen content of the glasses was obtained from the flat region of the hydrogen concentration profiles without etching the samples. A typical hydrogen depth profile is shown in figure 1.

Doubly polished plates of 0.5 or 5.0 mm thickness were prepared for MIR and NIR transmission measurements. Infrared absorption spectra were measured in the region from 6000 to 1400 cm⁻¹, with a resolution of 2 or 4 cm⁻¹. All spectra were related to 1 mm sample thickness. The reflection losses at the sample surfaces were eliminated by subtracting the absorbance values at 4250 cm⁻¹ from the MIR spectra and at about 4700 cm⁻¹ from the NIR spectra, respectively. Specular IR reflectance spectra of the 5 mm thick samples were collected using a reflectance device with a fixed 11° angle of incidence, in the MIR and FIR regions from 4000 to 50 cm⁻¹, with a resolution of 2 or 4 cm⁻¹. The spectra were normalized to the aluminium mirror reflectance.

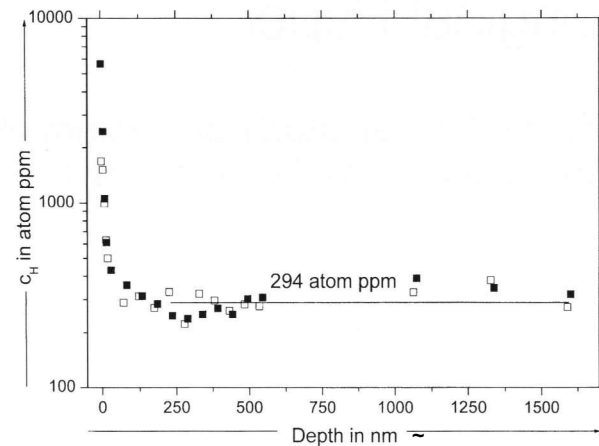


Figure 1. Hydrogen depth profile of the glass 27 $\text{CaO} \cdot 27 \text{Al}_2\text{O}_3 \cdot 46 \text{SiO}_2$. The symbols indicate the two sides of the sample. The line indicates the depth range used for the determination of the hydrogen content.

tance. All the IR spectra were obtained using a vacuum Fourier transform infrared spectrometer IFS 66v (Bruker, Ettlingen (Germany)).

Raman spectra were measured from the same 5 mm thick samples. For this, two pairs of the opposite faces of the samples were polished. The measurements were performed with 90° scattering geometry on a Dilor XY Raman spectrometer (Dilor, Bensheim (Germany)) equipped with an N₂-cooled CCD camera as detector. The samples were excited by an Ar⁺ laser (75 to 600 mW at 514.5 nm). Spectra were accumulated for 10 to 100 s.

3. Results

3.1 OH vibration bands

The OH bands in the MIR and NIR spectra of the glasses vary systematically with increasing x (figures 2 and 3). In the spectra of vitreous silica the OH stretching vibrations appear as a narrow asymmetric band at 3668 cm⁻¹. In contrast to this, in the spectra of the calcium aluminosilicate glasses broad and very asymmetric bands were observed, which shift from 3558 to 3519 cm⁻¹ with increasing x from 15 to 32. In the NIR spectrum the OH band was observed at 4522 cm⁻¹ with a shoulder at about 4450 cm⁻¹ for vitreous silica. In the spectra of the calcium aluminosilicate glasses the broad band shifts from 4514 to 4460 cm⁻¹ with increasing x .

The spectrum of vitreous silica shows a weak shoulder at about 3850 cm⁻¹. In the spectra of the calcium aluminosilicate glasses this shoulder appears at about 3900 cm⁻¹ and broadens to higher wave numbers with increasing x , or an additional band grows at about 4050 cm⁻¹ with increasing x .

Systematic changes in the spectra were also recorded in the range below 3000 cm⁻¹, where the measured ab-

