

Memory effects of raw materials in glass melts Raman spectroscopy investigations of glass defects

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The present work is based on investigations of aluminum oxide containing lead glasses. The aim was to decrease the costs in the production of lead glass by addition of alkalis other than potassium and soda. Feldspar and nepheline from different sources were employed. During the melting process inhomogeneities, cords, knots and blisters arise the origin of which could be detected by means of Raman spectroscopic measurement on the glasses. This could be achieved also for very tiny inclusions, where other methods such as light microscopy fail. Only results which can be generalized are considered in this work. Raman spectroscopy has proven to be an excellent method to determine the contents of gas bubbles by means of the rotational spectra of the gases or respectively to trace structural changes back from the mineral to the homogeneous glass via the vibrational spectra of the solids. Thus, the development within a cord can be demonstrated and the origin of knots can be explained. The use of this method in explaining defects, taking aluminum oxide containing lead glasses as an example, is presented by various investigations. The structural inhomogeneities in the glasses may be traced back to their origins. i.e., the glasses "have a memory" of their raw materials.

Zusammenfassung Ergebnis der Glasschmelzen an ihre Ausgangsrohstoffe ramanspektroskopische Untersuchungen von Glasfehlern

Die vorliegende Arbeit basiert auf Untersuchungen an aluminiumoxidhaltigen Bleigläsern. Es wurde versucht, durch Zugabe anderer Alkaliträger als Pottasche und Soda die Kosten in der Bleiglasproduktion zu senken. Hierfür wurden Feldspat und Nephelin verschiedener Herkunft eingesetzt. Beim Einschmelzen ergeben sich Inhomogenitäten, Schlieren, Knoten und Blasen, deren Ursprung im Glas mittels Raman-Spektroskopie ermittelt werden konnte, auch an sehr kleinen Einschlüssen, bei denen andere Methoden wie z. B. Lichtmikroskopie versagen. Es wird hier nur auf die verallgemeinerbaren Ergebnisse mittels Raman-Spektroskopie eingegangen. Die Raman-Spektroskopie hat sich als eine ausgezeichnete Methode erwiesen, einmal zur Ermittlung des Inhaltes von Gasblasen mittels der Rotationsspektren der Gase und zum anderen, um strukturelle Änderungen vom Mineral bis hin zum homogenen Glas anhand der Vibrationsspektren der Festkörper zu verfolgen. So kann die Entwicklung innerhalb einer Schlieren aufgezeigt und die Herkunft von Knoten aufgeklärt werden. Anhand zahlreicher Beispiele wird die Anwendung dieser Methodik in der Fehleraufklärung am Beispiel der aluminiumoxidhaltigen Bleigläser vorgestellt. In den strukturellen Inhomogenitäten der Gläser können deren Ursachen noch erkannt werden, die Gläser „erinnern sich“ an ihre Rohstoffe.

1. Introduction

Structural characteristics of bulk solids and inclusions that may be present in them can be determined by using Raman spectroscopy. In a Raman spectroscopic measurement, a laser beam with a frequency ν_0 passes through the investigated material. Structural species such as molecules or ions are perturbed to an excited state, and scatter light with the same frequency ν_0 when they return to their initial state. Such coherent scattering is called Rayleigh scattering. However, a very small portion of light is adsorbed during the scattering process which is scattered with a frequency $\nu_0 - \Delta\nu$. Such scattering produces Stokes-Raman scattering bands. Such bands are produced because the interacting molecules or ions find themselves after scattering light at various excited vibrational or rotational energy states with respect

to the initial energy state. In conventional Raman spectroscopy, a Raman spectrum is generated when the intensity of the Stokes-Raman scattered light is measured as a function of frequency shift $\Delta\nu$ from the Rayleigh frequency ν .

Crystalline materials exhibit sharp Raman-scattered bands at well-defined frequencies which correspond to optically active vibrations of the crystalline lattice. Such bands will only be observed in the Raman spectrum if there is a change in polarizability during the vibration. In contrast, glass materials produce broad bands (which are usually fewer in number) due to the lack of long-range order developing from the short-range order that is present in the glass network. The locations and intensities of the vibrational Raman bands can be analyzed in terms of the nature of the related glass or crystalline structure. Gas molecules can also produce rotational Raman spectra consisting of many sharp bands due to tran-

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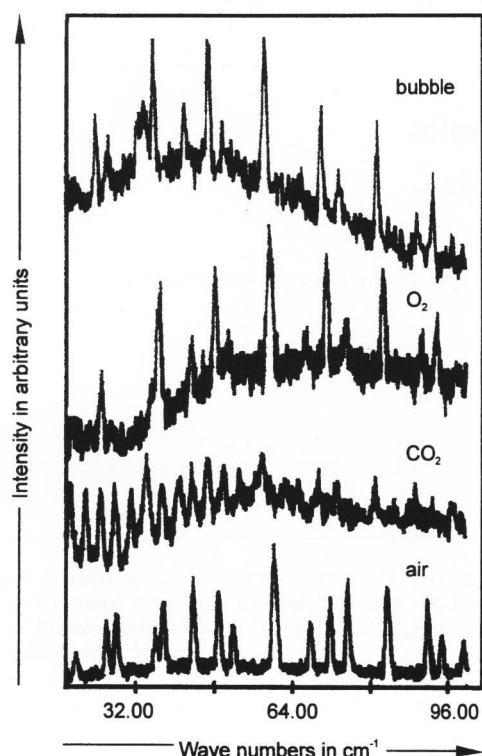


