OPTICAL FILTERS BASED ON COLOURED SILICA GLASS PREPARED BY SOL-GEL METHOD

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Abstract

The sol-gel method prepared silica gel glasses doped transition metals and rare-earth elements for optical filters was described. In this paper adduce the absorption spectra of silica gel-glasses doped chromium, cobalt, copper, cerium and neodymium

Introduction

Silica glasses doped transition metals and rare-earth elements compounds widely use in high-temperature and optical device-making as the optical filters and active elements laser systems and for protection from radiation in nuclear reactors [1-5].

The aim of this paper is working-out sol-gel process preparing silica glasses doped oxides of transition metals and rare-earth elements, in which realize straight transition sol-gel-glass.

Experiment

The starting substances for preparing samples are tetraethyl-orthosilicate $Si(OC_2H_5)_4$ (TEOS), hydrochloric acid (as a catalyst), fumed silica (aerosil), the salts of transition metals and rare-earth elements, dissolved in aqueous-alcohol solution. The reactives have been degree purity 99.99 %.

Samples of gel silica glass doped with different ions were prepared following the sol-gel process comprised of the following stages: hydrolysis of TEOS in a three-component system: TEOS-H_2O-HCl to obtain a sol, a fluoroplastic reactor with a blade mixer was employed to prepare sol in 30 to 40 min (mole ratio of the components was 1:16:0.01); then aerosil with the unit area 175 m^2/g was added to the resultant sol; the aerosil was mechanically dispersed (sonoactivation); different ions in the form of solid salt was added and dissolved by stirring for 30 min; hard particles and impurities were separated in a centrifuge at the velocity 3000 rev/min during 60 min; the sol-colloidal system was neutralized up to pH=6.5 to 7 with the help of an ammonia solution added to the mixture while stirring for 10 min; the liquid slurry was pored into square or circular containers made of a hydrophobic material; gel was formed during 20-30 min in sealed containers; then the containers were opened and the gels were exposed in water vapor atmosphere; the period of exposition was 10 to 16 h; the gels

thus aged were placed in special containers and dried in the thermal chamber at a temperature of about 60°C during to five days depending on the gel geometrical dimensions; xerogels were baked in a muffler in air following the program; the exposure temperature was between 1150 and 1200 °C; the time of exposure was 1 5 and 2 h.

The drying operation should not cause cracking or warping of large gels. This was ensured by using special containers to dry gels; accurate removal of humidity was provided; no mechanical stresses were accumulated. The yield of xerogels free of cracks and deformations makes up 80 %.

The absorption and transition spectra of samples of doped silica glasses were recorded on a spectrophotometre "Beckman-UV5270".

Results and Discussion

1. Cr-Doped Glasses

The Cr(III)-centers had been most full studied and easily realize in glasses. Usually, they is a polyhedron [CrO_6] in oxide glasses, although chromium can be in fourth or eighth coordination [6]. These centers are characterized in visible part of spectrum two wide ($\Delta\nu$~2500 cm^{-1}) intensive of absorption bands at the 470 and 660 nm, which are interpreted as the $^4A_2 \rightarrow {}^4T_{1,2}$ - transitions and narrow ($\Delta\nu$~200 cm^{-1}) weak of absorption bands, corresponding to transitions $^4A_2 \rightarrow {}^2E$, $^2T_1$. In UV part of spectrum about 310 nm is band, corresponding to allowed transition $^4A_2 \rightarrow {}^4T_1(P)$.

Fig. 1 (curve 1) shows the absorption spectrum of Cr-doped gel- glass, in which Cr(III) and Cr(II) centers are prevailed. The curve 1 is very similar to the spectrum of absorption of melting quartz glass with chromium [7].