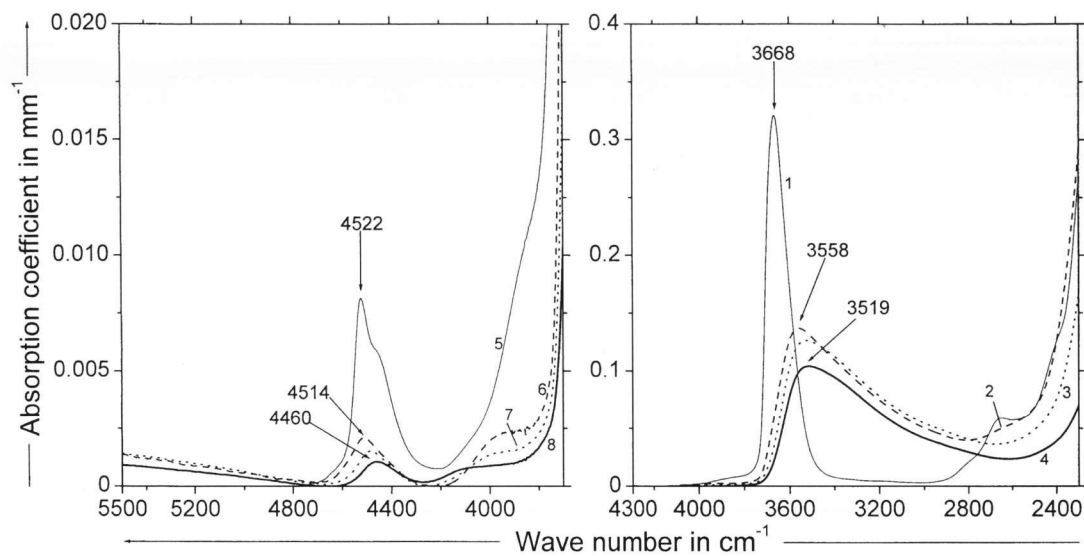


Figure 2. IR spectra of selected glass samples, scaled to 1 mm sample thickness and related to a water content of $0.02 \text{ mol} \cdot \text{l}^{-1}$; curve 1: glass no. 1, vitreous silica; curve 2: glass no. 2, $x = 15$ (broken line); curve 3: glass no. 10, $x = 25$ (dotted line); curve 4: glass no. 15, $x = 32$ (dark line); curve 5: glass no. 1, vitreous silica; curve 6: glass no. 3, $x = 15$ (broken line); curve 7: glass no. 11, $x = 25$ (dotted line); curve 8: glass no. 16, $x = 32$ (dark line).

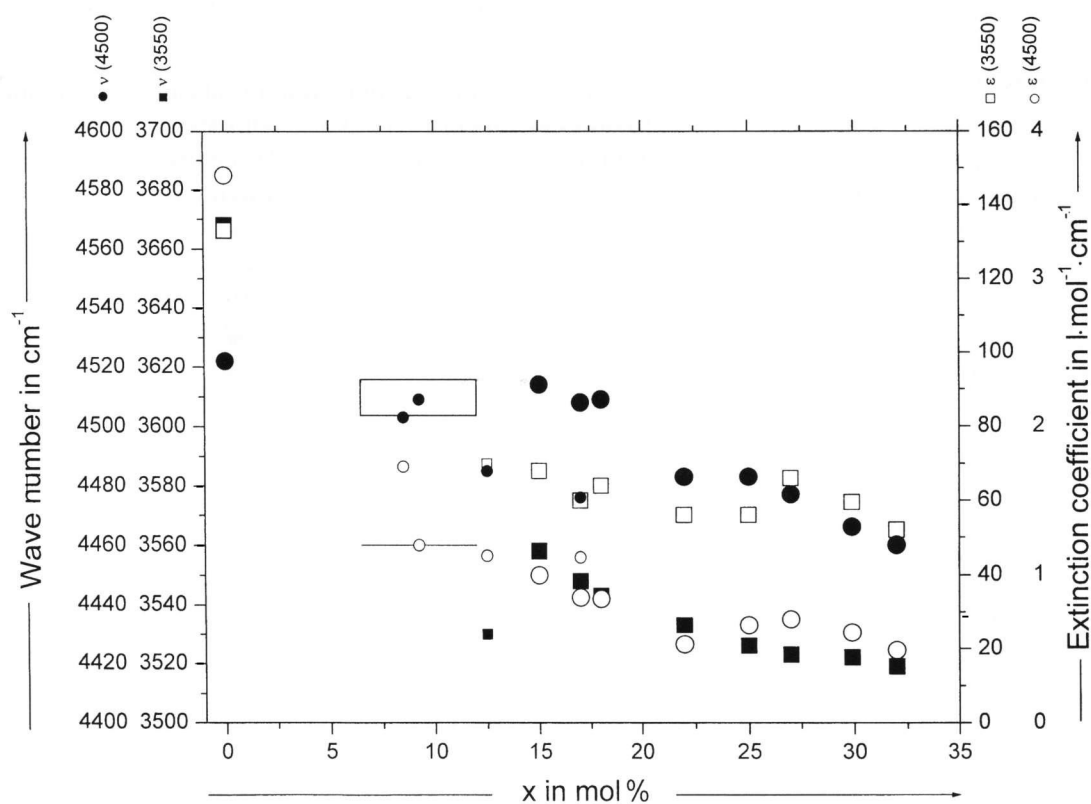


Figure 3. Positions of the OH bands $\nu(3550)$ and $\nu(4500)$ and corresponding extinction coefficients $\epsilon(3550)$ and $\epsilon(4500)$ as functions of x . Selected literature data are also included (smaller symbols) for $x = 8.5$ [12], $x = 12.5$ [13], $x = 17$ [12]; for $x = 6.73$ and 11.85 a frequency range 4515 to 4503 cm^{-1} (box) and a value of $1.20 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for $\epsilon(4500)$ (line) was reported in [12].

sorbance strongly increases due to the very strong absorption of the fundamental stretching vibrations of T–O–T bridges (T = Si, Al), which occurs at 1100 cm^{-1} with a prominent shoulder at approximately 1200 cm^{-1} in the spectra of vitreous silica. Only a combination band and the overtone of these bands can be observed at 2645 and at 2260 cm^{-1} , respectively, in transmission measurements of bulk glass samples [10]. It is well known that the stretching $\nu_{\text{as}}\text{T–O–T}$ vibration

bands shift to lower wave numbers with increasing amount of AlO_4 tetrahedra in the network. Thus, a systematic shift of the high-frequency slope of these bands with increasing x can be understood in the spectra of the aluminosilicate glasses.