Figure 1. Raman spectra of the reference samples (O_2 , CO_2 , and air). The spectrum at the top is that of an unknown gas bubble in a glass specimen. A comparison with the reference spectra shows the unknown to be mostly O_2 , with some CO_2 .

sitions between excited rotational energy states. These latter bands can be used to determine the nature of the gas components that are present and their concentration.

Raman spectroscopy, therefore, can be used to identify the gas components present in bubbles in glass or the crystalline phases included in glass. Also, the resulting Raman spectra for the bulk glass at different sample locations can show corresponding spectral characteristics of the short-range order of the precursor crystalline materials. This possibility allows cords in glass to be traced back to the appropriate starting raw materials.

The examples described in this work will demonstrate the capabilities of Raman microprobe analysis with respect to various glass problems. The presented results were obtained as part of the AiF-sponsored research project "Al₂O₃ and ZnO in lead crystal glass". Spectral/structural results will be presented to illustrate the determination of gas contents in bubbles in glasses along with the spectroscopic investigation of surface crystallization, stone and cord formation, and spectral analysis for understanding the development of structural inhomogeneity in glass. The title for this study is meant to indicate that one can unambiguously trace glass defects in the form of stones, cords and gas bubbles back to their origins by using the Raman microprobe technique. Obviously, this capability has extreme importance for identifying defects, and removing their sources (i.e., for guaranteeing product quality).

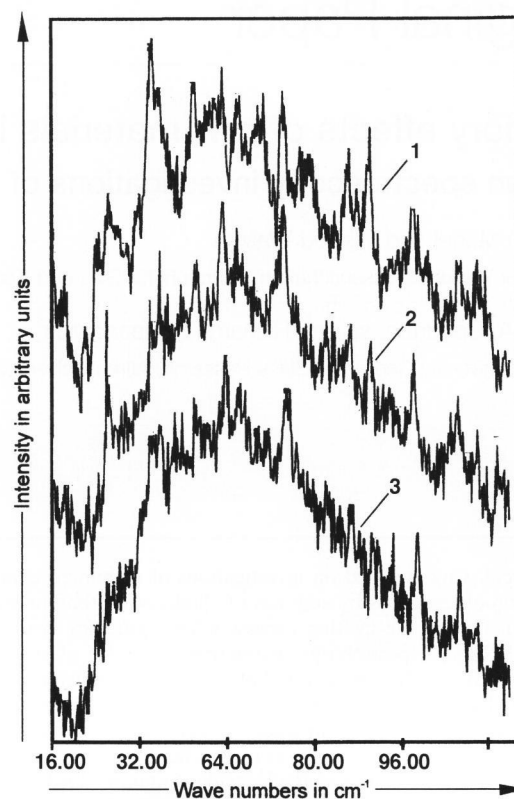


Figure 2. Raman spectra of gas bubbles in unfired lead crystal glass; the bubbles are mostly CO_2 . Spectrum 1: 1.0 mol% Al_2O_3 added as nepheline, spectrum 2: 1.5 mol% Al_2O_3 added as nepheline, spectrum 3: 1.5 mol% Al_2O_3 added as feldspar.

2. Experimental set-up

A Raman microprobe that is equipped with a microscope attachment [1] can be used to investigate inclusions as small as several micrometers which are as much as 1 mm below the glass surface. In this set-up the laser beam source is passed into the optics of the microscope by reflecting on a beam splitter, and the focussed onto a given position of the investigated specimen. The resulting beam from the sample position back-scattered into the optics of the microscope, and then passed through the beam splitter onto the entrance slit of a spectrometer so that a Raman spectrum can be measured for the given sample position. The Raman microprobe technique can be classified as a nondestructive technique, as long as the investigated sample can be positioned in the beam path without breaking it up. The technique is especially powerful for investigating non-destructively the gas contents in bubbles in glass.

3. Gas contents of bubbles in glass

Figure 1 illustrates the rotational Raman spectrum of a bubble in an industrial silicate glass in comparison to spectra of bubbles with air and pure gas components in standard glass specimens. Different gases produce spectra containing Raman bands at different band locations. The air spectrum is dominated by the bands of N_2 , as

shown by its comparison with the spectra of the pure gas components in bubbles. The rotational Raman spectrum of the gas bubble shown in figure 1 corresponds closely with that of a bubble containing mostly O₂ along with some CO₂.

