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Spectroscopic and dielectric characteristics of nickel-doped porous silica glasses

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The direct current conduction and electrical relaxation currents in nickel-doped porous silica glasses were investigated by using the thermally stimulated polarisation and depolarisation current techniques in a wide temperature range. Optical absorption measurements and transmission electron microscopy observations accompanied these studies. All characteristics were found to be affected by the porous matrix and the material filling the pores.

Keywords: nickel nanoparticles, porous glasses dielectric properties, optical absorption.

1. Introduction

Porous glasses are potentially important materials due to their large surface areas and controllable pore dimensions. An introduction of proper molecular species into the confined volumes of the pores could modify the physical and chemical properties of these materials. For effective applications and the fundamental research it is necessary to know the structure and composition of the interfaces between the constituent parts of the composite.

In the present paper, investigations of porous glasses, obtained from sodium-boro-silicate compositions and filled either with water molecules or nickel in the form of ions and nanosized particles, have been described. Measurements of thermally stimulated polarisation (TSP) and depolarisation (TSD) currents were performed to clarify the dynamic behaviour of different states of both fillers in the porous matrix. Complementarily, the optical absorption (OA) spectroscopy in a wide spectral range and the transmission electron microscopy (TEM) observations, with the high resolution TEM (HRTEM) and selected area electron diffraction (SAED) performances, were exploited to characterise the active matrix and the species related to the fillers.

2. Experimental part

2.1. Samples

Porous glasses can be understood as the leaching products of phase separated alkali -boro-silicate glasses. Heat treatment of these glasses (of a suitable composition) in a temperature range between 760 and 850 K initiates a phase separation into two interconnected phases. The first one is an alkali-rich borate phase soluble in hot mineral acids, and the second one is almost pure silica. The initial glass-composition, conditions of heat treatment (time and temperature) and the leaching conditions determine the structural and textural properties of the porous glass [1].

In order to understand the influence of disorder on the physico-chemical properties of glasses, the relationship between their properties and the structure is one of the basic problems of the glass-science. The porous materials can be produced in a wide range of densities and pore size distribution, which give further degree of structural disorder.

The samples used in the work described were prepared at the Institute of Electronic Materials Technology (Warszawa, Poland) from originally boro-silicate glasses with a nominal composition as follows: 62.55% of SiO_2, 30.40% of B_2O_3 and 7% of Na_2O. After 165 h of annealing at about 760 K strong phase separation was induced. This phenomenon results in interconnected and randomly oriented pores with nearly uniform pore-size distribution. To guarantee such uniformity, the samples should be thinner than about 0.5 mm. After phase separation, samples were washed in distilled water and 0.5 M HCl, and dried at 429 K during 20 minutes. Nevertheless, some of the samples contained amorphous silica gel deposited at the internal surfaces of pores.

After extraction of the sodium-borate phase and additional annealing under vacuum at 520 K for 3 h, the specific surface area of specimens was determined by the Brunamer–Emmet–Teller (BET) method. The value obtained equals to 63 m^2/g, and the corresponding size of the pores ranged between 2 and 50 nm. The large specific area of the porous glasses provides a large contact of samples with the ambient, and the porous matrix is a very active material. Water molecules from the humid air atmosphere can easily be adsorbed and desorbed from the silica surfaces. The geometrical confinement and interactions with the active surface sites should affect the properties of the adsorbed particles.

The impregnation with nickel was performed by dipping the samples in 0.5 M solution of $Ni(NO_3)_2 \times 6H_2O$ for about 5 h and drying them at 390 K for different time periods. After evacuation of the residual solvent, samples underwent the permeation of gaseous hydrogen in order to decrease the valence of the dopant possibly up to the atomic state which could be the nucleus of metallic and metal oxide nanoparticles.

The sol-gel samples have been performed by dr. Hreniak from the Institute of Low Temperature and Structure Research (Polish Academy of Sciences, Wrocław, Poland). Technological conditions are based on the general ones for preparations of the SiO_2 sol-gel specimens [2].

2.2. Measurements

The dielectric characteristics of porous silica glasses were up to now mainly investigated by dielectric spectroscopy [3, 4], and we hope that our measurements permit to gain further insight into the complex relaxation behaviour of this composite.