The extinction coefficients of the OH bands (table 2, figure 3) were estimated on the base of the NRA data of the glass samples (table 2) by using the equation

Table 2. Extinction coefficients ϵ_{3550} and ϵ_{4500} and water content $c_{\text{H}_2\text{O}}^{\text{NRA}}$ and $c_{\text{H}_2\text{O}}^{\text{IR}}$

| glass no. | x in mol% | ϵ_{3550} in $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ | ϵ_{4500} in $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ | $c_{\text{H}_2\text{O}}^{\text{NRA}}$ in $\text{mol} \cdot \text{l}^{-1}$ | $c_{\text{H}_2\text{O}}^{\text{IR}}$ in $\text{mol} \cdot \text{l}^{-1}$ |
|-----------|-------------|--|--|---|--|
| 2 and 3 | 15 | 68 | 1.0 | 0.019 | 0.019 |
| 4 and 5 | 17 | 60 | 0.85 | 0.018 | 0.017 |
| 6 and 7 | 18 | 64 | 0.84 | 0.016 | 0.016 |
| 8 and 9 | 22 | 56 | 0.53 | 0.019 | 0.016 |
| 10 and 11 | 25 | 56 | 0.66 | 0.020 | 0.018 |
| 12 | 27 | 66 | 0.70 | 0.018 | 0.018 |
| 13 and 14 | 30 | 60 | 0.61 | 0.019 | 0.016 |
| 15 and 16 | 32 | 52 | 0.49 | 0.022 | 0.018 |

$$\epsilon = \frac{A}{c_{\text{H}_2\text{O}}^{\text{NRA}} \cdot d}$$

where A denotes the measured, reflectance-corrected IR absorbance in accordance with recommendation given in [11]. For the determination of the absorbance of the 4500 cm^{-1} band a linear baseline between the minima at both sides of the band was chosen. It should be noted, however, that quantitative results of hydroxyl concentrations are less precise because of the low hydroxyl contents in the studied glasses.

OH vibration bands were published and interpreted for a wide variation of glass compositions and extinction coefficients of all the various OH bands were proposed. Among these there are data for aluminosilicate glass compositions $x\text{R}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) and $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$, which are immediately comparable with our experimental results [12 to 17].

IR spectra of vitreous silica were extensively studied [18]. Shoulders on the low-wave number side of the 3672 cm^{-1} silanol band suggest that more than one hydrous species are present in this low-water-content glass. Therefore, Davis et al. distinguished between three types of silanol groups with bands at 3672, 3663 and 3608 cm^{-1} . Three bands were assumed for representing the 3800 to 3400 cm^{-1} envelope in the water-related spectrum of vitreous silica [19]. The 4522 cm^{-1} band is usually assigned as combination of OH bending and stretching in silanol groups. The shoulder of this band at about 4450 cm^{-1} possibly arises from asymmetric distribution of silanol vibration frequencies due to varied degrees of hydrogen bonding [20]. The 3850 cm^{-1} shoulder was assigned as a combination of OH stretching and an SiO_2 network vibration at 280 cm^{-1} [21] or it was attributed to a combination, possibly, of stretching and torsion of SiOH ; and a weak shoulder at about 4100 cm^{-1} was noticed as an unidentified OH combination band [18]. Bands in the range below 3000 cm^{-1} were scarcely interpreted. They are due to combination vibrations of the network [22]. Extinction coefficient of the OH band at 3670 cm^{-1} in the spectra of vitreous silica varies from 86 to 186 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (see [23]). Our value of 133 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ satisfactorily agrees with val-

ues of 152.8 or 155.0 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, which were very precisely determined by Davis et al. [23]. Ilievski et al. [24] proposed extinction coefficients between 137 and 182 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The extinction coefficients of the OH band at 4522 cm^{-1} are 3.71 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in this study and 3.06 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in [23]. Thus, both the measured band positions and the extinction coefficients given in our study are in good agreement with literature data for SiO_2 glasses.

Moreover, for calcium aluminosilicate glasses our findings are also in accordance with spectroscopical literature data of glasses with similar compositions. Selected literature data are included in figure 3. Scholze published the OH band at 3484 cm^{-1} in the IR spectrum of 20 $\text{Na}_2\text{O} \cdot 20 \text{Al}_2\text{O}_3 \cdot 60 \text{SiO}_2$ among other spectra of silicate glasses [14]. The long low-frequency tail of this band is very similar to the band shape in our spectra. In the range between 3800 and 2600 cm^{-1} a comparable asymmetry of this band was found in the spectra of hydrous albite glasses ($x = 12.5$) [13]. A comparison with these spectra is possible because the band becomes narrower with increasing water content [13]. Stolper presented extinction coefficients from 52 up to 88 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for the fundamental OH vibration band at about 3550 cm^{-1} in the spectra of water-rich albite glass, hydrated obsidian, and rhyolitic glasses with about 80 mol% SiO_2 in the dry glass network [15].

