Structure and IRR spectra of copper-exchanged soda-lime silica glass

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Abstract. Multi-component soda lime silica glass (SLSG) specimens, with composition from the miscibility gap in the SiO2–Na2O system, were investigated after the substitution of copper for sodium and after thermal treatment of the exchanged samples in gaseous hydrogen. The behaviour of the obtained composite materials was studied by infrared reflection spectroscopy (IRRS). Some optical absorption micro-spectrophotometry (OAMS) measurements and X-ray-diffraction (XRD) analyses complemented these investigations. It has been stated that after exchange in the CuCl molten bath, the dopant was present in the glassy matrix in the form of cuprous and cupric ions. The cuprous ions participate in the formation of semiconducting Cu2O nanoparticles. Hydrogenation of the exchanged specimens leads to the formation of metallic copper atoms which due to the van der Waals interactions precipitate in the form of colloidal copper nanoparticles. Changes of the matrix morphology are mainly related with the presence of cupric ions which behave as glass forming cations and such as these participate in the formation of mixed copper-sodium silicates. The effectiveness of these processes is substantially dependent on the exchange and hydrogenation parameters.

1. Introduction

Ion exchange between an oxide glass and a molten salt is used for preparation of composite materials for a variety of applications, such as chemical strengthening of glasses [1], formation of gradient index materials [2], and fabrication of passive integral optical devices [3, 4]. Although the formation of copper-colloids in these glasses is well documented [5, 6], the ion exchange process, in which a part of the univalent cations in a silica glass is replaced by other univalent cations from a molten salt, has been conducted to date without paying much attention to the alteration of the glass structure. It has been shown recently [7], that some structural changes occur during the exchange of soda lime silica glass and lead to distinct modifications of the phase separated occlusions already present in not-exchanged specimens, cf. figure 3 in [7].

The purpose of the work described was to study the interrelations between the exchange conditions, copper valence state, optical properties and the structure of copper-doped multi-component soda-lime silica (SLS) glass. The local structure of the glass network was investigated by infra-red-reflectance
spectroscopy (IRRS). Measurements of optical absorption micro-spectrophotometry (OAMS) and powder-X ray-diffraction (XRD) were made to obtain supplementary data.

2. Experimental part: specimens and measurements

A multicomponent soda-lime silica glass (SLSG), produced according to the Fourcault procedure (Torgau-factory, Germany), was used. The content of the main components (SiO$_2$/73 mol % and Na$_2$O/13 mol %) corresponds to the miscibility gap in this system [8].

Doped samples have been prepared by the ion exchange method, and to the first time for this type of glasses molten CuCl salt was used at the exchange temperature of 903 K for times between a few min. and 168 h. To avoid the formation of a metal lustre, samples were exchanged in the air atmosphere. Under these conditions, the dopant enters the matrix as cuprous and cupric ions, and the equilibrium between both valence states depends in a quite complex way on the temperature and time of exchange. To transform the copper ions into atoms and metallic nanoparticles, it was necessary to anneal the exchanged samples in gaseous hydrogen at temperatures $\geq 573$ K; for the purposes of the present work 5 h at 773 K have been chosen. Not-exchanged specimens were used as a reference material.

According to the previously obtained EDX data, see figure 1 in [9], the copper concentration-profile in the SLSG specimens has a rectangular shape with a constant value of the concentration from the sample surface up to the end of the penetration depth. For each temperature, this depth increases with the increase of the exchange time. The sodium concentration-profile gives the degree of the Cu/Na-exchange. It has been stated that at the surface about 90 % of sodium has been exchanged independently of the exchange time.

To determine the local atomic arrangement around the copper ions and copper nanoparticles in the exchanged and hydrogenated specimens, respectively, infra-red reflectivity (IRR) measurements have been performed. The IRR spectra were measured with a BIORAD 575 C FT-IR spectrofotometer in the 1300-400 cm$^{-1}$ range with a spectral resolution of 2 cm$^{-1}$. The measurements were performed at near normal incidence of 10° using a fixed-angle specular reflectance accessory.