Figure 2 illustrates the rotational Raman spectra of some gas bubbles formed during the early stages of the melting process in lead-containing crystal glasses that were investigated in the earlier mentioned AiF project. Al₂O₃ was placed into the lead-containing glass by the addition of either nepheline or feldspar. These additions into the initial crystal glass caused foaming in the resulting glass, and sometimes led to different melting behavior. The rotational spectra of the gases present in such bubbles in these glasses could be easily investigated by using the Raman microprobe technique. The Raman spectra of glass specimens which were melted with 1.0 or 1.5 mol% Al₂O₃ added in the form of nepheline of different sources (see the two upper spectra in figure 2) or with 1.5 mol% Al₂O₃ added as feldspar (see lower spectrum in figure 2) indicate bubbles which are dominated by the presence of CO₂. Presumably, such CO₂ was produced from organic species which were introduced during the processing of the raw materials. Such bubbles are only detected during a very early stage of the melting process, and, as a general rule, are associated with batch stones (i.e. with remnants of the raw materials). These bubbles were found near stones.

However, the vast majority of all of the analyzed bubbles exhibit spectra such as the one shown in figure 3, which, in turn, is similar to the upper spectrum in figure 1. The investigated bubbles, therefore, contain mostly oxygen. The following interpretation seems to be the most likely explanation: The oxygen solubility of the glass not containing nepheline or feldspar is changed by the addition of the natural raw material. The oxygen contents of the resulting glasses are no longer in equilibrium. As a consequence, reboiling occurs which causes the formation of oxygen bubbles.

Melting behavior studies

Experiments relating to melting behavior were conducted with all raw materials in the research project. Glass melts were quickly cooled from 1300°C by pouring them out, in order to evaluate the dissolution of the grains using a microscope. As a result, it was concluded that the minerals first began to dissolve on cleavage surfaces and at inhomogeneities. The grains were observed to break up into finer chunks, which led to cords and schlieren in the glass, if insufficient time was available for melting and reaching homogeneity (figures 4 and 5).

Structural nature of stones in various investigated glass samples

Stones originating from raw materials that are used for forming glasses can be readily identified by Raman

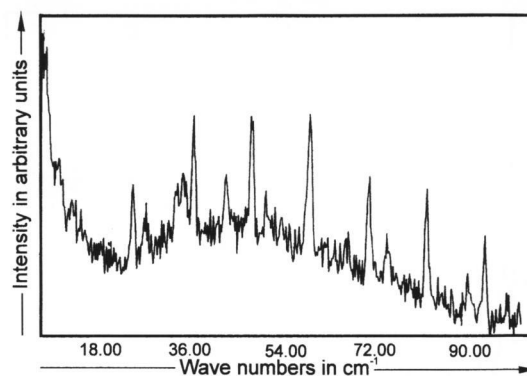
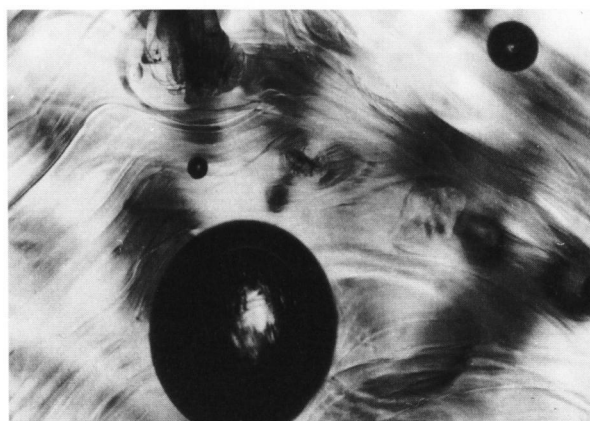


Figure 3. Raman spectrum of bubbles in lead crystal glass; these bubbles are mostly O₂, with some CO₂.



1 mm

Figure 4. Stones and bubbles with schlieren in an early stage of melting investigated under transmitted polarized light.



1 mm

Figure 5. Breaking up of nepheline into finer pieces with transformation to carnegieite (investigated under transmitted polarized light); note dissolution on the cleavage surfaces and the formation of cords or schlieren.

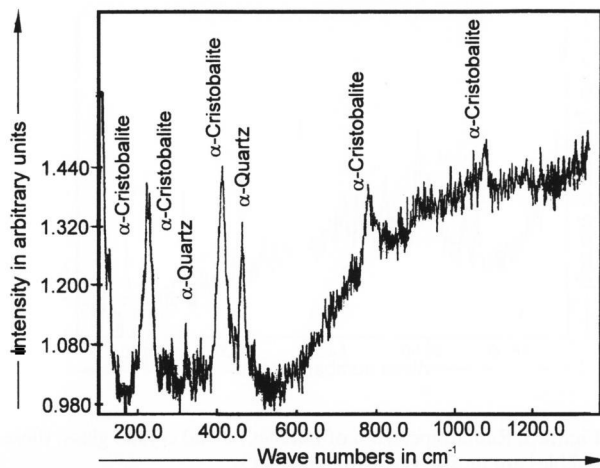


Figure 6. Raman spectra of solid silica inclusions quartz and cristobalite [1].



