

# WEATHERING OF THE CRYSTAL GLASS IN MOIST AND POLLUTED ATMOSPHERES

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*The weathering of commercially available crystal glasses (PbO and BaO containing glasses) was investigated under conditions, in which relative humidity was about 53 % or 97 % and pollutant i.e. CO<sub>2</sub> or SO<sub>2</sub> concentrations were as in normal atmosphere or increased by approx. 1 vol.%. The influence of cyclic temperature changes on weathering of the glass samples was also investigated. After exposure surfaces of these glass samples were studied by means of optical microscopy, scanning electron microscopy with energy dispersive X-ray microanalyses and Raman spectroscopy. During the above experimental conditions of weathering, solid products formed on the glass surfaces. Their chemical composition and structure significantly depend on the type of crystal glass as well as on environmental composition used during weathering tests. It was found that larger solids or crystalline aggregates usually consist of various sulphates and carbonates (e.g. CaCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, BaSO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub>).*

## INTRODUCTION

Glass is generally a stable and resistant material, but when in contact with either liquid or vapor waters it is vulnerable to damage. In the past a chemical resistance of medieval glass as well as those for laboratorial, pharmaceutical or technical applications was mainly studied. The number of papers dealing with the corrosion resistance of commercial table glassware has increased only in last years [1-5]. This is associated with a growing production of different kinds and shapes of products, the necessity of their long-term storage, long distance transport through areas with various climatic conditions and atmospheres. All the above-mentioned factors can also lower the optical quality of an original product.

The degradation of a glass surface due to interaction with the atmosphere [6] is referred to as "weathering". Heat and humidity cycling or storing glass in a confined space as well as increased concentration of aggressive gasses such as SO<sub>x</sub>, CO<sub>2</sub>, and NO<sub>x</sub> usually promote weathering.

According to [7], the weathering mechanism generally covers water adsorption by the glass surface, ion exchange of hydrogen ions mainly for alkali ions in the glass followed by formation of particular hydroxides and finally absorption of oxides with "acid properties" from surrounding environment and in the end the production of a salt solution. The considerably increased

concentration of these oxides leads to extensive damage of the glass surface. Afterwards, the solid layers or flat formations may precipitate from salt solutions on the glass surface and thus producing a so-called "weathering crust" [8].

The time required for the process of weathering to produce deleterious damage may range from few hours to many years. Duration of this process depends on various factors i.e. the glass composition, homogeneity and damage of the glass surface, the composition and temperature of surrounding atmosphere and the final application of glass product as well.

Deterioration mainly of the optical quality of glass surfaces by weathering causes serious problems to both producers and consumers of tableware glasses. On account of that the main purpose of this work was to investigate the weathering process of crystal glasses exposed to various atmospheric environments in order to establish the influence of temperature, relative humidity and the composition of environment.

## EXPERIMENTAL

### Sample preparation and exposure

Two different crystal glasses were used in this study. Their average chemical composition is given in table 1 but that obtained from the near glass surface was partly different (compare to figures 2 and 3). The speci-

mens were that of typical manufactured glass, i.g. barium crystal and polished lead crystal glass, respectively. Circular rings (diameter approx. 7 cm) were prepared by cutting the wine glass using a diamond saw and then sectioned to the samples under investigation (3.0 cm × 1.5 cm). Finally, the glass samples were cleaned in deionised water, ethanol and acetone and then dried at 60°C. The samples were exposed for 50 days in different atmospheres at the cyclic temperature between 25°C and 60°C. The test conditions for these cyclic temperature experiments are given in table 2.

The weathering test was carried out by placing the glass samples in a desiccator on a glass sheet vertically and raised 3 cm above a dish of tap water solution. These assemblies - desiccators were placed in an oven maintained ± 1°C. Samples were exposed for two different nearly fixed values of relative humidity (RH), i.g. 53 ± 4 % or 97 ± 1 %. This was achieved by placing the glass samples above the saturated water solutions of NaBr and K<sub>2</sub>SO<sub>4</sub>, respectively [9].

In order to investigate the effects of common pollutants some samples were exposed in environments to which either SO<sub>2</sub> or CO<sub>2</sub> were added. Thus the concentrations of SO<sub>2</sub> or CO<sub>2</sub> were either that of normal air (samples 1 to 4, see table 3) or were increased by addition of about 1 vol.% of SO<sub>2</sub> or CO<sub>2</sub> (samples 5 to 12). The surrounding environments have been renewed every ten-day. After the weathering tests all glass samples were dried at 40°C and stored in a desiccator before being analysed.