Optical absorption micro-spectrophotometry (OAMS) allowed to measure the extinction spectra of doped samples (nominal thickness was about 25 $\mu$m) for a fixed value of wavelength ($\lambda$) as function of the penetration depth in steps equal to 0,5-1,0 $\mu$m [10]. Optical profiles of the copper incorporation into the SLSG samples were determined by using the ARL EMX SM 32 electron-probe microanalyzer.

The powder X-ray-diffraction (XRD) data were collected with the aim of a STOE powder X-ray diffractometer using the (Cu-K$_\alpha$) radiation.

3. Results and discussion

3.1. The SiO$_4$ tetrahedron vibrational unity

The soda lime silica glasses are Si-O networks in which the SiO$_4$ tetrahedra are joined together by the oxygen atoms located at the vertices. These SiO$_4$ tetrahedral connections become modified by incorporation of the Na, K, Ca, Mg, Al and Fe ions (present in the SLSG specimens) which alter the polymerization degree of the glass framework. Also the dopant ions and/or particles affect the polymerization degree of the matrix. Five structural units (Q$^0$-Q$^4$) correspond to the SiO$_4$ tetrahedra with different number (4-0) of the bridging oxygen atoms [6]. The IRR spectra obtained for the exchanged and hydrogenated specimens reflect the modifications of the SiO$_4$ tetrahedral vibrational units. Mostly, the intensity, line-width and spectral position of the associated reflection bands are considered in terms of the symmetric stretching modes; this description is essentially the same as that presented in terms of the modes originating from bending of the SiO$_4$ units [11-13].

3.2. IRR spectra
Figure 1 shows representative IRR spectra detected for not exchanged (curve a), copper exchanged (curve b) and hydrogenated (curve c) SLSG samples for which the exchange time at 903 K was equal 168 h. For shorter exchange times, the results were qualitatively similar.

For not-exchanged samples the strongest bands are located at 1060 cm$^{-1}$ and 462 cm$^{-1}$, and are related with the Q$^3$ stretching and bending vibrational modes, respectively. The shoulders, detected on the high and low vibration side of the 1060 cm$^{-1}$ band, correspond to the Q$^4$ (1150 cm$^{-1}$) and Q$^2$ (930 cm$^{-1}$) units, respectively.

After the ion-exchange, the width of the main bands decreases (in comparison with not-exchanged specimens), suggesting that the glass framework became more ordered. Moreover, the frequency of the stretching Q$^3$ band strongly increases (1060 → 1109 cm$^{-1}$), the frequency of the bending Q$^3$ band also increases but not so much (462 → 473 cm$^{-1}$), the frequency of Q$^2$ slightly decreases, and the intensities of Q$^4$ and Q$^2$ remain nearly unchanged. This behavior could be explained in terms of some de-polymerization which occurs in the glass framework, but in conflict with this suggestion is the detected increase of the stretching Q$^3$ frequency. On the other hand, assuming that a part of the stretching Q$^3$ units disappears giving a mixture of (Q$^4$ + Q$^3$), the frequency of the stretching Q$^3$ band would increase and this increase should be accompanied by a decrease of the bending Q$^3$ frequency. Also this supposition is in conflict with the experimental observation. Moreover, the expected intensity increase of the Q$^3$ and Q$^2$ bands has not been detected. Taking into account the experimental data and all the mentioned incompatibilities one has to consider that the results are consequences of interactions between the dopant ions and the oxygen atoms from the silica framework.

Hydrogenation, performed after the ion-exchange, leads to a slight increase of the stretching Q$^3$ frequency (1109 → 1115 cm$^{-1}$), suggesting further decrease of the corresponding (Si-O) bond length, an increase of the interaction force and a slight decrease of the polymerization degree. The appearance of a new band at about 1007 cm$^{-1}$ has been tentatively ascribed to the formation of some silicates, the structure of which comprises chains of connected SiO$_4$ tetrahedra [6]. The absence of bands characteristic of the Q$^0$ and Q$^1$ units indicates that clustering is limited to two cations per one SiO$_4$ tetrahedron, at least below the di-silicate composition.

The XRD-data (figure 2), have been accepted as confirmation of this hypothesis although a proper identification of the newly created phase was unsuccessful on the basis of the present data. Probably
the number of the corresponding particles per unit area of the sample surface is very small and they are amorphous at this stage of the sample preparation.