In the NIR spectral region water-rich calcium aluminosilicate glasses with similar compositions $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ ($x = 6.73$ and 11.85) were investigated by Silver et al. [12]. The presented band position of 4515 to 4503 cm^{-1} and the corresponding extinction coefficient of $1.20 \pm 0.59 \text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ can be connected to our data for $x \geq 15$ (figure 3). Behrens et al. [16] investigated NIR spectra of hydrous glasses with alkali feldspar compositions (12.5 $\text{R}_2\text{O} \cdot 12.5 \text{Al}_2\text{O}_3 \cdot 75 \text{SiO}_2$ with $\text{R} = \text{Li}, \text{Na}, \text{K}$) and proved that both wave number and extinction coefficient depend on alkali type. The determined extinction coefficients of 1.32 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ($\text{R} = \text{Li}$), 1.28 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ($\text{R} = \text{Na}$) and 1.58 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ($\text{R} = \text{K}$) agree with values presented in this study (table 2, figure 3). An extinction coefficient of 1.11 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ was determined for a 10 $\text{Li}_2\text{O} \cdot 10 \text{Al}_2\text{O}_3 \cdot 80 \text{SiO}_2$ glass [17].

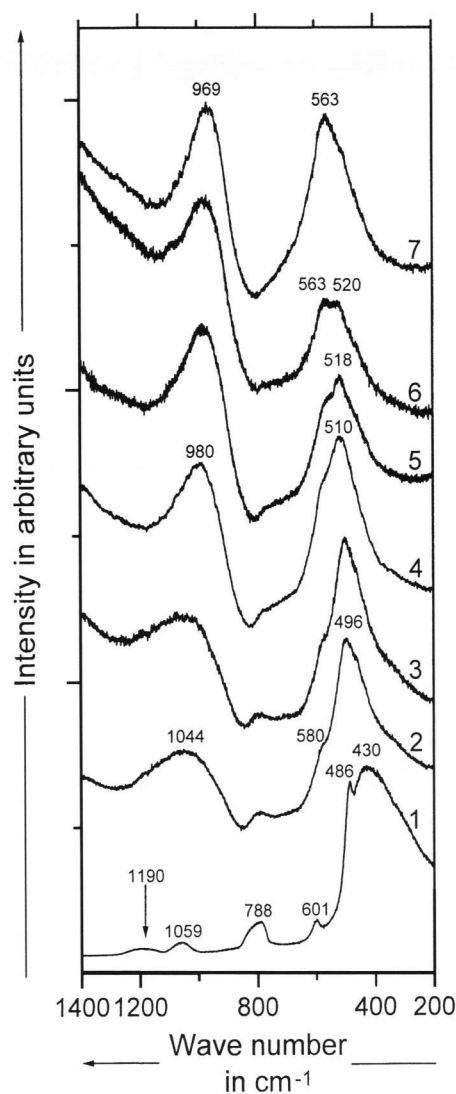


Figure 4. Raman spectra of calcium aluminosilicate glasses with composition $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$; curve 1: glass no. 1, vitreous silica; curve 2: glass no. 5, $x = 17$; curve 3: glass no. 7, $x = 18$; curve 4: glass no. 11, $x = 25$; curve 5: glass no. 12, $x = 27$; curve 6: glass no. 14, $x = 30$; curve 7: glass no. 16, $x = 32$.

3.2 Network vibrations

3.2.1 Raman spectroscopic measurements

The Raman spectra (figure 4) of the calcium aluminosilicate glasses vary systematically with increasing x . All the spectra are dominated by a strong complex envelope of overlapping bands between 450 and 600 cm^{-1} . This broad band shifts from 483 to 520 cm^{-1} with increasing x from 15 to 30. A new band at 563 cm^{-1} appears with increasing x . This band is the dominant one in the spectrum of the glass with $x = 32$. Both the bands at 520 cm^{-1} and at 563 cm^{-1} were recorded for $x = 30$. The spectral range between 800 and 1300 cm^{-1} significantly changes in the spectra of calcium aluminosilicate glasses in comparison with the spectrum of vitreous silica. A broad unresolved band shifts continuously from

1083 to 969 cm^{-1} with increasing x from 15 to 32. In addition, intensity of the 1000 cm^{-1} band grows with x in relation to the 500 cm^{-1} band intensity. The 800 cm^{-1} band disappears with increasing x . The measured spectra closely agree both in band positions and in relative band intensities with Raman spectra of the $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ glass series, reported by McMillan et al. [1] for x up to nearly 50. Our spectra are also in good agreement with Raman spectra of calcium aluminosilicate glasses with $x = 16.7$ and 33.3 [25], with $x = 15, 20$ and 25 [4] and with Raman spectra of anorthite glass ($x = 25$) [26 and 27]. But the high band intensity obtained in the high-frequency range in the spectra of anorthite glass and of vitreous silica [3] was not observed in this study.

In general, the Raman spectra have been interpreted in a structure model of fully polymerized, three-dimensional aluminosilicate network, with aluminium and silicon in tetrahedral coordination to oxygen [1, 3, 4, and 25 to 27]. But in detail, different assignments were proposed for both the low-frequency and the high-frequency spectral regions. Different interpretations were given also for the Raman spectrum of vitreous silica. For spectrum-structure correlations various types of structural groups in the glass network were assumed, as TO_4 tetrahedra, T-O-T bridges, rings etc. The spectra interpretations mainly differ in proposed degree of coupling between vibrational motions and in suggested envelope deconvolution of overlapping bands.