Dielectric characteristics of the porous glass specimens filled either with nickel ions or nickel nanoparticles were measured in a dc-field and critically compared with data obtained for as prepared samples. The thermally stimulated polarisation (TSP1 and TSP2) and depolarisation (TSD) currents were measured in vacuum in a temperature range between 230 and 450 K by using electric fields up to about 500 V/cm at a linear heating rate equal to about 5 K/min.

The linear portion of the TSP2-curve was used to calculate the dc-conduction from the relation $\sigma = id/VA$. In this relationship, i is the measured current, d – the specimen thickness, V – the dc-voltage applied, and A – the area of the sample. The exponential temperature dependence of σ ($\sigma = \sigma_0 \exp(-E_{dc}/kT)$) gave the activation energy of the related process from the slope of σ *vs.* $1/T$. On the other hand, for TSD runs the activation energy was determined by using the partial discharge procedure.

The optical absorption at room temperature (RT) was measured within the 200–6000 nm spectral range by using a Cary–Varian and Bruker spectrophotometers, respectively. Besides these measurements the samples were characterised by using the TEM observations accompanied by the HRTEM and SAED performances. For these purposes a 200 kV-Philips microscope, providing a 0.24-nm resolution, was used. Fine powder samples and carbon shadowed replicas from the sample surface were prepared. In the former case, the massive sample was grinded in an agate mortar and ultrasonically dispersed in methanol. A droplet of this suspension was deposited on a microscope grid covered by the carbon film.

3. Results and discussion

Figure 1 shows TEM microphotographs of the porous matrix (**a**), the nickel nanoparticles distributed within the matrix (**b**) and the HRTEM image of a nickel nanoparticle (**c**). The morphology of the material corresponds to randomly interconnected structure of

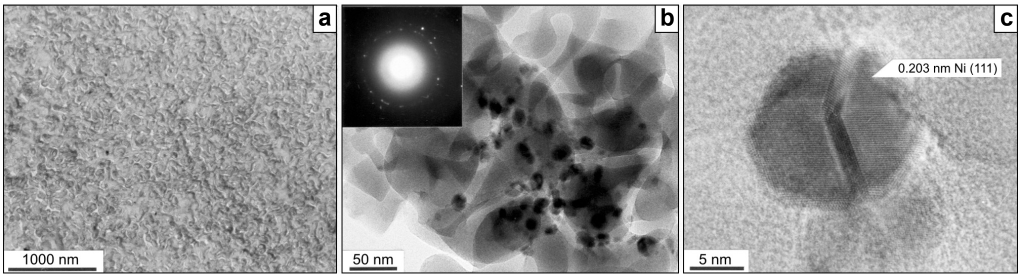

Fig.1. TEM microphotographs of the porous matrix (**a**), the nickel nanoparticles distributed within the matrix (**b**) and the HRTEM image of a nickel nanoparticle (**c**).

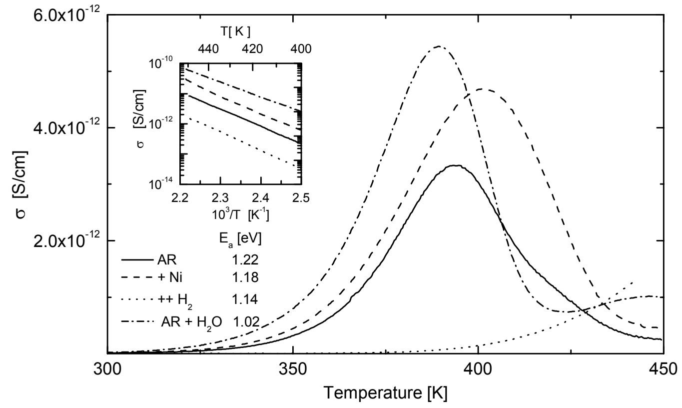

Fig. 2. Spectra of thermally stimulated currents of differently treated porous glass samples; the inset shows the corresponding linear parts of the TSP2-runs which permit to determine the activation energy of the related process.

two interpenetrating phases. They are the solid one (nearly pure silica) and the framework of pores. The lattice fringes ≅ 0.203 nm correspond to the (111) planes of nickel the presence of which has been confirmed by the SAED image. The particles are more or less regular in shape and have an average size of 15 nm. In the HRTEM image, a ⟨111⟩ stacking fault in the nickel particle and a few planes corresponding to NiO particles have been also detected.

