STRUCTURE AND HARDNESS OF COPPER-DOPED SODA-LIME SILICA GLASS

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Introduction

In the last decades several works have been published in the literature concerning nano-meter-sized metal particles in glasses. Especially interesting are the noble metal particles because of their unique linear and nonlinear optical properties associated with the strong surface plasmon resonance due to the d-d optical transitions, cp. [1]. For the potential optical applications, mechanical characteristics of the composed materials are of great importance.
The purpose of the work described was to introduce copper into the soda-lime silica (SLS) glass by the ion exchange procedure and to study the effect of the exchange conditions upon the copper valence state, the structure of the doped material and the Vickers micro-hardness (VH). The structure was followed by transmission electron microscopy (TEM) and the powder X-ray-diffraction (XRD) technique. Measurements of the linear thermal expansion ($\Delta L/L$) were also performed.

Experimental

The method of sample preparation and the conditions of the ion exchange were essentially the same as those described in a previous report [2]. For the exchange, cuprous chloride was mainly used at T≅723-903 K for times between a few min. and 168 h. After exchange, the specimens were annealed at 773 K for 5 h in a hydrogen atmosphere.
The XRD data were collected with a STOE powder X-ray diffractometer using the Cu-K_α radiation. For TEM observations two types of replica were prepared from the surface of specimens. The PHILIPS-CM 20 microscope was used at 200 kV with a 0,24 nm point-to-point resolution.
For the micro-hardness data, the Vickers pyramid (ZWICK 3212 tester) was applied for loads ranging between 1 and 30 N. The diagonal lengths of the indentation marks were exploited to calculate the VH values.
Thermal expansion was measured with a quartz capacitance dilatometer cell [3]. The measurements have been performed in a temperature (T) range from 293 K to 413 K during the cooling at a rate of 0,5 K/ min. The sensitivity of measurements was 10^{-7}, and the accuracy was about 5%.

Results and Discussion

Structure
Figure 1 presents a HRTEM micrograph of the glass sample in which the Cu nanoparticles were surrounded by Cu_2O in the form either of globules or layers. The identification of both components of the core-shell structure has been confirmed by the surface area electron diffraction performance.

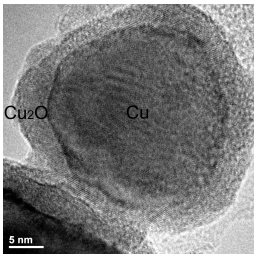

Fig.1 HRTEM micrograph of a soda lime silica glass exchanged with copper.

It has been stated that the quantity, size and distribution of the Cu and Cu_2O nanoparticles depend upon the preparation conditions. These conditions also affect the size and shape of the matrix particles separated yet in as obtained specimens [2]. The matrix morphology was altered only in samples exchanged above the glass transformation temperature ($T_G \cong 840$ K).
The XRD data (cp. Fig. 2) suggest the formation of a new phase the identification of which was, however, not possible on the basis of the present results. On assuming, that rearrangement of the glass morphology relates with the formation of new phases, changes of the linear thermal expansion coefficient of the material are expectable.

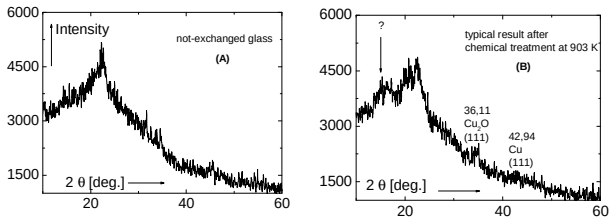

Fig. 2 XRD-spectra of samples as-obtained (A) and hydrogenated after 168 h of exchange (B).

Figure 3 compares the thermal deformation of specimens chemically and thermally treated with

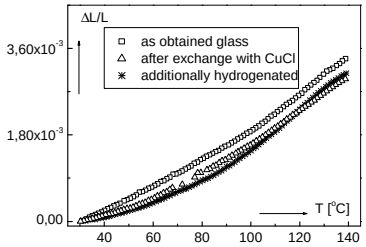

Fig. 3 Thermal expansion curves of the glass samples studied.

data characteristic of the as obtained ones. The detected decrease of the thermal expansion could be related with the formation of some mixed sodium-copper silicates [4, 5].

Microhardness

Variations of the Vickers-hardness as function of the indentation load are shown in Fig. 4. A distinct increase of hardness was detected for heavily doped specimens ($t \geq 24$ h). After hydrogenation, the VH

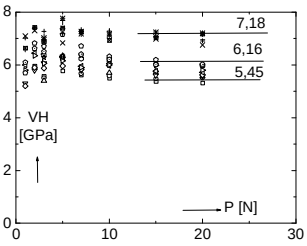

Fig. 4 VH versus indentation load for specimens exhanged up to72 h at 903 K.

values were nearly the same as those obtained directly after exchange. On the other hand, the exchange below T_G shows a detectable increase of VH only after relatively long exchange time (t). For instance, 168 h of exchange at 723 K yields a VH value nearly equal to that obtained after two h at 903 K. It should be stressed that the annealing of not exchanged SLS glass specimens in air for times and at temperatures typical of the copper exchange and/or hydrogenation induces only minor changes of the microhardness.

Conclusion

The results obtained indicate that copper enters the glass network as cupric and cuprous ions which induce gradual changes of the glass morphology. Creation of strong bonds between copper and the non-bridging oxygen ions of the matrix results in the formation of monovalent copper oxide and some mixed sodium/divalent copper silicates. The related compressive stresses are responsible for the detected increase of microhardness. Differences in strengthening of samples exchanged below and above T_G are related with the differences in the oxidation degree of copper. The formation of cupric ions prevails at $T \geq T_G$. In hydrogenated specimens the strengthening effect is comparable with that characteristic of the exchanged specimens although a part of the cuprous ions forms colloidal particles The additional strengthening contribution comes from the changed geometry of particles present in the phase separated matrix.

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