3.3. Structural interpretation of the spectral features

The described results have shown that more complex structural modifications of the matrix must be considered to account for the behavior of the copper-doped soda-lime silica glass.

First of all, one has to stress that the mentioned changes of the glass morphology are characteristic only for specimens exchanged at temperatures above the glass-transformation temperature [7]. Under these conditions, the concentration of cupric ions is distinctly larger than that of the cuprous ions. Moreover, according to the optical microspectrophotometry the divalent copper ions are still present in the hydrogenated specimens. Figure 3 exemplifies the results of the OAMS after 168 h of exchange.

![Figure 3](image)

Figure 3. The optical microspectrophotometry figures characteristic of SLSG specimens exchanged for 72 h (upper part) and hydrogenated afterwards (lower part).

The dark zone, which in the hydrogenated sample corresponds to the copper colloids, is followed by other colored zones related with the presence of cupric ions probably in the form of some silicates, see Section 3.2. The narrow and sharp zones in the "optical profiles" are compatible with the copper concentration profiles [9], and are characteristic of transitions between the compression and tension zones in exchanged and thermally treated specimens.

With respect to the IRRS results, substitution of sodium ions in the SLS glasses by other metal ions should affect the frequencies of both $Q^3$ modes (stretching and bonding) by shifting their frequencies towards lower or higher values. These changes are consequences of the altered glass framework where the number of the bridging Si-O-Si bonds, represented by the $Q^2$, $Q^3$, and $Q^4$ modes, and the bonding strength between the matrix oxygens and the dopant ions were changed.

While the cuprous ions are comparable in size with the exchanged sodium, the cupric ions are distinctly smaller and each divalent copper replaces two univalent sodium ions. The matrix becomes more tight and the shorter (Si-O) bonds could be responsible for higher frequencies of the related $Q^3$ units. For changes induced only by the structure (morphology), the frequencies of the stretching and bending $Q^3$ modes should be shifted in opposite directions. This means that for increasing number of the bridging-oxygens the frequency of the stretching band (1050-1100 cm$^{-1}$) should increase while the frequency of the bending $Q^3$ (450 cm$^{-1}$) should decrease. And for decreasing number of the bridging oxygens, the opposite effect should be observed. The bonding strengths, characteristic of both $Q^3$ modes, should be affected approximately in the same way. In the described case, the intensities of the $Q^2$, $Q^3$, and $Q^4$ bands are relatively small, and the frequencies of both $Q^3$ modes are shifted towards higher values. Although, this behavior could be explained in terms of the formation of a more tight glass network, it is also possible to consider that the divalent copper ions are not only located at positions anticipated for the glass-modifiers but are also able to enter the matrix as the glass-formers and form new silica phases. This possibility was, among others, considered for the phosphate glasses where the (Cu-O) bonds are relatively strong and have a large covalent contribution (similar to the case of Cu in SLSG). The glass-forming position for divalent copper was also evidenced for the silica
glasses on the basis of some optical and magnetic characteristics [15-17]. The detection of a new IRR band (1007 cm\(^{-1}\)) in the hydrogenated SLSG specimens strongly confirms these suppositions.

4. Summary
Combined studies of the optical and structural characteristics of copper-doped SLSG specimens show that:

- Distinct morphology changes of the glassy matrix occur due to the joint effect of divalent copper and the high temperature treatment;
- These changes are related with the formation of strong chemical bonds between the dopant and the non-bridging oxygens of the matrix;
- The Cu-O interactions, induce the decrease of the Si-O bond lengths and result in an increase of the compactness of the glass framework;
- Some mixed sodium/copper silica phases could be formed in the exchanged SLS glass, and suitably sized voids in the hydrogenated specimens accommodate the copper nanoparticles;
- The described phenomena suggest that the divalent copper ions in the ion exchanged glasses not only replace sodium ions (one for two) but are also responsible for the alteration of the glass network;
- These preliminary investigations deserve further studies, and more work is needed to understand the role of the divalent cations in perturbing the network of the soda lime silica glasses.

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