

Incorporation of copper and its oxides and chalcogenides into silica sol-gel materials*

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Recent results concerning fabrication and optical features of the sol-gel materials are reviewed. The nanoparticles of copper, copper oxides, sulfides and selenides have been produced by means of the modified silica-based sol-gel technique within two types of materials: amorphous silica films and monolithic glasses. Features of the optical absorption are discussed in dependence on the chemical composition. Optical properties are varied with element composition of the compounds, size of particles, their concentration, etc. The quantum confinement and partial surface chemical modification of the nanoparticles are considered as possible reasons for appearance of optical features of the copper multivalent compounds.

Key words: *sol-gel films, glasses, nanoparticles, copper, copper oxide, copper sulfide, copper selenide*

1. Introduction

Glassy materials doped with transition metal ions, nanoparticles and clusters of different chemical composition including oxides, sulfides and selenides have been found to be of great scientific and practical interest [1, 2]. Optical materials fabricated from doped glasses and films are widely used in optics and optoelectronics as selective filters, passive laser elements, optoelectronic switches, etc. Silica matrices provide stable samples for study of novel physical phenomena associated with low-dimensional em-

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bedded objects (excitation and relaxation of rare earth ions [3] and quantum-confined semiconductors [4], surface plasmon resonance in metals [5], light-induced transformations in nanoparticles [6], etc.).

Historically, the main method of doped glass fabrication consisted of melting components (oxides, fluorides or another glass-forming base) with the addition of dopants which underwent some chemical transformation resulting in final products responsible for their optical properties. Also, there is a number of preparation methods for glassy films that can be distinguished by the starting phase state of components – direct evaporation-deposition, chemical vapour deposition or reactive sputtering with participation of gaseous reactions and deposition from liquid solutions with dipping or spin-coating. The last method is similar to the familiar sol-gel technique [7–9], the main idea of which is the realization of complete sequence “sol → gel → solid” selecting chemical composition of precursors allowing these phase transformations. Organic derivatives of silicon, titanium and other polyvalent elements favour well this idea due to easy hydrolysis and polycondensation processes to form oxide structures. Doping in this case can be done at different stages. The sol-gel technique is successfully applicable also to fabrication of monolithic glasses. However, detailed methods of doping can be slightly different as compared with those for the films.

In this paper, we consider from one viewpoint the two types of sol-gel derived materials: thin films and monolithic glasses. The preparation technique was developed specially for doping with copper compounds dispersed as nanoparticles within the stiff silica matrix. The known advantages of the sol-gel-based methods are the lower temperature of final heat treatment (comparing with fused technique), flexibility in composition and intermediate chemical treatments favour the complex composition of the materials. Similar materials with transition metal compounds cannot be prepared with conventional molten glass technology. Liquid state of the precursor sols provides the best condition for homogeneity, and subsequent gaseous phase reactions retain also this aspect. At the same time new effects appear for some sample compositions, (as surface segregation [10]) that can also be used for preparation of special materials.

2. Samples preparation and characterization

The first fabrication step of *bulk monoliths* (Fig. 1) is conventional for the sol-gel technique and consists of preparation of precursor sol by mixing alcohol-aqueous solution of tetraethoxysilane (TEOS) at the molar ratio $\text{TEOS}/\text{H}_2\text{O} = 1/8$. Different acid catalysts – HCl, HNO_3 , H_2SO_4 (with molar ratio $\text{acid}/\text{TEOS} = 1/50$) were studied to promote hydrolysis of TEOS. Aerosil (SiO_2 powder with the grain size on the order of 20 nm and surface area 150–400 m^2/g) was added to sol before gelation to avoid strong volume contraction under drying. A part of agglomerated aerosol was separated