#### Sample analysis and measurements

In the present study samples were preliminary observed by optical microscopy to obtain morphological information. A scanning electron microscopy (SEM, TESLA BS 300, 15 kV) was used for detailed characterization of the glass surface and the morphology of the products formed by weathering. The samples were coated with a thin layer of gold prior to SEM measurements. The chemical composition of large crystals as well as that of some glass surfaces without crystals was determined by energy dispersive X-ray spectroscopy (SEM/EDX, JEOL JXA-840 A, Kevex, 15 kV). Before being analysed the samples were coated with a thin layer of carbon. Analyses from at least three various areas on the surface as well as on the same crystalline product, respectively, of all samples were carried out. By this technique it was not possible to determine of elements lighter than Na.

To determine the chemical structure of large crystals or crystalline aggregates the Raman spectroscopy was used. The Raman spectra of the glass samples were recorded on a Labram I spectrophotometer. The excitation source was a He-Ne laser operating at 632.8 nm.

## RESULTS AND DISCUSSION

High relative humidity values in combination with cyclic temperature changes predetermine that surfaces of weathered samples would be disrupted in all of used environments.

Results obtained from optical microscopy positively confirmed the surface damage of all weathered samples. However, only small particles spread on the surface of samples weathered in normal atmosphere were usually observed (samples 1 to 4). On the other hand the images obtained from SEM at higher magnifications showed that even relatively "undisturbed" surfaces observed by optical microscopy are actually disturbed by creation of pits and/or craters (figure 1a). The EDX microanalyses of samples 1 to 4 showed that these disturbed surfaces (but without any crystalline products) are usually richer in Al<sub>2</sub>O<sub>3</sub> and partly in SiO<sub>2</sub>. The Na<sub>2</sub>O

Table 2. The cyclic temperature conditions during the weathering tests.

Change of temperature	temperature (°C)	time (h)
increase	from 25 to 60	3.5
dwel	60	8
decrease	from 60 to 25	4.5
dwel	25	8

Table 3. The relative humidity and the composition of atmosphere during the weathering tests.

sample no.	class of glass	relative humidity (%)	atmosphere (addition of pollutants)
1	Ba	53 ± 4	normal air
2	Pb	53 ± 4	normal air
3	Ba	97 ± 1	normal air
4	Pb	97 ± 1	normal air
5	Ba	53 ± 4	(CO <sub>2</sub> , 1 vol.%)
6	Pb	53 ± 4	(CO <sub>2</sub> , 1 vol.%)
7	Ba	53 ± 4	(SO <sub>2</sub> , 1 vol.%)
8	Pb	53 ± 4	(SO <sub>2</sub> , 1 vol.%)
9	Ba	97 ± 1	(CO <sub>2</sub> , 1 vol.%)
10	Pb	97 ± 1	(CO <sub>2</sub> , 1 vol.%)
11	Ba	97 ± 1	(SO <sub>2</sub> , 1 vol.%)
12	Pb	97 ± 1	(SO <sub>2</sub> , 1 vol.%)

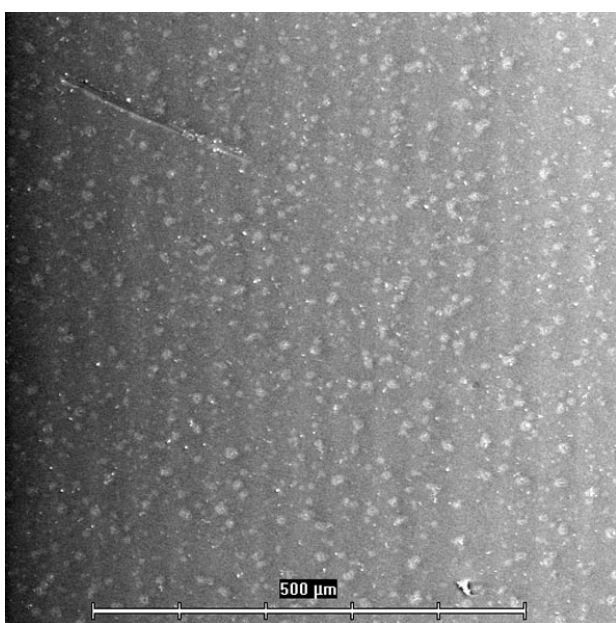
Table 1. The average chemical composition (wt.%) of studied crystal glasses.