McMillan et al. in [1] comprehensively investigated the Raman spectra of aluminosilicate glasses with compositions along the joins $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ and $x\text{R}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ ($\text{R} = \text{Na}, \text{K}$) and discussed the band assignment in relation to corresponding crystal spectra. Former published Raman investigations of alkali and alkaline earth aluminosilicate glasses as well as of vitreous silica were reviewed and discussed. These systematic investigations have shown that both intensities and band contours in the high-frequency region from 850 to 1200 cm^{-1} in the spectra of aluminosilicate glasses are highly sensitive to the glass composition. They concluded that the molecular structure of glasses along the $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ join may be described as fully polymerized networks of AlO_4 and SiO_4 tetrahedra, with Ca^{2+} filling cavities in these networks. They suggested the appearance of four discrete fixed-frequency bands at 1140, 1000, 925 and 890 cm^{-1} , which have been related to symmetric stretching vibrations of silicate tetrahedra with one, two, three and four Al-O bonds, respectively. They summarized that the high-frequency range is much more determined by the Si-O stretching bands than by Al-O vibrations, although the network is geometrically a fully polymerized structure of silicate and aluminate tetrahedra. Such a type of bonds causes the high band intensity in the high-frequency region, which is similar to that observed in spectra of silicate glasses with NBO. In the spectral range from 400 to 600 cm^{-1} the polarized

bands have been associated with a transverse motion of oxygen atoms in T–O–T bridges. These bands are similar to the 430 cm^{-1} band in SiO_2 glass spectra. They are observed at 520 cm^{-1} and at 560 cm^{-1} in the spectra of anorthite glass and calcium aluminate glass, respectively.

An opposite interpretation of Raman spectra was given by Mysen et al. [25]. In the high-frequency range, they strictly distinguished between Si=O stretching vibrations in Si=O (NBO) bonds and in Si–O–Al bridges. In this model the wave number of the T–O–T stretching vibrations decreases with increasing charge-balanced Al^{3+} . Such decrease is caused by the decreasing T–O–T angle associated with increasing Si–O bond length due to growing Al^{3+} content in the network. Thus, the Si–O bond weakens as the neighboring Si^{4+} is replaced by Al^{3+} . This fact is well known for crystalline aluminosilicates [28].

A comparison of the Raman spectra of anorthite glass and of anorthite crystal was used to draw conclusions about the glass structure in the near and medium range [26 and 27]. Because of the similarity between the features in the spectra of crystalline anorthite and of anorthite glass, the bands were attributed to corresponding types of vibration. In Matson et al. [27] the Raman spectra of glasses along the orthoclase-anorthite and nepheline-anorthite joins were investigated and an interpretation of the spectrum of anorthite glass as the end-member glass was proposed. It was suggested that the band position of the symmetric stretching vibration $\nu_s(\text{T–O–T})$ in the low-frequency region can be related to the most probable T–O–T angle and to the ring size [26]. In the case of anorthite the crystal band at 503 cm^{-1} and the corresponding glass band at 508 cm^{-1} were attributed to this symmetric stretching vibration of the oxygen in the T–O–T bridge [27]. Thus, the ring structure of anorthite glass is similar to that of crystalline anorthite, consisting predominantly of four-membered rings of TO_4 tetrahedra. In the high-frequency region the strong band at 974 cm^{-1} and the shoulder at about 1100 cm^{-1} were attributed to antisymmetric stretchings of Si–O–Al and Si–O–Si bridges, respectively. It was suggested that antisymmetric stretching features can be directly related to the silicon/aluminium ratio of the glass. Hence, the presence of a weak Si–O–Si band indicates a small degree of Si–Al disorder in the anorthite glass [27].

3.2.2 IR reflectance measurements

The reflectance spectra of the samples (figure 5) show gradual trends with composition. Significant features of all the spectra are the high-frequency bands at 1000 to 900 cm^{-1} and the band at 500 to 400 cm^{-1} as well as a weak band at 800 to 650 cm^{-1} . Compared with the spectrum of vitreous silica, the spectra of calcium aluminosilicate glasses show broad bands with unresolved con-