Figure 7. Nepheline remnant close to the surface of a crystal glass surface investigated under transmitted polarized light.

microprobe analysis as long as their location in the glasses are within the working distance of the objective lens in the microscope. One good example is the identification of crystalline silica remnants present in silicate glaze glasses after firing porcelain bodies. Even though some of these silica stones are too small to be clearly defined in the light microscope, they can be clearly identified by their Raman microprobe spectra. The presence and composition of such problematic inclusions are influenced by the glaze firing conditions. Incomplete reaction of the raw materials in the glaze can cause the retention of crystalline remnants in the glaze material. It has been observed a Raman microprobe spectrum of a solid inclusion that was found in the glassy matrix of such a glaze specimen which had been fired in a normal firing atmosphere [1]. This inclusion was in a long distance from any bubbles in the glass. The observation of the

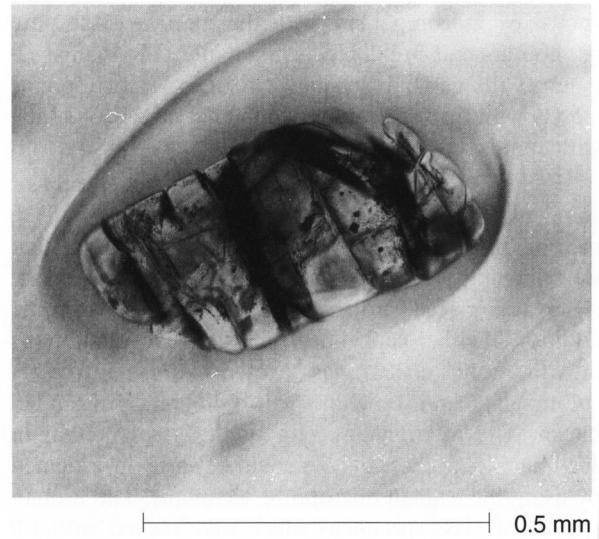


Figure 8. Carnegieite remnant in a crystal glass melt investigated under transmitted polarized light.

strong Raman band at $\approx 463 \text{ cm}^{-1}$ demonstrates that this solid inclusion is essentially composed of α -quartz. There is no indication for any of these types of inclusions that any transformation occurs from the α -quartz phase to the α -cristobalite phase, which would be expected for fired specimens involving sufficient higher firing temperatures and/or longer firing periods. In contrast, the Raman microprobe spectra (figure 6) for solid inclusions found on the surface of bubbles in the same glaze specimens indicated that both α -quartz and α -cristobalite were present. Raman bands at 127, 224, 413, 780 and 1081 cm^{-1} were associated with the α -cristobalite phase. Slight shifts in their wave numbers may be due to stress effects on the polycrystalline inclusion. Analysis of the Raman spectra of the glaze specimens fired at higher temperatures and longer periods of time indicated larger α -cristobalite/ α -quartz concentration ratios for solid inclusions found either embedded on the surfaces of bubbles or immersed in the glassy matrix than were indicated for the specimens that were fired under previously described conditions. Optimization of the firing conditions for the glaze materials generate glassy glaze matrices into which crystalline SiO_2 has completely dissolved so that no Raman microprobe spectra could be obtained for any solid inclusion. Similar spectra are found of remnants relating to undissolved quartz in glasses or of stones from silica refractories.

Another good illustration of conveniently identifying stones in glass by Raman microprobe analysis involves the investigation of solid inclusions formed in crystal glasses using nepheline as a starting material [2]. For instance, the observed Raman microprobe spectra of investigated crystalline inclusions either sitting on the surface of the glass or embedded in the glass (figures 7 and 8) indicate that they originate from a carnegieite phase.

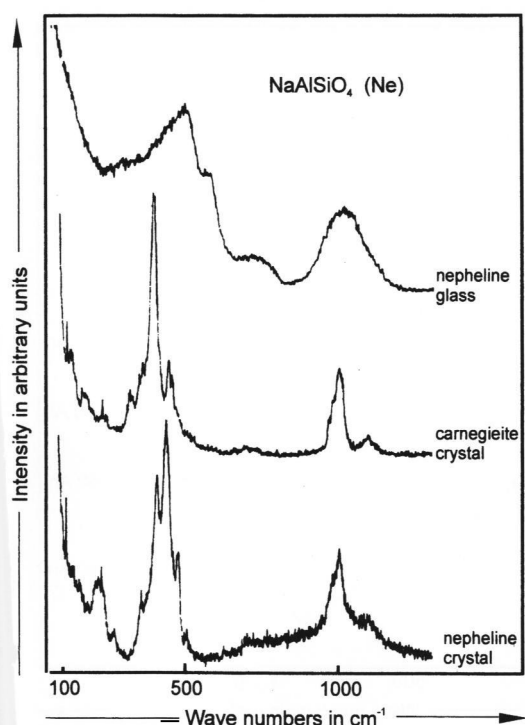


Figure 9. Raman spectra of nepheline crystal, carnegieite crystal and nepheline glass [2].

rather than a nepheline phase (figure 9). There are slight differences in their band locations with respect to those of the pure phase due to differences in cation substitution. Apparently, nepheline crystals converted to the carnegieite form under the full cycle of heat treatment conditions for this investigation.