glass/oxides	SiO <sub>2</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	BaO	PbO	Al <sub>2</sub> O <sub>3</sub>	ZnO	other oxides
Ba-glass	68.2	5.2	10.4	8.2	6.0	-	1.2	-	0.8
Pb-glass	59.2	11.8	2.2	-	-	24.4	0.3	1.4	0.7

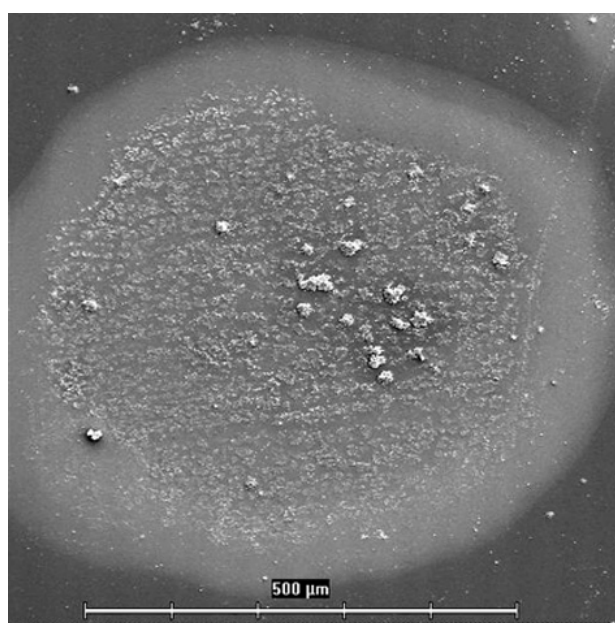
content in Ba-glass and the PbO content in Pb-glass always decrease whereas that of K<sub>2</sub>O in Ba-glass increases. The contents of the others oxides were nearly constant or changed irregularly. A comprehensive comparison of the above results with those obtained from unweathered samples ("virgin glass") is given in figures 2 and 3.

The more aggressive environments with increased concentration of CO<sub>2</sub> or SO<sub>2</sub> produced occurrence of both larger solids and crystalline aggregates (figure 1b). Almost all of solid weathering products were analyzed by EDX spectroscopy. On the other hand, we failed to obtain relatively good Raman spectra for a lot of small crystalline products deposited on the surface of weathered glass samples.

The weathering products obtained in relatively mild aggressive environments (RH about 53 %, increased concentration of CO<sub>2</sub> or SO<sub>2</sub>, samples 5 to 8) were investigated mainly by EDX microanalyses. The small crystals observed on the surface of sample 6 were essentially rich in Na, K and S. Unfortunately their chemical structure was not determined by the Raman spectroscopy. The crystals observed on the surface of sample 7 were always rich in Na, Al and S and those observed on the surface of sample 8 in K, Al and S. The structures of some of these crystals were determined on the basis of Raman spectra. The presence of sodium dithionate, Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>, in the sample 7 (figure 4a) and potassium sulphate, K<sub>2</sub>SO<sub>4</sub>, in the sample 8 (figure 4b) were unambiguously confirmed [10].



a)



b)

Figure 1. SEM micrographs of : (a) sample 1 weathered in normal atmosphere at RH ≈ 53 %; (b) sample 9 weathered in atmosphere with increased concentration of CO<sub>2</sub> at RH ≈ 97 %.

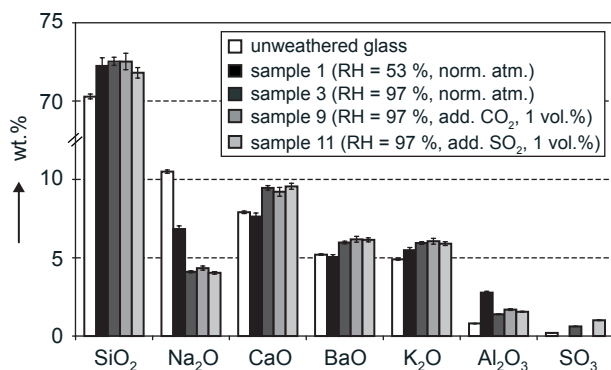


Figure 2. Comparison of results of EDX microanalysis obtained from surfaces of samples (places without any crystalline products) weathered in different atmospheres with that of unweathered Ba-glass.