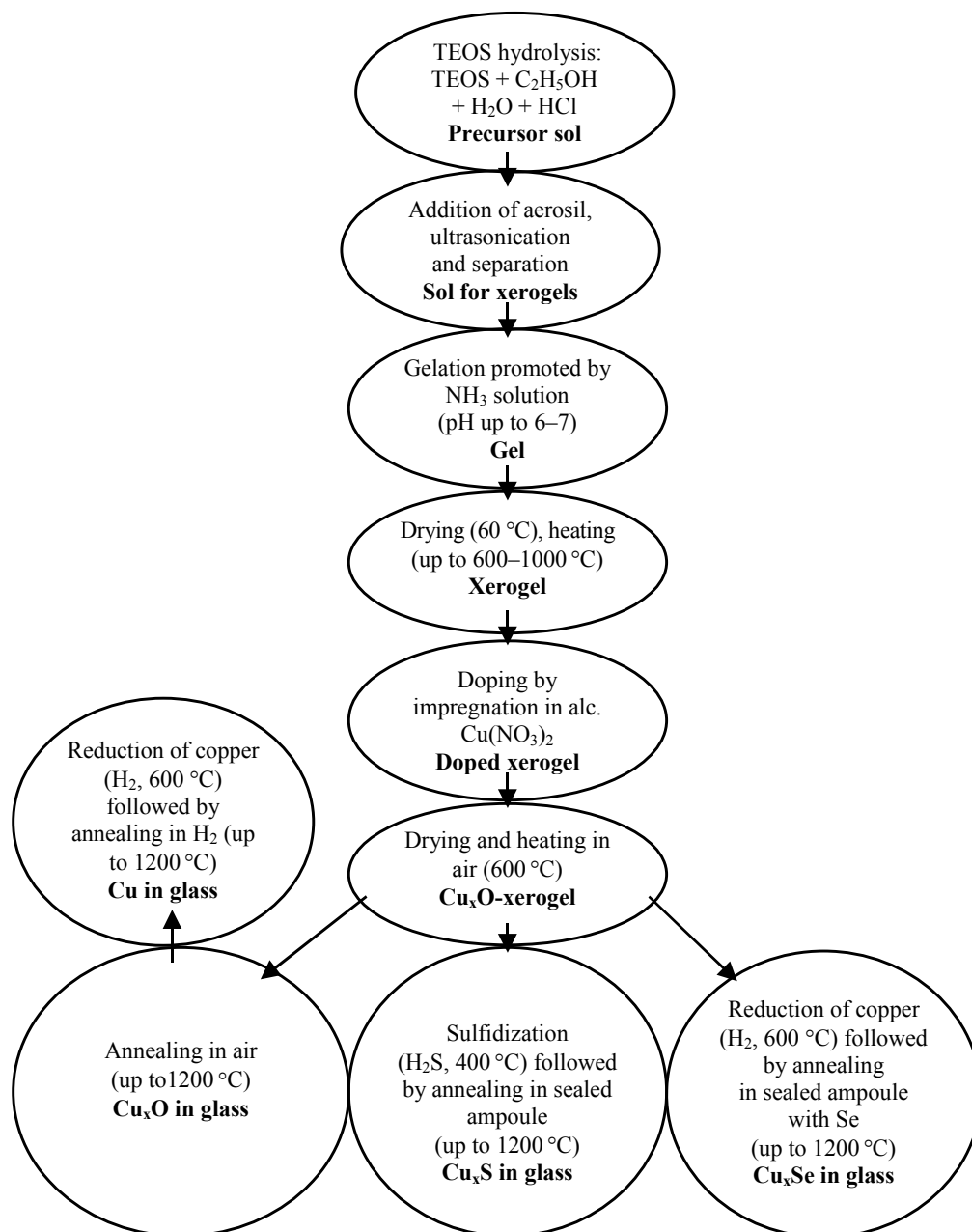


Fig. 1. Fabrication scheme of the silica sol-gel glasses

by centrifugation. Such sols had density of 1.05 g/cm^3 and could be stored at $3\text{--}5^\circ\text{C}$ without spontaneous gelation for 15–20 days. The gelation occurred when pH was increased up to 6–7 with addition of ammonia solution. In order to fabricate mono-

lithic glasses of definite shape, the sols were poured into polystyrene containers, and gelation proceeded for 24 h. The gels were dried at 60 °C and heat-treated up to 600–1000 °C for 2 h to remove sorbed water and organic remnants of TEOS. The temperature regime influences the properties of xerogels (porosity, amount of remnant hydroxyl groups, etc.) and was used as one of the experimentally controllable factors influencing final materials features. Such products, as *xerogels* resulted in finally annealed pure silica glassy monoliths heated treatment up to 1200 °C in the air. The doping was carried out via two routes: (1) mixing of metal salts ($\text{Cu}(\text{NO}_3)_2$) with precursor sols, (2) impregnation of porous xerogels (before the high-temperature annealing step) in alcoholic $\text{Cu}(\text{NO}_3)_2$ solutions for 8 h.