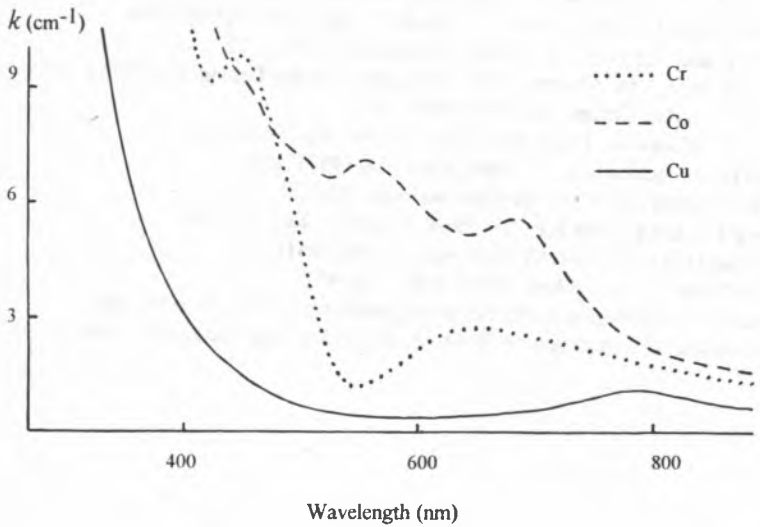

Fig. 1 Absorption spectra of Cr-, Co-, Cu- doped silica gel-glasses

2. Co-Doped Glasses

The cobalt can enter in glasses in type two- and three-charge ions, possessing configuration of "optical electrons" d^7 and d^6, accordingly, that determine rather strong sensitivity of position and structure of absorption bands to coordination of complexes, symmetry and force of ligands field [8-10]. The ions of two-charge cobalt can form both octahedron [8] and tetrahedron oxocomplexes [8-10]. The tetrahedron complexes of Co(III) are characterized two complicated bands in visible and hear IR ranges, corresponding to transitions $^4\Gamma_2(F) \rightarrow {}^4\Gamma_4(P)$, $^4\Gamma_4(F)$. The Co-doped glasses are characterized intensive absorption band in UV-region of spectrum and weak- intensive band at the 690 nm [11].

Fig. 1 (curve 2) shows the absorption spectrum of Co-doped gel-glass. In the gel-glasses contain considerable share of Co(III), moreover, correlation of Co(II)/Co(III) can change depending on synthesis conditions, nature of matrix and activator concentration.

3. Cu-Doped Glasses

Fig. 1 (curve 3) shows the absorption spectrum of Cu-doped gel- glasses. This spectrum is characterized intensive violet absorption with comparatively sloping long-wave bound at the $\lambda<500$ nm, weak diffusion band at the $\lambda\sim800$ nm. The weak-intensive band in the red and hear infrared regions of spectrum is connected with Cu(II) and intensive absorption in short wave region caused Cu(I) and, possibly, the band of charge transference between oxygen and Cu(0) [12, 13].

4. Ce-Doped Glasses

Absorption spectra of Ce-doped silica gel-glasses were measured at room and liquid helium temperatures. They are shown in Fig. 2. One can see that the broad band in the UV region is inhomogeneously broadened and consists of two maxima at 290