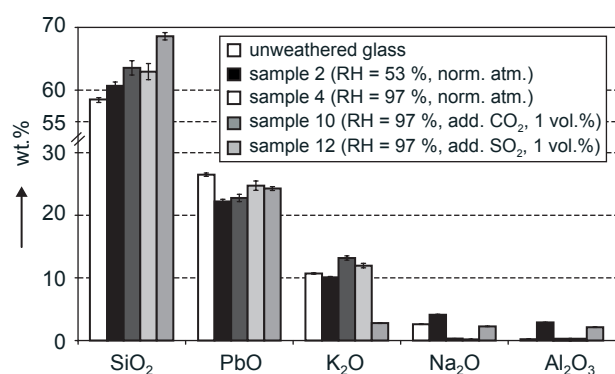


Figure 3. Comparison of results of EDX microanalysis obtained from surfaces of samples (places without any crystalline products) weathered in different atmospheres with that of unweathered Pb-glass.

The greatest changes were observed in environments both with high relative humidity (RH about 97 %) and with increased concentration of CO<sub>2</sub> or SO<sub>2</sub> (samples 9 to 12). During weathering tests some visible droplets have been also formed on the glass surface. Moreover, it can also be observed (figure 1b) that larger solids or crystalline aggregates have usually been formed on places after evaporation of these droplets. On the other hand, small crystalline particles were usually observed on the whole surface of weathered samples.

The composition of the intact glass surface beneath the crystalline weathering products depends significantly on the crystal glass type (figures 2 and 3). By EDX microanalysis of samples 9 and 11 we found that the Na<sub>2</sub>O content in Ba-glass always decreases, whereas that of the others oxides partially increases. On the other hand the changes in the contents of the oxides in Pb-glass (samples 10 and 12) are significantly different and they characterise each the aggressive gas used for the weathering test. The weathered surfaces, however, are always richer in SiO<sub>2</sub> and poorer in PbO one.

The chemical composition and the structure of all the larger weathering products deposited on the surfaces of the samples 9 to 12 have been examined by EDX microanalysis and by Raman spectroscopy, respectively. In some cases the compositions found at various points of the same weathering products were significantly different. Moreover, it has been found that the solid products deposited on Ba-glass in the sample 9 contained the small amount of SO<sub>3</sub>. This suggests that during the weathering tests various components from glass have been gradually extracted into water droplets. In the presence of reactive gases such as CO<sub>2</sub> and SO<sub>2</sub>, however, metallic ions could form various compounds that may slowly crystallize or precipitate as mixtures of

solids on the surface of a glass sample. The results have been partially confirmed by Raman spectroscopy, however, good Raman spectra with intense and narrow bands have been obtained for some weathering products only (figure 6).

The size and the shape of solid weathering products deposited on the surfaces of the samples 9-12 were usually different. The largest aggregates reach a diameter of 100 μm (figures 5a to 5d). The larger solids with shapes like flowers as well as the smaller needlelike crystals were observed on the surface of the sample 9 (figure 5a). While the latter product is significantly richer in Na, S and partially in K and Ca, the composition of the former depends on spots chosen for EDX measurements. In some regions this product was richer in Na, K and S, but in another one mainly in Ca. The good Raman spectrum of these solids from regions with increased content of Ca is shown in figure 6a. It is evident that this part of weathering products contains mainly calcite in the form of calcium carbonate, CaCO<sub>3</sub>, and partially barium sulphate, BaSO<sub>4</sub> [10].