Some representative TSC-spectra of thermally stimulated depolarisation currents of differently treated porous glass samples have been shown in Fig. 2. The inset shows linear parts of the corresponding TSP2-runs used to determine the activation energy of the related process. It has been found that the activation energy characteristic of as prepared (AR) specimens are nearly the same when determined for the TSP1 and TSP2 runs, while for impregnated specimens the energy values determined from TSP2 are larger than those obtained from TSP1 by about 0.2 eV. The current values are always larger (about two times) for TSP1 than for TSP2, indicating that the band is not electronic in origin. The TSDC run gives mainly one depolarisation band followed by the so-called high temperature background (HTB). The polarisation conditions for the detected band were as follows: the polarisation temperature $T_p = 395$ K, polarisation time $t_p = 5$ min and the polarisation voltage $V_p = 25$ V for a 0.5 mm thick sample, which corresponds to the polarisation field $E_p = 500$ V/cm. It can be seen that the impregnation of AR samples either with water or nickel affects both the location and intensity of the TSDC band. The activation energy, determined by the partial discharge procedure, was equal to 0.83, 0.81 and 0,91 eV for the AR, water-containing and nickel-doped specimen, respectively. The depolarisation current band reaches saturation with increasing T_p suggesting that it is not a space charge polarisation. Another way of distinguishing whether a band is due to dipolar or space charge polarisation is to reverse the dc-TSPC-measurement. The obtained band was of opposite sign twice as large as the original one suggesting a dipolar-type of polarisation. Using

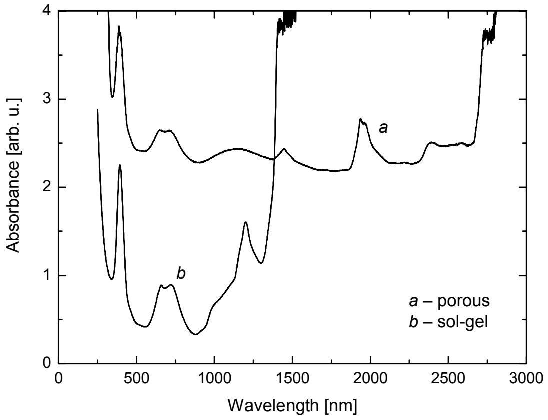

Fig. 3. Optical absorption spectra of the nickel-doped porous glass (curve *a*) compared with a spectrum characteristic of nickel-doped silica obtained by the sol-gel technology (curve *b*).

the blocking electrodes (thin sheets of Teflon located between the sample and metallic electrodes), one has stated that the TSD-current appearing at temperatures higher than 400 K has to be ascribed to dc-conduction. This statement results from the fact that with Teflon "electrodes" the TSDC above 400 K and the TSPC2 disappear, while the TSDC band detected below 400 K shifts toward lower temperatures and its intensity decreases by one order of magnitude. The precise mechanism producing the TSDC-band is still unknown, but the motion of some water-related species could be in principle responsible. It should be noted that the results obtained in the work described are hardly comparable with those previously obtained by using the dielectric spectroscopy [3, 4]. Hence, also the models describing the non-Debye slow-decay dynamics, used in the previous works, seem to be not applicable for the results described in the present paper.

In order to verify if the dielectric response observed was affected by the presence of fillers (adsorbed water and the nickel-related species), which interact with the surface of pores, optical absorption was measured at RT in a wide spectral range. In Figure 3 the UV-VIS-NIR spectrum characteristic of a porous sample filled with nickel (*a*) has been compared with a spectrum of nickel comprised in a sol-gel silica (*b*). It is clear that the first three bands, located at the highest energy, relate to the presence of nickel comprised in the framework of pores. XPS measurements and some literature data [5] have also confirmed this result. After hydrogenation the absorption spectrum is strongly shifted to the lower energy side "covering" the original bands. Thus, the colloidal nickel-nanoparticles (see the TEM-data) could not be detected by the OA measurements.