Structural/spectral relations between crystals and glasses with similar compositions

In many cases, the average short-range order of glasses and crystals with the same elemental composition is similar. It is well-known that this similarity causes interrelations between the Raman spectra of related homogeneous glass and crystalline phases. In other words, important effects of the short-range order of the crystalline phase is seen in the Raman spectrum of the related glass. One finds that the Raman spectrum of the glass forms usually a broad envelope spectrum of the Raman spectrum of the related crystalline phase. This relation holds for glass compositions of interest in this paper. Figures 9 to 11 illustrate the Raman spectra for anorthite, orthoclase and nepheline compositions, respectively [3]. Figure 9 illustrates the spectra of nepheline, carnegieite (the high-temperature modification) and nepheline glass. Figure 10 shows the spectra for the potassium-rich side of the feldspars, i.e., sanidine (the isochemical high-temperature modification of orthoclase), and orthoclase glass, additionally the potassium homologon of nepheline, leucite. Figure 11 illustrates the

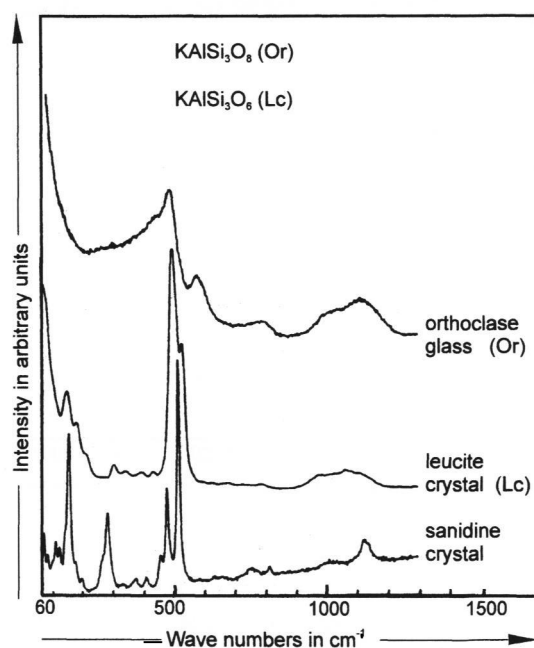


Figure 10. Raman spectra of sanidine crystal, leucite crystal and orthoclase glass.

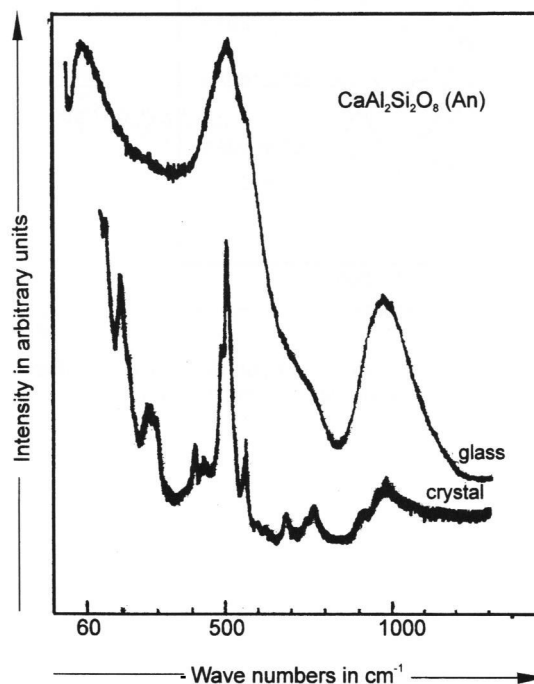


Figure 11. Raman spectra of anorthite crystal and corresponding glass.

spectra for the calcium-rich corner of the feldspars (anorthite and anorthite glass). In general, most of the Raman bands of the related phases can be interrelated to each other. Furthermore, there is usually a systematic change in the Raman spectra as one proceeds from one glass composition to another, indicating a systematic

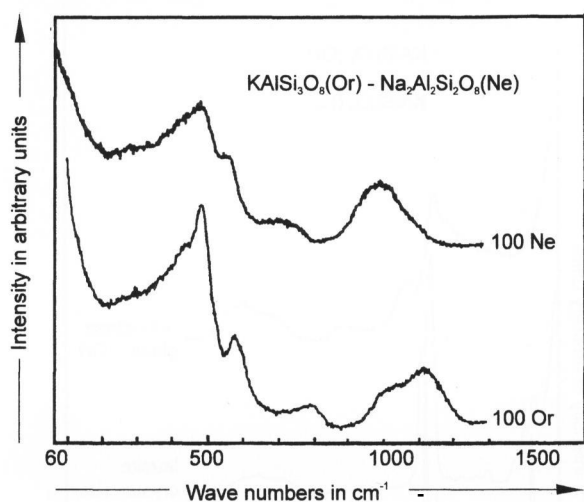


Figure 12. Comparison of the Raman spectra of nepheline glass and orthoclase glass.