On the other hand, the weathering products formed on the surface of the samples 10 and 11 were usually observed as bulky compact solids of irregular oval shapes (figures 5b and 5c). It also indicates that these weathering products have been mainly formed by the simultaneous crystallization, precipitation and/or evaporation from water droplets containing various compounds. It has been found that the larger weathering products on the sample 10 were richer in Na, Ca and Al compared with the virgin Pb-glass. Moreover, these solids always contain some amount of S. On the other hand, the solid weathering products on the sample 11 contain mainly Na, S and Al. The Raman spectra of solids recorded from the samples 10 and 11 were of bad

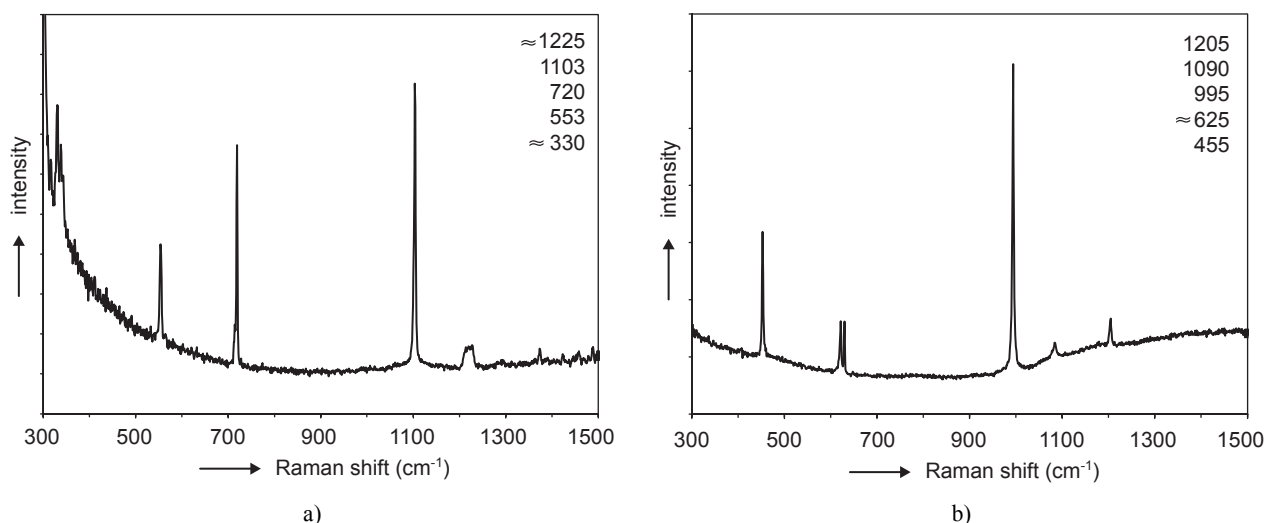


Figure 4. Raman spectra of some crystals from samples weathered in atmosphere with increased concentration of SO<sub>2</sub> at RH ≈ 53 %; (a) sample 7 (Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>), (b) sample 8 (K<sub>2</sub>SO<sub>4</sub>).

quality. It seems, however, that the mixture of weathering products formed on the sample 11 consists mainly of various sodium compounds such as sulphates ( $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$ ) and carbonates ( $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ).

It is obvious from figure 5d that large aggregates deposited on the surface of the sample 12 consist of smaller crystals with different size and shape. Their chemical composition is often significantly different. While all the crystals are considerably rich in Na and S, some of them are also richer in K and Ca. The Raman spectrum obtained from one part of the crystalline

aggregate is shown in figure 6b. It is evident that the spectrum has been measured from a mixture of crystals with different composition and structure. However, the positions and the intensities of the bands observed in this spectrum lead to the conclusion that crystalline aggregates contained potassium sulphate,  $\text{K}_2\text{SO}_4$ , sodium sulphate,  $\text{Na}_2\text{SO}_4$ , as well as potassium carbonate,  $\text{K}_2\text{CO}_3$ . We also obtained the different Raman spectrum from another part of the crystalline aggregate that contains mainly potassium carbonate and partially other compounds such as various sulphates.