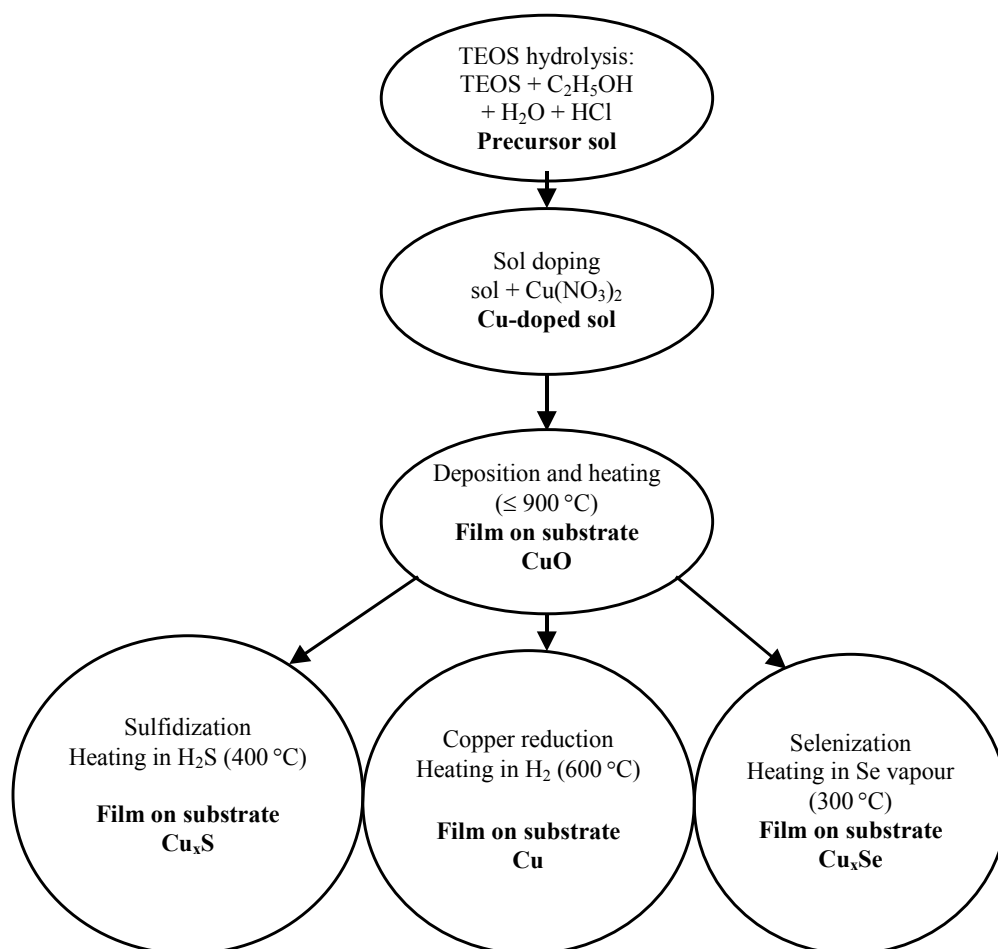


Fig. 2. Fabrication scheme of the silica sol-gel films

Subsequent chemical transformations of copper compounds introduced by doping were performed via different routes leading to formation of nanoparticles of metal, oxide, sulfide or selenide (Fig. 1): (1) heating and annealing of the doped xerogels (~ 1200 °C) in H_2 , (2) heating and annealing of the xerogels (~ 1200 °C) in the air, (3) heating in the air followed by H_2S (400 °C) and annealing in a closed quartz ampoule up to 1200 °C, (4) heating in H_2 (600 °C) followed by annealing in Se vapour in a closed quartz ampoule up to 1200 °C. This final annealing step resulted in production of transparent glassy samples (*monoliths*) of high optical quality and good mechanical strength.

The fabrication of doped silica *films* (Fig. 2) proceeded with the simpler sequence without the high-temperature annealing. The homogeneous sol-gel films were formed by spin-coating process on polished silica substrates. The doped sols were prepared by dissolving copper nitrate in sols yielding partially hydrolysed copper nitrate, $Cu_2NO_3(OH)_3$, characterized directly by XRD analysis [11]. The following four different types of processing for the films were developed: (1) heating in hydrogen (600 °C, 1 h) resulted in reduction of copper up to the metallic state, (2) heating in the air up to 900 °C (this temperature retained amorphous character of the silica matrix) to produce the films doped with copper oxide, (3) heating in the air (900 °C) with subsequent treatment in H_2S atmosphere (400 °C, 1 h) to obtain copper sulfide nanoparticles embedded into the silica matrix, (4) similar heating in the air (900 °C) and subsequent processing in H_2 (600 °C, 1 h) followed by heating in selenium vapour (300 °C, 1 h). The last step resulted in formation of copper selenide nanoparticles dispersed in silica matrix. The thickness of films was in the range of 300–1000 nm and controlled by amount of spin-coated sols deposited on substrates under constant rotation speed (2000–5000 min^{-1}).