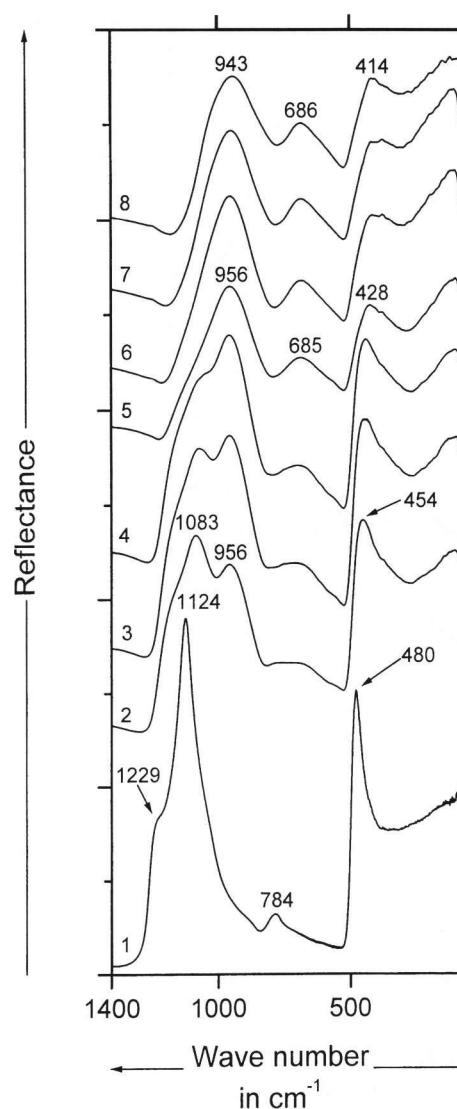


Figure 5. IR reflectance spectra of calcium aluminosilicate glasses with composition $x\text{CaO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$; curve 1: glass no. 1, vitreous silica; curve 2: glass no. 3, $x = 15$; curve 3: glass no. 5, $x = 17$; curve 4: glass no. 7, $x = 18$; curve 5: glass no. 11, $x = 25$; curve 6: glass no. 12, $x = 27$; curve 7: glass no. 14, $x = 30$; curve 8: glass no. 16, $x = 32$.

tours. The band at 1124 cm^{-1} shifts to lower wave numbers and disappears and the shoulder at 956 cm^{-1} becomes more pronounced with increasing x . For $x = 32$ only a broad band at 943 cm^{-1} was obtained. The intensity of the 690 cm^{-1} band increases while the 784 cm^{-1} band disappears. The 480 cm^{-1} reflectance band shifts to 414 cm^{-1} in the spectrum of glass with $x = 32$. It should be noted that the measured reflectance spectra were related to changes in the glass composition without performing Kramers-Kronig transformation. This transformation was extensively treated in the literature [5, 29 and 30]. It is connected with the assumption of crystal-like long-range order in the glass structure.

Our finding can be compared with IR reflectance investigations reported for calcium aluminosilicate glasses

in literature [5 and 30]. The measured reflectance spectra satisfactorily agree with literature data of corresponding glasses. Similar changes in reflectance spectra in dependence on x were found, as published by Merzbacher et al. [30], for calcium aluminosilicate glasses with a $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of 1.5 and increasing SiO_2 content from 0 up to 80 mol%. All the bands in the experimental reflectance spectrum of anorthite glass are shifted by nearly 10 cm^{-1} to higher wave numbers in relation to the published spectrum by Merzbacher [5]. The features in the measured reflectance spectra can also be roughly compared with IR absorbance spectra obtained for so-called KBr pellets of glass powders [31 and 32].

In a paper by Merzbacher and White [5] IR reflectance spectra and Raman spectra were used to study the structure of calcium and magnesium aluminosilicate glasses. Two series of glass compositions were investigated, with $\text{NBO}/\text{T} = 1$ and with constant 50 mol% SiO_2 . Kramers-Kronig transformation was performed on the IR reflectance spectra and the results were discussed in terms of crystal-like transverse and longitudinal optic modes (TO and LO). For calcium silicate glasses with $\text{NBO}/\text{T} = 1$, it was found that the high-frequency TO and LO modes shift to lower wave numbers with increasing aluminium content. These bands were assigned as asymmetric stretching vibrations of the tetrahedral network. In the low-frequency region a band between 350 and 200 cm^{-1} was attributed to $\text{Ca}-\text{O}$ vibrations. This spectral range allows to distinguish between Ca^{2+} , acting as charge balancer, and Ca^{2+} , acting as a network modifier, because the vibration band of the charge-balancing Ca^{2+} appears at higher wave numbers than the vibration band of the network modifier. A direct comparison of the detailed structural conclusions, drawn by Merzbacher et al., is complicated because of the different compositional series of studied glasses. IR spectra of glasses with composition $x\text{RO} \cdot x\text{Al}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$, $\text{R} = \text{Mg, Ca, Sr, Ba, Pb}$ and $5 \leq x \leq 27.5$ were investigated by Roy [31] using the KBr pellet technique. With increasing x from 5 to 17.5 a linear decrease of wave number from 1094 to 1063 cm^{-1} of the most intense band in the IR spectra of the calcium aluminosilicate series was obtained. Besides, a shoulder at about 955 cm^{-1} grows with increasing substituted Al^{3+} , and the bands at 799 and 470 cm^{-1} shift by 74 and 10 cm^{-1} , respectively, to lower wave numbers. These results can be qualitatively related to our findings using reflectance spectra. As described above, in the reflectance spectra these trends continue with $x \geq 17.5$. In [31] spectra analysis was based on the following band assignments. The 1100 cm^{-1} band is attributed to the $\text{Si}-\text{O}$ stretching vibration in SiO_4 tetrahedra, modified by Al^{3+} and R^{2+} . The 800 cm^{-1} band is mainly related to a corresponding $\text{Al}-\text{O}$ stretching vibration in AlO_4 tetrahedra. The 470 cm^{-1} band is assigned to $\text{T}=\text{O}=\text{T}$ bridges. Huang et al. [32] studied the role of aluminium in calcium aluminosilicate glasses with a wide range of compositions, also by using IR spectra. The assignments of vibrational

bands are the same for both IR and Raman spectra. Although the spectroscopical findings are similar to the referred literature data, we partially suggest other interpretation of the spectra, as described below.