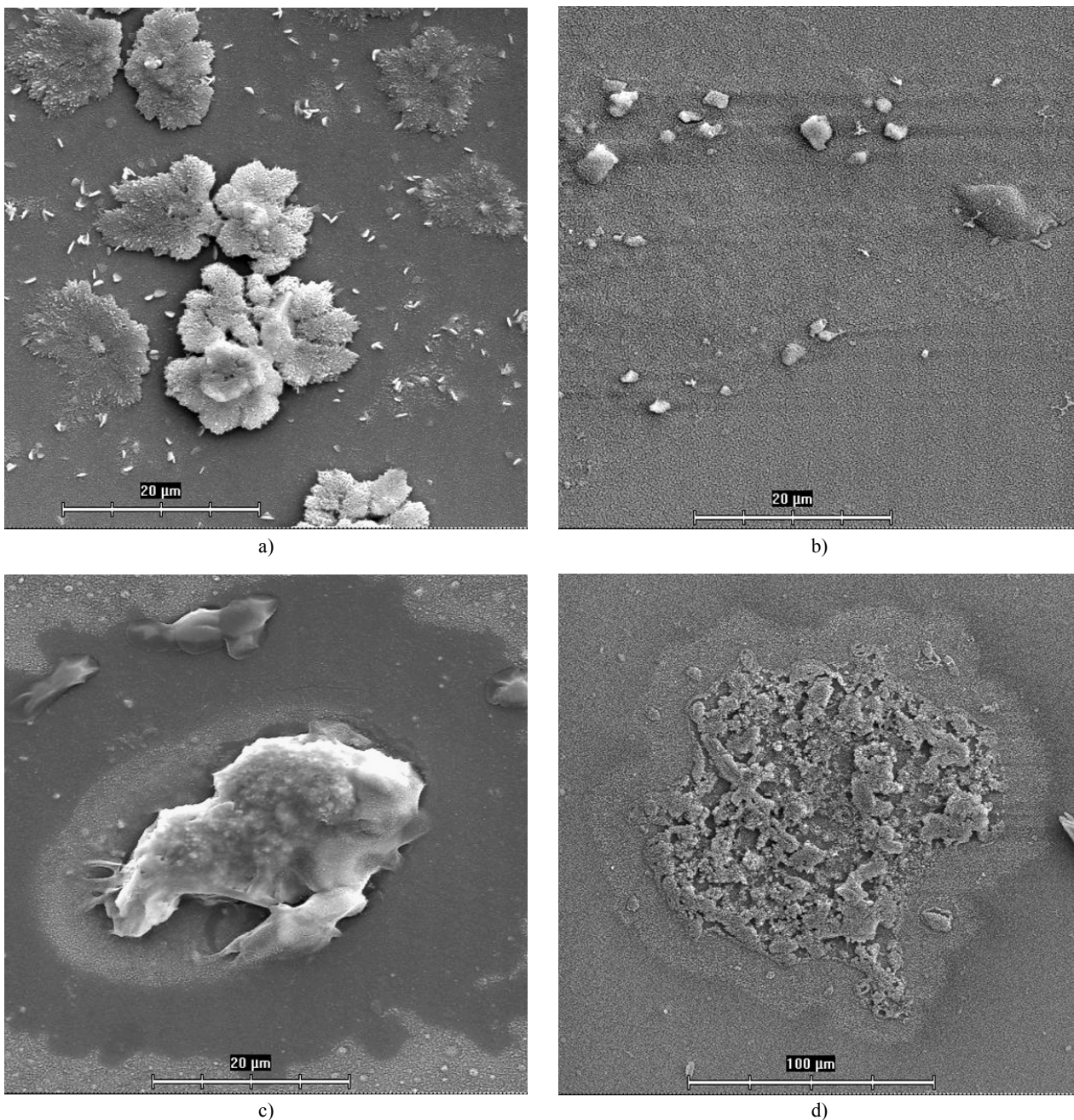


Figure 5. SEM micrographs of some solid products from samples 9 to 12 weathered in atmosphere with increased concentration of  $\text{CO}_2$  or  $\text{SO}_2$  at  $\text{RH} \approx 97\%$ ; (a) and (c) from samples 9 and 11, respectively (Ba-glass) (b) and (d) from samples 10 and 12, respectively (Pb-glass).

Another goal of this work was to investigate the possible effect of used environments on permanent changes of glass surfaces quality. To remove weathering products the glass samples were washed using standard detergent, rinsed with deionised water and then dried. Investigation of permanent defects caused by weathering process showed that surfaces all of the samples weathered at high relative humidity (about 97 %) were either partially or significantly damaged. Whereas the environments with normal atmosphere as well as with increased concentration of SO<sub>2</sub> did not caused significant permanent flaws on the glass surface of both

weathered crystal glasses that with increased CO<sub>2</sub> concentration caused a considerable damage over the whole surfaces (figure 7).