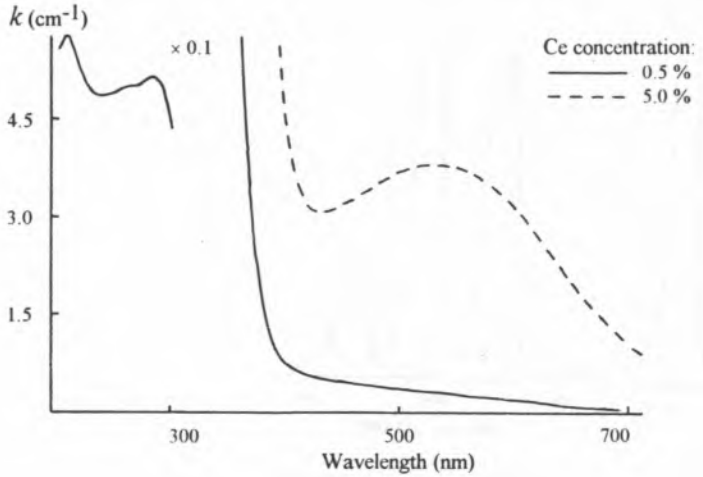

Fig. 2 Absorption spectra of Ce-doped silica gel-glasses

and 260 nm which may be associated with the different Ce^{3+} sites present in silica gel glass. These two bands could be associated with two transitions from the ground state to the splited orbital. The energy separation in our case is estimated to be about 45[illegible] cm^{-1} which is remarkable smaller than that reported by Szczurek and Schlesinger [14] for purely ionic $CaF_2:Ce^{3+}$ crystals.

The spectrum measured at T=4.2 K was taken for the sample of the thickness 0.1 mm and with the nominal concentration 0.25 mol. %. We did not observe any substantial the band with the maximum at 530 nm. The spectra in visible range have been measured for a series of concentrations for the same thickness of samples and demonstrated an increase of intensity with concentration. This band may be combined with the electron transfer Ce^{4+} ion to the ligand.

5. Nd-Doped Glasses

The best results were obtained on the sol stage when glass doped at the same time Nd and Ce salts. In this case was received concentration Nd_2O_3 up to 2 mol. % (concentration Ce_2O_3 - 0.5 mol. %). In the Fig. 3 absorption spectrum of the prepared silica gel glass is adduced. The volume concentration of the Nd in this sample is 6.4×10^{20} ions/cm^3. The similar results was obtained at the same time doping Nd and Al.

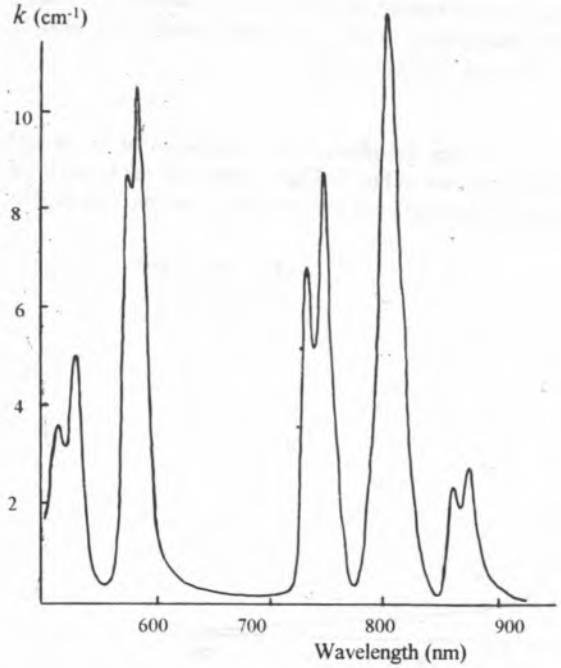

Fig. 3 Absorption spectrum of Nd-doped silica gel-glas

When activation was conducted only Nd ions, these concentrations receive impossibly because of their segregation. Moreover, in this case takes place essential

violation the Bouguer-Lambert-Beer law, adducing to decrease specific absorption with increase concentration activator.

The investigated samples were homogeneous and characterized with weak opalescence. The peak absorption index in region of basic valence vibrations of hydroxyl ions for these glasses makes up about 30 cm^{-1}.

Conclusions

The new silica glasses, doped transition metals and rare-earth elements was prepared sol-gel methods. The absorption spectra silica gel glasses doped with Cr, Co, Cu, Ce and Nd ions were investigated.

Specimens of coloured filters have been made from the doped silica glass in the form of the plate measured up to 100×100×5 mm^3, discs and tubes measured up to 75 mm and 30 mm in diameter, respectively. Optical filters from coloured silica glass are designed for an application in quantum electronics devices, for pumping system of powerful solid lasers; they can serve for eye protection and for the protection of other objects from UV laser radiation, solar radiation, for display screens and manufacturing thermostable coloured - optical components.

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