The above-described different preparation sequences were designed to form nanoparticles including a series of copper compounds (Cu_xO , Cu_xS , and Cu_xSe) or metallic copper. However, production of a broader range of other compounds is also possible. The chemical composition of the above series of compounds with the variable stoichiometry both in the case of films and monolithic glasses has been established using several methods: XRD (mainly for films) [11–13], XPS (also for films [13] and some glasses with higher concentration of dopants), RBS (both for films and glasses) [14, 15]. Transmission electron microscopy (TEM) studies have revealed that the materials are nanoparticles (in the range of 10–100 nm) embedded into amorphous glassy matrix [14]. The size of nanoparticles depends on the concentration of the dopants and particulars of the heat treatment of xerogels. Nanoparticles in the monoliths have usually relatively low concentrations (from 10^{12} – 10^{13} cm^{-3}), and the aggregation degree of them is not large, so in the most cases they may be considered as separate ones surrounded by glassy matrix rather than in contact with other particles. The concentration of particles in the films was 2–3 orders of magnitude larger (due to the more relative amounts of dopants), possessing the sizes similar to those observed for the monolithic glasses.

3. Optical properties

Optical absorption spectra of the sol-gel silica films and glasses doped with different copper compounds are summarized in Fig. 3. In spite of their similar general chemical composition, their optical properties reveal remarkable differences. The optical properties depend on particulars of the preparation, the particles concentrations and features of the matrices.

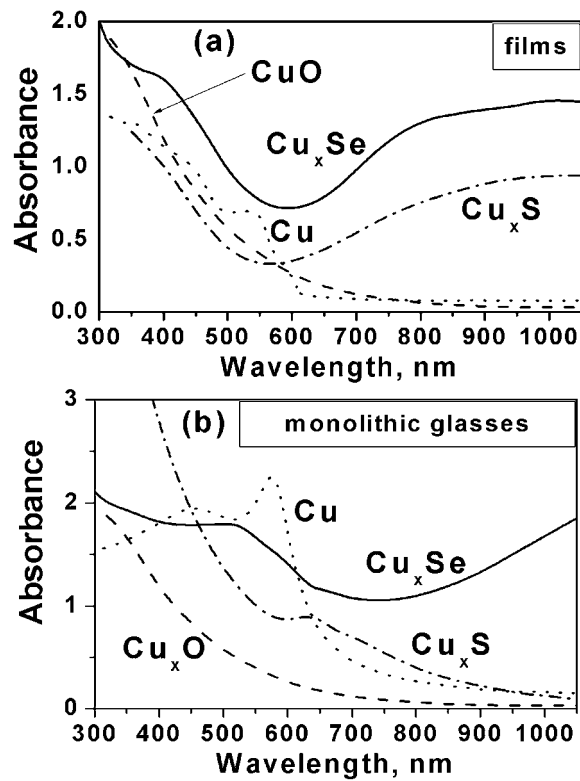


Fig. 3. Absorption spectra of the sol-gel silica films (a) and glasses (b) containing nanoparticles of different copper compounds indicated by their chemical formulas

The spectra of Cu_xO-doped films are similar to those of monolithic glasses and show the sloping monotonous spectrum with a very weakly developed shoulder in the short-wavelength range ($\lambda < 350$ nm). Such spectra are characteristic of indirect-gap semiconductors and are consistent with properties of CuO or Cu₂O. Size effects are virtually absent. According to the XRD data [11], in such films the chemical form of CuO is dominating. Recent photoluminescence results [16] suggest that Cu⁺ ions in Cu₂O nanoparticles occur in glasses. This difference in composition of films and

glasses can be caused by differences in concentration of the dopants (much higher for films than monoliths) and higher maximum temperature of heating during the preparation (900 and 1200 °C, respectively). The higher temperature, evidently, can lead to decomposition of Cu(II) oxide ($4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$).