### CONCLUSION

The surface of twenty crystal glass samples was investigated. They have been obtained by the weathering in six different environments for 50 days at cyclic temperature ranging between 25°C and 60°C. The creation of solid products as well as the degradation of the

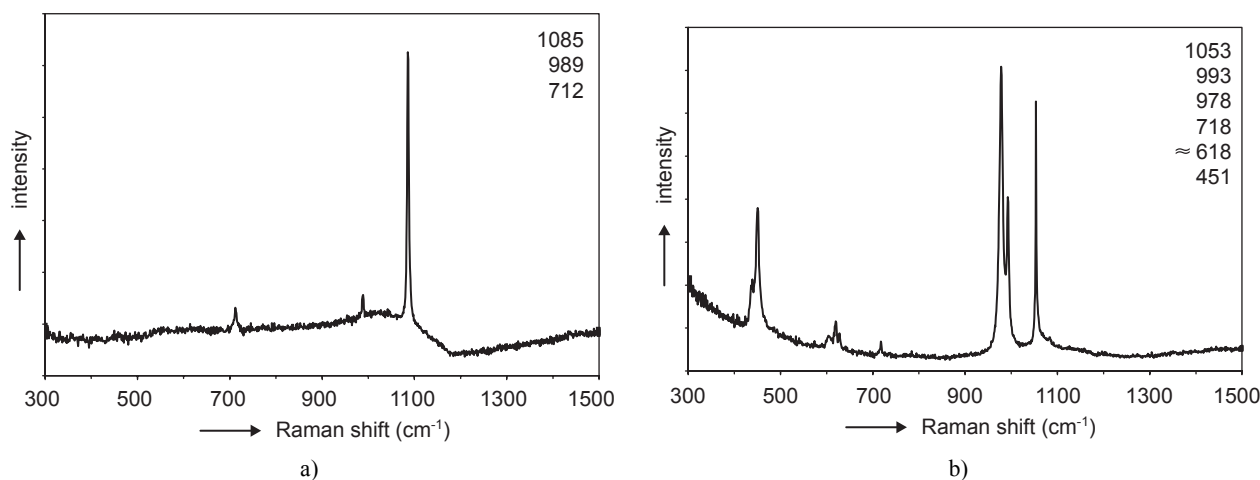


Figure 6. Raman spectra of some crystals from samples weathered at RH ≈ 97 %; a) in atmosphere with increased concentration of CO<sub>2</sub> - sample 9 (mixture of CaCO<sub>3</sub> and BaSO<sub>4</sub>), b) in atmosphere with increased concentration of SO<sub>2</sub> - sample 12 (mixture of K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub>).