4. Discussion

The overall network structure of calcium aluminosilicate glasses is manifested in both the Raman (figure 4) and IR reflectance spectra (figure 5). As referred to above, these spectra can be successfully interpreted in terms of fully polymerized network of TO_4 tetrahedra, and significant changes in the spectra were observed as a function of the glass composition. These gradual changes reflect the substitution of Al^{3+} for Si^{4+} and the corresponding increase of Ca^{2+} in the network with growing x . Increasing x correlates in the Raman spectra with decreasing wave number of the asymmetric stretching vibration bands $\nu_{\text{as}}\text{T}-\text{O}-\text{T}$ from 1083 to 969 cm^{-1} . In the IR reflectance spectra the contour of the high-frequency band significantly changes with x and the bands also shift to lower wave numbers. In the spectral range below 600 cm^{-1} the Raman bands show a less resolved contour and the bands shift to higher wave numbers, while the IR reflectance band shifts to lower wave numbers with increasing x . The fact that Raman and IR bands shift in opposite directions with x demonstrates that these bands do not correspond to the same vibrations. This observation was not surprising because Raman and IR bands are generally caused by different origins. If changes in dipole moment or polarizability occur during the vibrational motion, bands appear in the IR and Raman spectra, respectively. As a result, the selection rules are different for these two vibrational spectroscopic methods [33].

We followed the interpretation of McMillan et al. [1 and 2] and assigned the Raman bands below 600 cm^{-1} to symmetric bending vibrations of $\text{T}-\text{O}-\text{T}$ bridges, where the oxygen vibrates along the bisecting line of the $\text{T}-\text{O}-\text{T}$ angle. The high degree of polarization of this Raman band requires an assignment as a total symmetric vibrational motion. This assignment is generally confirmed for silicates and aluminosilicates by numerous investigations, for example by Lazarev [34]. By using quantum chemistry methods Gibbs et al. [28] have explained the correlation which was observed between the bridging bond length and the angle as well as between stretching and bending force constants of the disiloxyl unit in silicates and siloxanes. Moreover, the studies have been extended to $\text{Si}-\text{O}-\text{Al}$ bridges by Gibbs et al. [28]. As the angle widens, the $\text{Si}-\text{O}$ bridging bond length is observed to shorten. In addition, the stretching force constant of the bridging bond has been observed to increase with increasing angle while the angle bending force constant decreases. Thus, in our case the opposite shifts of the $\text{T}-\text{O}-\text{T}$ stretching and $\text{T}-\text{O}-\text{T}$ bending vibration bands in the Raman spectra of calcium alumi-

nosilicate glasses can be understood. However, the IR bands at about 450 cm^{-1} should be rather attributed to deformation vibrations of TO_4 tetrahedra. The selection rules causes that for an ideally symmetric TO_4 tetrahedra a deformation vibration should be IR active. This band assignment as an intra-tetrahedra deformation vibration is usual for crystalline aluminosilicates, for example zeolites.

However, it should be noted that subtle information about a complete absence of NBOs in the studied glasses could not be inferred from the network spectra. The formation of NBOs in silicate glasses gives rise to high-frequency bands of significant intensity nearly 1000 cm^{-1} in the Raman spectra of the glasses. For a small number of NBOs such a band is impossible to detect under the intense high-frequency band of the studied glasses. In the IR spectra NBOs are usually indicated by a band at about 930 cm^{-1} . But a weak band at 930 cm^{-1} would be obscured by the intense broad band at about 950 cm^{-1} in the measured spectra. It is also difficult to estimate the degree of disorder of Al^{3+} in the network, although the Raman band at 563 cm^{-1} is probably due to Al-O-Al bridges [2] and a band-broadening effect of aluminum is clearly visible in the high-frequency range of both the Raman spectra and the IR reflectance spectra of the calcium aluminosilicate glasses in comparison with the corresponding spectra of SiO_2 glass. Nevertheless for the anorthite glass sample the asymmetry of the 956 cm^{-1} band in the IR reflectance spectrum probably demonstrates the existence of Si-O-Si bridges and in the Raman spectrum the shoulder at nearly 563 cm^{-1} indicates Al-O-Al bridges. Thus, in the network the alternation Si-O-Al is probably interrupted. This result agrees with the NMR measurements of Stebbins et al. [35], who discussed a considerable silicon/aluminium disorder in anorthite glass. It should be noted that the general behaviour of the vibrational bands of the studied glasses does not confirm the results of Engelhardt et al. [6], who discussed a glass structure with $76\text{ Q}_4^4 + 24\text{ Q}_3^3$ and $50\text{ Q}_4^4 + 50\text{ Q}_3^3$ for low-silica glasses with $x \approx 29.8$ and 33.3 , respectively. No hints were found in the Raman and IR reflectance spectra for such a large number of NBOs, connected with Q_3^3 units.