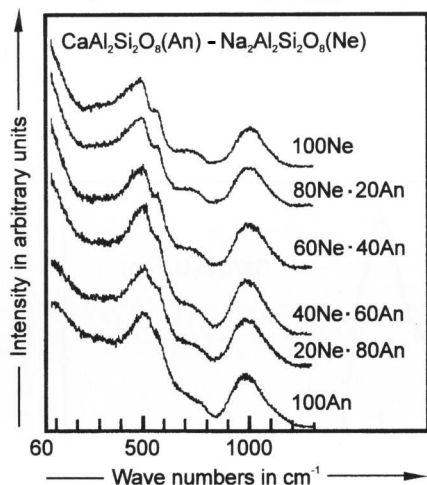


Figure 13. Raman spectra of feldspar glasses having different compositions along the nepheline-anorthite join [3].

change in its glass structure. Figure 12 compares the spectra of nepheline and orthoclase glass. Figure 13 illustrates this systematic change with the Raman spectra for the nepheline-anorthite series [3] and figure 14 the analogous change for the orthoclase-anorthite glass series.

Nepheline raw materials had been employed from Canada and Norway in the AiF-sponsored research project. The Raman spectra of these two raw materials are shown in figure 15, and it can be seen that they are clearly different. More detailed analyses showed that additions of feldspars in paragenesis with the nepheline occur in both raw materials; these additions determine the proportion of alkali in the raw materials. Furthermore, one could determine that the Raman spectra of different crystallographic orientations of the same mineral differed from one another (i.e., the anisotropy of the lattice was clearly reflected in the spectra).

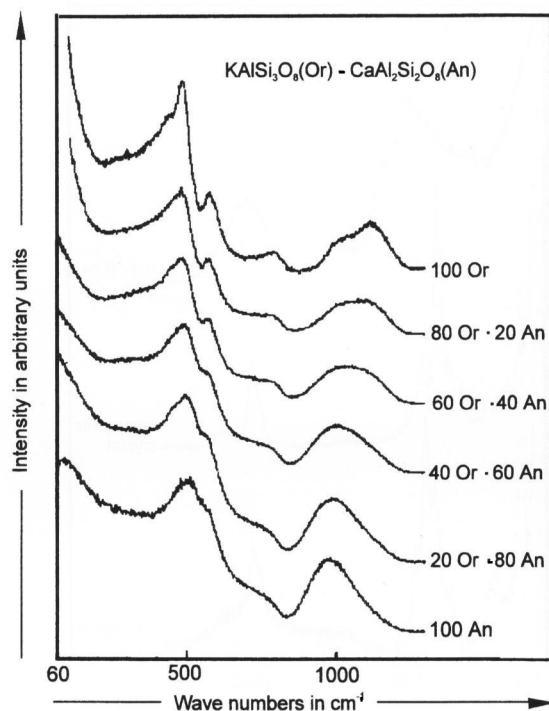


Figure 14. Raman spectra of feldspar glasses having different compositions along the orthoclase-anorthite join [3].

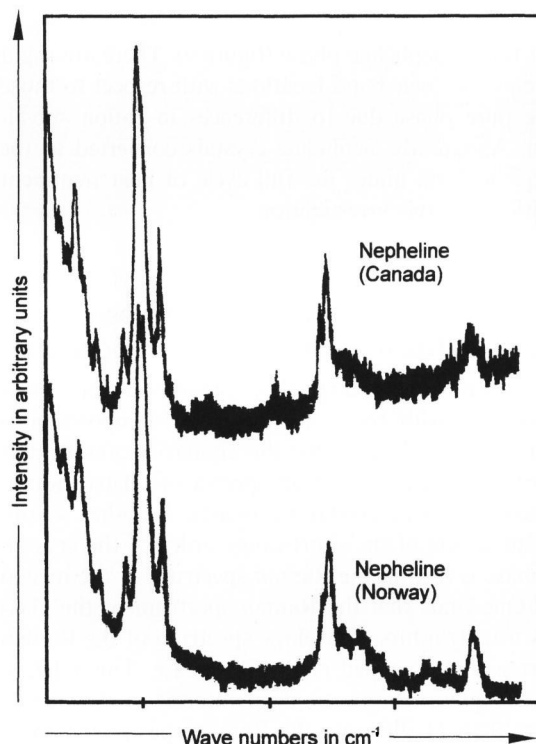


Figure 15. Raman spectra of nephelines from different sources.