Besides the nickel-related absorption, optical absorption of porous silica specimens, measured up to 6000 nm, shows the presence of several other bands, see Figs. 3 and 4. Most of them are well known from the literature [6, 7]. The internal surface of porous glasses could be characterised by OH-groups, different types of SiOH

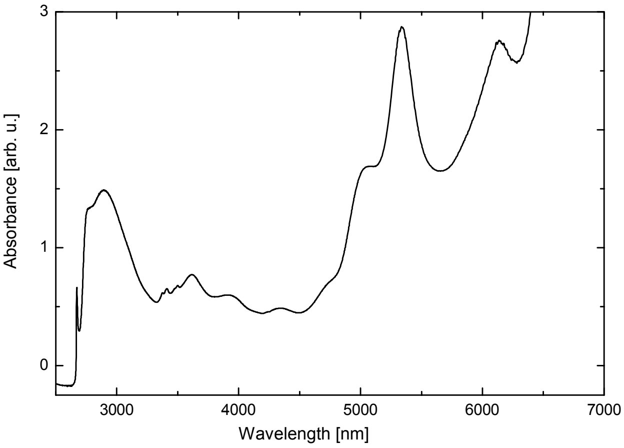

Fig. 4. Optical absorption of porous silica in the infrared spectral range.

groups (isolated and hydrogen-bounded), siloxane species and probably some rest of species related with boron. For instance, according to AGAMALIAN *et al.* [7] for a porous layer in a Vycor glass the presence of three types of adsorbed water has been anticipated: one physicosorbed and two chemisorbed ones assigned to stretching vibrations of shared pairs of OH groups within H_2O molecules. The first one can be desorbed by heating the samples at about 360 K, the second – above 460 K, and the third one is more strongly sorbed, which means that it should consist of many molecules connected to each other by hydrogen bonds and forming an ordered array of water molecules. In the case of our specimens, the effect of 30 minutes-annealing at temperatures ranging between 330 and 970 K was detected for the bands located

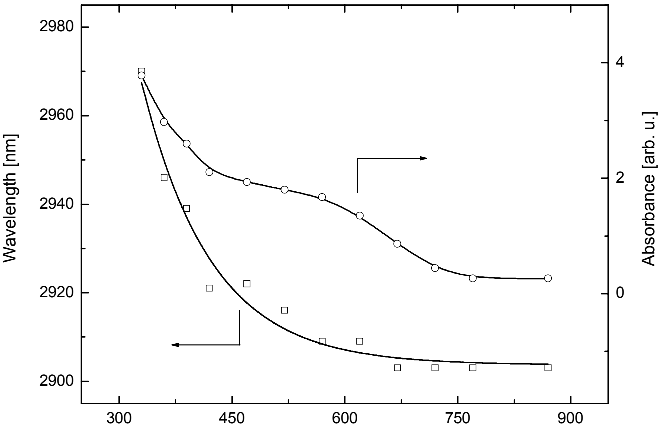

Fig. 5. Changes of the location (left-hand axis) and absorbance (right-hand axis) of one of the "water" related bands with the annealing temperature; the annealing time was 30 minutes at each temperature.

at about 1950, 2670, 2750, and 2940 nm. Additionally, the bands corresponding to the presence of ionic nickel were also decreasing. Figure 5 exemplifies the temperature -induced changes of both the intensity and the location of the "2940 nm" band. It can be seen that some characteristic absorption changes occur at about 420 and 620 K, being in reasonably good agreement with the literature data for de-sorption of the physically and less strong chemically bounded water species. This behaviour was also detected for the band located at about 2670 nm. Further work is, however, necessary to distinguish between chemical and physical contributions to the changes observed in the properties of the fillers confined in the investigated porous silica glasses.

4. Summary

It has been stated that the dielectric behaviour of the prepared porous silica glass samples is complex, and the relaxation is associated with the complex dynamics of the water molecules. This dynamics is due to interactions with the pore surfaces, and is affected by the geometrical nano- and mesostructural features of the porous matrix and different material filling the pores.

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