A reductive heat treatment in hydrogen is known to lead to easy transformation of copper oxides to metallic copper ($\text{Cu}_x\text{O} + \text{H}_2 \rightarrow x\text{Cu} + \text{H}_2\text{O}$). However, the size and concentration of particles affecting the optical response can be different for films and glasses due to variations in matrix properties and initial chemical compositions. Usually, absorption features of small copper particles are described well (at least, in the first approximation) using the Mie theory explaining maxima in absorption spectra as a combination of a λ -dependent dielectric function ($\varepsilon_2(\lambda, R) \sim R^{-2}$) occurring in the total expression $\varepsilon = \varepsilon_1 + i\varepsilon_2$ [17] and medium dielectric constant ε_0 . The typical spectra of copper nanoparticles possess main maxima in the range of 500–600 nm (properly, the plasmon resonance from the Mie theory) and additional features originate from the complicated $\varepsilon(\lambda)$ dependence on the band structure of metallic copper. The more pronounced maxima observed for copper nanoparticles in glasses, as compared to the films, as well as a small (several tens of nanometers) blue shift of the band position can be the consequence of a more homogeneous size distribution of the particles in the glasses with much lower concentrations and particle–particle interactions.

It should be emphasized that we have shown only some selected representative spectra of the copper nanoparticles: they vary with changing properties of the xerogels and dopant concentrations retaining similar general principal appearance with the plasmon resonance maximum in the range of 500–700 nm. This feature can be used for designing of cut-off filters. Production of copper chalcogenides (sulfides and selenides) nanoparticles embedded in the sol-gel films and glasses is the principal purpose of the preparative part of this work; oxides and metallic particles appear mainly as intermediate steps of the reaction sequence. Chalcogenides of different metals are the subject of studies of the size effects through observation of certain non-trivial optical features [18]. Copper sulfide particles have been produced within fused glasses [19, 20], and ultrathin nanostructured films have been fabricated by means of the Langmuir–Blodgett technique [21, 22]. The sol-gel technology allows studies of both copper sulfide and selenide within matrices of similar composition. The typical absorption spectra of films with the chalcogenides (Fig. 3a) reveal the two principal features: (i) the fundamental absorption band and (ii) the intense and rather broad (in particular with the λ -dependence presentation) absorption peak in the near IR range. They both are composition-dependent. However, their positions may be associated to the corresponding ranges of E_g (both direct and indirect): 1.2–2.2 eV [23] including the possible blue shift. This shift is observable only for copper compounds and has been interpreted recently by us [24–26] as midband levels due to the partial change of the copper valence state (accompanied also by partial or surface oxidation of nanoparticles).

In the case of monolithic glasses, the behaviour of sulfide and selenide nanoparticles is different (Fig. 3b), and the IR-band is observable only in the selenide case. It can be assumed that the main reason of this difference is variation of stoichiometry of nanoparticles. The composition of Cu_xS nanoparticles is close to CuS , however Cu_xSe is a very variable compound retaining the similar features of the absorption spectra. The monolithic glasses with Cu_xS were not analysed directly in order to establish for the chemical composition, however, the spectrum is consistent with that given in [19, 20] for Cu_2S nanoparticles. Thus, as well as in the case of oxide nanoparticles, the conditions of preparation of monolithic glasses favour the lowest valence state of copper, Cu(I) . Copper selenides are produced with a substantial excess of selenium (partial Se pressure of about 1 atm sufficient due to the small size of samples in ampoules). To control composition of the selenides, we used porosity of xerogels with the same overall selenium amount. In the case of sulfides there was no possibility to control the sulfur amount because of the higher volatility of sulfur, instead, copper sulfide (CuS , dominantly) was pre-produced within porous xerogels prior to the annealing step without providing any additional source of sulfur. Under these conditions CuS decomposes during subsequent heat treatment up to $1200\text{ }^\circ\text{C}$. Cu_xSe phases are formed according to the Cu-Se phase diagram [27, 28].

4. Conclusions

Two types of nanostructured sol-gel derived optical materials: silica thin films on solid substrates and monolithic silica glasses containing copper, copper oxide and chalcogenide nanoparticles have been developed. Absorption spectra reveal various features of nanoparticles of Cu , Cu_xO , Cu_xS , and Cu_xSe . The exact chemical composition of those nanoparticles depends on the type of material, details of the preparation procedure and can be controlled within certain experimental limits.

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