7. Structural nature of cords and schlieren in various investigated glass samples

Cords or schlieren appear in glass due to variations in the glass composition or structure at the associated loc-

tions in the glass (see figures 4 and 5). Raman microprobe spectra can be obtained for such glass defects by focussing the microprobe on the defect and running its spectrum. Analysis of these spectra with that of the bulk glass will generate glass structural information concerning the defects.

The vibrational Raman microprobe spectrum of a cord in a silicate glass along with that of the bulk glass in which it resides are illustrated in [4]. Only subtle differences may be seen between these spectra. Significant differences can only occur in the spectra if there are significant differences in the related structures. One may note that a broad band at about 800 cm^{-1} becomes less intense in the spectrum of the cord with respect to that of the bulk glass. Bands appearing in this region may be due to vibrational modes involving bridging oxygens. Brawer et al. [5] showed that the intensity of a Raman band at about 800 cm^{-1} for alkali silicates decreased with increasing alkali content, indicating a decrease of bridging oxygens with respect to non-bridging oxygens. This spectral difference is probably due to more network modifiers being present in the cord region than in the bulk glass. The network modifiers could be introduced by corrosion of refractories in the glass melting tank. The variations in the relative intensities of vibrational bands in the Raman microprobe spectra can change depending upon which location on the cord is focussed during the microprobe measurement.

Schlieren can appear in a glass around a crystalline inclusion due to incomplete dissolution of the crystalline phase. This glass defect is due to incomplete and inhomogeneous dissolution of the crystalline phase into the glass around itself. One should see progressive changes in the Raman microprobe spectra/glass structure when one measures the spectra at various short distances from the inclusion if this schlieren effect is apparent. Figure 16 demonstrates the spectral development of a cord from a carnegieite crystal when measurements are taken at $40\text{ }\mu\text{m}$ intervals until the end member is reached. The homogeneous glass contains 1 mol% Al_2O_3 that was introduced by using nepheline. Clearly, there is a change in the spectra as one moves the focussing spot away from the inclusion. Figure 12 illustrates the Raman spectra for nepheline and orthoclase glass. Clearly, comparison of the spectra in figures 12 and 16 indicates that there is a change in the glass composition approximately along the nepheline-orthoclase join as one moves away from the crystalline inclusion.

Analysis of the vibrational spectra from the Raman spectrometer enables the recognition that the glass structure of the schlieren depends upon the long-range order of the dissolving crystals. That means that the form of the spectrum approaches that of the lead glass with increasing distance away from the nepheline relic. The change in the intensity of the band in the wave number region between 800 and 1000 cm^{-1} (the location of the Si-O stretching vibrations) verifies the change in the Al_2O_3 content as the crystal is approached. Therefore, a

cord analysis using Raman microprobe spectroscopy can give information about the aluminum supplier (i.e., about the aluminum-containing mineral). In other words, by investigating a glass cord, it is possible to determine whether feldspar, nepheline or another aluminum-containing mineral was the source of the cord. This would not be possible through chemical analysis alone. The short-range order of the glass develops from the long-range order of the crystalline mineral, as long as homogeneity has been reached.

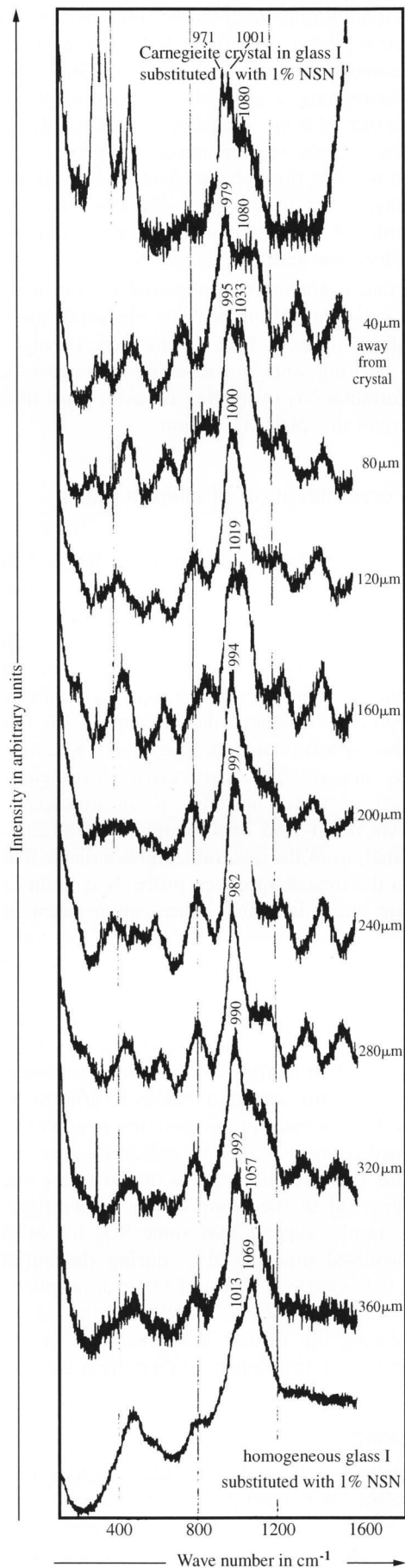
The fact that nepheline was observed to transform into carnegieite before melting explains why nepheline is especially difficult to melt. That is, why more energy is required for melting and for reaching homogeneity. Theoretical formulations of melting behavior must also take into account this phase transition.