Gradual changes in dependence on x were found not only in the network spectra of the studied glasses but also for the OH vibration bands (figure 3). While in the SiO_2 glass all the SiO-H groups interact with oxygens in Si-O-Si bridges, with increasing x an increasing number of SiO-H groups interact with oxygen of Si-O-Al bridges. The decreasing wave number of the fundamental OH stretching vibration band at about 3550 cm^{-1} with increasing x may be caused by such a change in interaction, because of a wide variability of interactions between SiO-H and network. As x increases, the wave number of the OH combination band at about 4480 cm^{-1} decreases in nearly the same way as the fundamental OH vibration band. This band is usu-

ally assigned as combination of the OH stretching vibration and SiOH deformation vibration, $\nu\text{OH} + \delta\text{SiOH}$. Thus, the determined wave number of δSiOH is nearly the same for all the x . The value varies between 966 cm^{-1} for $x = 18$ and 941 cm^{-1} for $x = 32$. But for SiO_2 glass the corresponding wave number of δSiOH is significantly lower with a value of 854 cm^{-1} . As noticed above the shoulder at about 4000 cm^{-1} clearly broadens with increasing x . But the interpretation of the weak shoulder in this region is uncertain even for vitreous silica [15 and 18]. For the calcium aluminosilicate glasses a similar interpretation seems possible assuming for the low-energy mode a wide variation due to an increasing amount of Al^{3+} and Ca^{2+} in the glass network.

The extinction coefficient of the 3550 cm^{-1} band varies from 68 to $52\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for $x = 15$ and 32, respectively. A slight decrease of the extinction coefficient can be suggested with increasing x . Thus, the water content of these glasses can be estimated with an extinction coefficient of approximately $60\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The situation is different for the SiO_2 glass with an extinction coefficient of $133\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. For the extinction coefficient of the 4500 cm^{-1} band the decrease is more pronounced. It varies from 1.0 to $0.49\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for $x = 15$ and 32, respectively. It is not clear why these two extinction coefficients show such a different behaviour as a function of x . Further measurements are necessary for a more precise determination of extinction coefficients.

As noticed above the fundamental OH stretching vibrations appear as an asymmetric band at about 3550 cm^{-1} , which broadens and reaches up to nearly 2600 cm^{-1} . Thus, a significant band intensity was recorded at wave numbers around 2800 cm^{-1} . It is well known that the stretching vibrations appear at about 2800 cm^{-1} for SiO-H groups with strong hydrogen bonds to NBO in the network. For the studied glass spectra the interpretation is given without assuming NBOs in the network structure. Nevertheless it can be noted that the so-called two-band model [13 and 36] with the extinction coefficients $\epsilon_{3550} = 80\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $\epsilon_{2800} = 170\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ [37] seems to be applicable to calculate the water content of the glasses $c_{\text{H}_2\text{O}}^{\text{IR}}$ by the equation

$$c_{\text{H}_2\text{O}}^{\text{IR}} = \frac{1}{d} \left(\frac{A_{3550}}{\epsilon_{3550}} + \frac{4}{3} \frac{A_{2800}}{\epsilon_{2800}} \right).$$

A_{2800} was measured at 2900 cm^{-1} because a maximum cannot be reliably found in the studied spectra, but maxima were observed at about 2900 cm^{-1} in the spectra of calcium aluminosilicate glasses (for example $42\text{ CaO} \cdot 2\text{ Al}_2\text{O}_3 \cdot 56\text{ SiO}_2$) with a large number of NBOs. In table 2 the IR spectroscopically determined water contents, $c_{\text{H}_2\text{O}}^{\text{IR}}$, were listed and compared with the values obtained by nuclear reaction analysis, $c_{\text{H}_2\text{O}}^{\text{NRA}}$. The agreement is satisfactory within the error of measurement. The largest

difference was obtained for the low-silica glass with $x = 32$.

Thus, two interpretations are possible for the spectral range around 2900 cm^{-1} : firstly, an interaction of strongly varying strength between SiO–H hydroxyls and BOs in T–O–T bridges or secondly, SiO–H hydrogen bonded with NBO. Although we could not locate NBOs in the measured network spectra, it should be mentioned that Stebbins et al. [35] proved the existence of a small amount of NBOs in two anorthite glass samples by using ^{17}O MAS NMR techniques. In contrast Engelhardt et al. [6] reported that up to $x = 25$ the glasses are fully polymerized, whereas glasses with $x = 29.8$ and 33.3 have 24 and 50 % Q^3 units, respectively. In the OH vibration region of the IR spectra no evidence was found for such a strong increase of NBOs for the low-silica glasses.

It has been demonstrated that the network vibrational spectra as well as the OH vibration bands reflect the glass structure of the studied calcium aluminosilicate glasses, and all changes in these spectra are gradual with the composition parameter x . Further studies of the vibrational spectra of alkaline earth aluminosilicate glasses may be useful for more detailed structural information from the spectra. Further work is required to confirm the interpretation of the spectra and to understand the behaviour of the extinction coefficients as a function of glass composition. For this reason it seems useful to analyse the vibrational spectra of aluminosilicate glasses with various alkaline earth cations and with systematically changed number of NBOs.

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The authors are thankful to Mrs. M. Nofz (BAM) for providing all the samples of calcium aluminosilicate glasses and they thank her and W. Pilz (BAM) for many useful discussions. Thanks are also due to the anonymous reviewer for helpful comments. Financial support from the Deutsche Forschungsgemeinschaft Bonn-Bad Godesberg (Germany) is gratefully acknowledged.

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