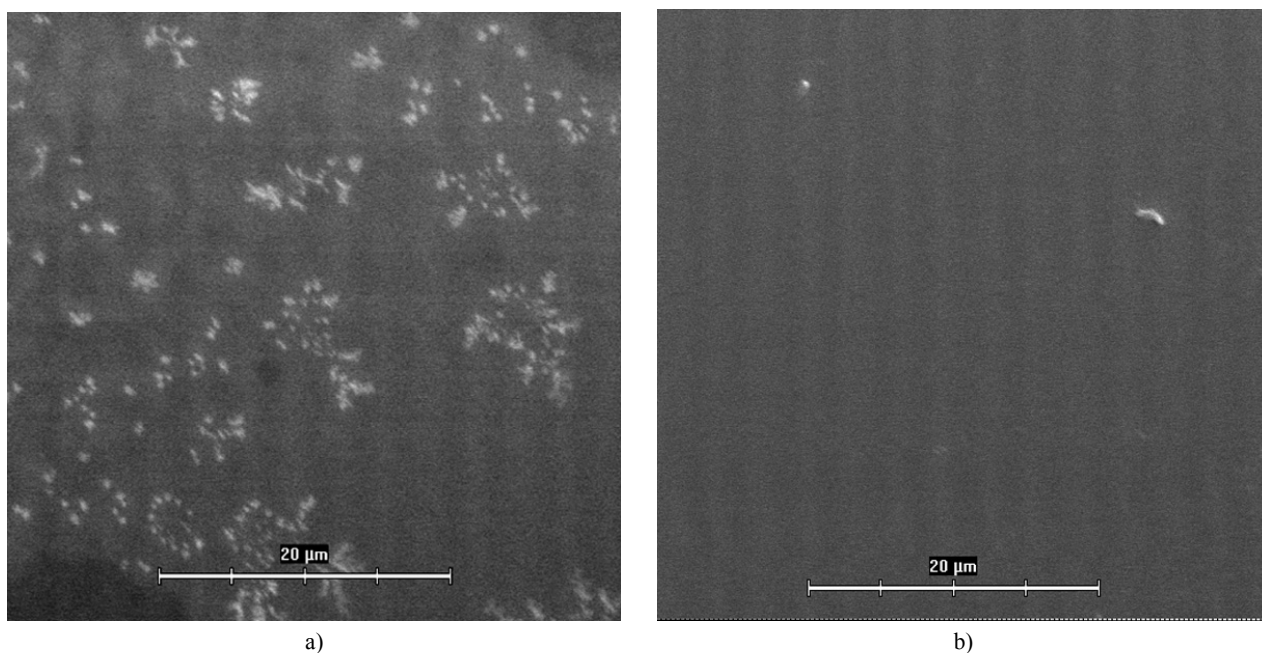


Figure 7. SEM micrographs of samples 10 and 12 weathered at RH ≈ 97 % after washing up weathering products (Pb-glass); a) sample 10 weathered at increased concentration of CO<sub>2</sub>, b) sample 12 weathered at increased concentration of SO<sub>2</sub>.

glass surface on all the weathered samples was observed. It follows that cyclic temperature changes in combination only with normal but moist atmosphere are sufficient to damage the surface of the crystal glasses under study.

Increased concentration of aggressive acid oxides such as CO<sub>2</sub> or SO<sub>2</sub> in the surrounding environment causes more extensive weathering of the glass surfaces. The greatest changes were observed in environments of both one with the high relative humidity (about 97 %) and the other with increased concentrations of CO<sub>2</sub> or SO<sub>2</sub> (about 1 vol.%).

The size and the shape of solid weathering products deposited on the surfaces of the samples differed significantly, e.g. from small particles distribute on the whole surface to the large crystalline aggregates reach a diameter of 100 μm. Their chemical composition and structure significantly depend on the type of crystal glass as well as on the environmental composition used during weathering tests. The EDX microanalysis showed that they are usually rich in Na, K, Ca, Ba, S or Al, the content of C not being determined. The structure some of these solid products was unambiguously determined from Raman spectra. It was found that larger solids or crystalline aggregates usually consist of various sulphates and carbonates, the presence of sodium dithionate being also confirmed.

Alkaline solutions of various carbonates are assumed to be created as the main end products in a liquid film or droplets created on the surface of samples weathered in the environment with increased CO<sub>2</sub> concentration at high relative humidity. These solutions can further cause damage to the sample surface following the mechanism characteristic for so-called "corrosion of glass" in alkaline solution [6] that results from the occurrence of permanent defects on the glass surface (figure 7a).

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#### ZVETŘÁVANIE KRIŠTÁLOVÉHO SKLA V ATMOSFÉRE SO ZVÝŠENÝM OBSAHOV VLHKOSTI A PLYNNÝCH ZLOŽIEK

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Sledoval sa proces zvetrávania krištáľových skiel s obsahom PbO a BaO, v závislosti od zmeny relatívnej vlhkosti a zmeny koncentrácie plyných zložiek (CO<sub>2</sub> alebo SO<sub>2</sub>) v okolitej atmosfére. Hodnota relatívnej vlhkosti bola 53 % alebo 97 % a koncentrácia plyných zložiek bola rovnaká ako za bežných podmienok, alebo zvýšená prídavkom 1 obj. % danej zložky. Rovnako sa pozoroval vplyv cyklickej zmeny teploty okolitej atmosféry na zvetrávanie uvedených krištáľových skiel. Zvetraný povrch vzoriek sa sledoval použitím optickej mikroskopie, riadkovej elektrónovej mikroskopie, röntgenovej mikroanalýzy a Ramanovej spektroskopie. V priebehu zvetrávacích experimentov sa na povrchu vzoriek tvorili rôzne tuhé produkty, ktorých morfológia a chemické zloženie významne závisia od typu krištáľového skla a zvetrávacích podmienok. Pozorovalo sa, že tuhé kryštalické produkty zvetrávania vo väčšine prípadov obsahujú rôzne sírany a uhličitany (napr. CaCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, BaSO<sub>4</sub> a K<sub>2</sub>SO<sub>4</sub>).