8. Surface crystallization of silicate glass samples

Finally, Raman microprobe techniques can be used to analyze the nature of inclusions formed on glasses due to surface crystallization resulting from different types of surface treatment. Figure 17 illustrates the Raman microprobe spectrum which was obtained for a bloom that was formed upon heat treating a soda-lime silicate glass specimen in an SO_2 -containing atmosphere [6]. For all cases of the applied treatments, the resulting Raman spectra were similar. The particularly investigated specimen was heat-treated at 700°C in an atmosphere containing 2 vol.% SO_2 and 2 vol.% moisture. The comparison and analysis of the spectral features indicate that the bloom on the treated specimen probably contains a sodium sulfate phase in which other cations such as Ca^{2+} or Mg^{2+} are also possibly substituted for Na^{2+} ions. Similar Raman microprobe spectra were noted for crystalline coatings on the surfaces of bubbles in soda-lime silicate glasses prepared with sodium sulfate. It is also interesting to note that when the bloom is wiped from the surface of the glass, and the specimen is reheated in an air atmosphere, a bloom returns to its surface whose Raman microprobe spectrum is similar to that of the earlier formed bloom, indicating that the bloom contains a sulfate phase that is similar to the one which was observed in the blooms after earlier treatments. These results suggest that some SO_3 (or SO_2) must have dissolved into the glass during the initial treatment of the glass in the $\text{SO}_2/\text{H}_2\text{O}/\text{air}$ atmosphere, and must have diffused back to the glass surface along with Na_2O during the further heat treatment of the wiped glass in the air atmosphere to form fresh bloom.

9. Conclusions

During the melting of glass, the raw materials lose their mineral structure, their structural long-range order and are distinguished by a short-range order which has characteristics of the former long-range order. Gases are either trapped in bubbles or are set free during melting.



◆ Figure 16. Development of the Raman spectra of cords and schlieren starting from carnegieite and ending with the homogeneous lead crystal glass. (NSN: Nepheline Syenite from Norway)

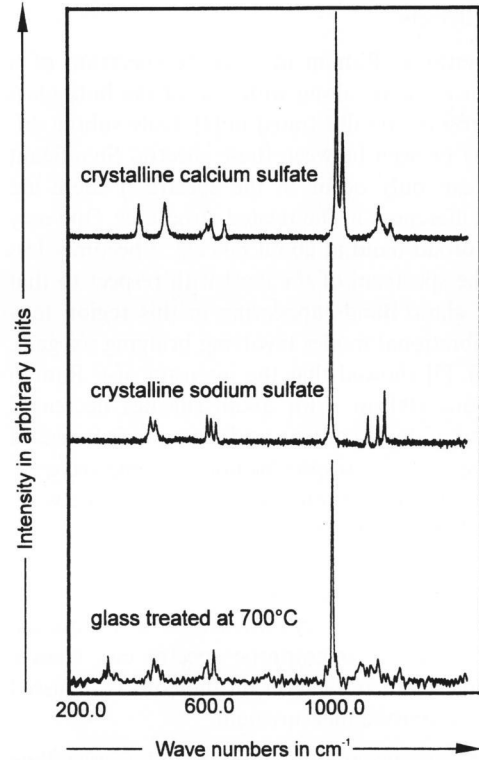


Figure 17. Raman spectra of surface devitrification on a float glass which was exposed to flowing SO₂ gas [4].

Raman spectroscopy enables compositional and/c structural analysis of gases, using rotational spectra, and solids, using vibrational spectra. Thus, Raman microprobe spectroscopy can be applied to the identification of crystalline particles in glass (i.e., a mineral analysis). Any phase conversion of the crystalline inclusions can be determined from the microprobe data. The melts display the corresponding characteristics of the short-range order, whereby cords in glass can be related to the starting materials, and gas bubbles can be analyzed with respect to their form and composition. The so-called Raman microprobe apparatus, equipped with a microscope, can be used to examine inclusions as small as several micrometers which are up to 1 mm below the surface of the glass. The Raman microprobe technique is classified as a nondestructive technique, as long as the specimen can be placed in the laser path. It is especially useful that the content of closed bubbles can be determined nondestructively, at the very least on a qualitative level.

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