PHYSICS, CHEMISTRY AND APPLICATION OF NANOSTRUCTURES, 2003

SOL-GEL SYNTHESIS OF Fe-CONTAINING SILICA GLASSES

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Fe-doped glasses and composites were prepared by hybrid sol-gel process, modified in the part of doping technique. The UV-VIS spectra and XRD-investigation show both the presence of oxide and fluoridecomplexes in the glass matrices.

1 Introduction

Fe-containing silica glasses and nanocomposites can be used as ferromagnetic materials and colored filters. Utilization of the sol-gel process for synthesis of silica glass is preferable because of its low sintering temperature and high efficiency [1]. Incorporation of fluorine into xerogel simultaneously with Fe-ions reduces bubble formation upon consolidation by sintering and results in the formation of Fe-containing clusters in the network of silica gel-glass.

2 Methods

Fe-doped glasses and composites were prepared by a hybrid sol-gel process [2], modified in the part of doping technique. The flowchart of the hybrid sol-gel process incorporates the following stages: tetraethoxysilane (TEOS) hydrolysis in the system $Si(OC_2H_5)_4$- C_2H_5OH-H_2O-HCl with mole ratio 1:2:16:0.01 by vigorous mixing in fluoroplastic reactor in air; addition the fumed silica with a specific surface 200 cm^2/g into the sol as filler, ultrasonic dispergation and centrifugal separation from agglomerates and dust particles. Then, the sol was neutralized up to pH=6.5 with the help of ammonia solution and cast into fluoroplastic moulds to prepare the solid gels shaped as disks. The wet gels were formed during 20-30 min in sealed containers; then the containers were opened and the gels were washed by bidistilled water.

The resulting gels were dried slowly at 30-60^{0}C in the period of 7-14 days in air and presintered at 600^{0}C in 2 h. After heat-treatment the xerogels were impregnated by water or organic solutions of $Fe(NO_3)_3$ and $FeCl_3$.

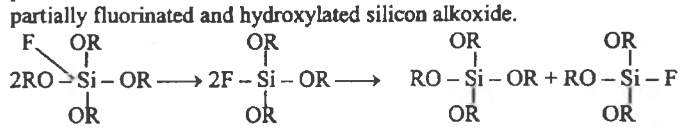
Using of Fe-containing aqueous solutions for xerogels impregnation results in the preparation of hydroxylated silica gel-glass doped ferrum(III). The presintered xerogels impregnated by the organic solutions (mixture: acetone, HF) and then by the acetone solution of $FeCl_3$ lead to the formation of opalescent composites. The following thermo-treatment of Fe-containing porous materials at 1200°C in air lead to formation of silica glass.

3 Results and discussion

Optical absorption spectra were measured using the glass and composite samples of 2-4 mm thickness in the IR, visible- and UV-regions. The pore-size distribution in the gel structure measured by BET-method has a complex character: the network contains micro- (3.0 nm), meso- and macro-pores (5-25 nm). The pore size can be increased by chemical attack of silica network by fluorine ions in solution and also in vapor phase until heating and dissociation of F-containing compounds (HF, NH_4F).

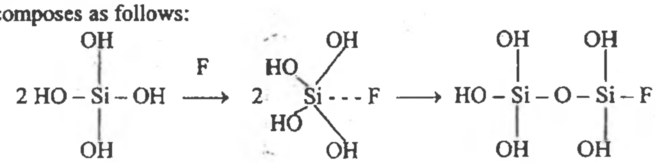
Hydroxyl content in dense glasses and composites was evaluated from IR-absorption spectra using the relationship [3]: $[OH]ppm=(1000/t)\log(T_a/T_b)$, where t is the sample thickness (mm), T_a is the transmission at 2.2 μm, T_b is the transmission at 2.72 μm.

The reaction (1) shows that fluorine severely catalyses hydrolysis reaction [3]. In the hydrolysis reaction, because of the smaller ionic radius of the fluorine, which approaches a molecule of TEOS in the solution forming a highly unstable pentacovalent activated intermediate. This complex rapidly decomposes, forming a partially fluorinated and hydroxylated silicon alkoxide.


(1)

This process can continue until nearly all of the ethoxide bonds are replaced by OH. More that likely, however, the polymerization reaction begins before all TEOS is fully hydrated.

The polymerization reaction forms a hexacovalent intermediate, it rapidly decomposes as follows:


(2)

The process of gas-phase fluorine doping reduces hydroxyl level in the xerogels by the attack of gel network and the reaction takes place:

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-OH + HF \rightarrow SiF_4\uparrow + H_2O\uparrow. \qquad (3)$$

The impregnation of fluorine-containing gels by the acetone solution of $FeCl_3$ and subsequent thermal treatment at 1200^0C in air results in the formation of fluorinated Fe-containing compounds in the form of nanosize amorphous clusters, dispersed in the matrix of silica-like opalescence material.

The IR-spectrum of composite samples demonstrates the hydroxyl groups on the level of 100-150 ppm (Fig. 1). The UV-vis transmition spectra of Fe-containing glasses and composites are shown in Fig. 2.

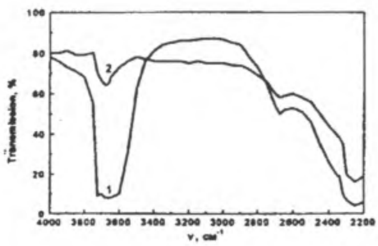


Figure 1. IR-spectra of composite and glass samples: 1 – silica gel-glass; 2 – $FeOF_x$ containing composite.

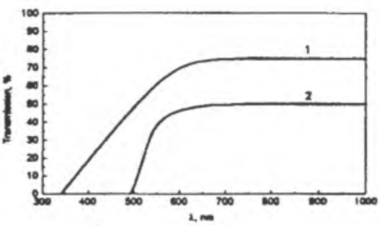


Figure 2. The transmition spectra of Fe-containing glasses(1) and composites(2).

The scheme of Fe-ions transition in impregnated xerogels is probably following:

$$Fe(NO_3)_3 \rightarrow [Fe(OH)_x(NO_3)_{3-x}]_n \xrightarrow{F_2} FeOF_x. \quad (4)$$

The incorporation of Fe(III) into the silica matrix was verified by UV-vis spectra. A Fe(III) ion incorporated into the silica network demonstrates the broad band below 350 nm with diffuse edge and Fe-containing composites demonstrates UV-absorption edge shifts to longer wavelength. The absorption band at ~500 nm has been attributed to the presence of $FeOF_x$-complexes in the structure of silica composite.

References

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3. G. Sijian, G. Zhenan, *Proc. XVI Int. Congress on Glass* (Madrid, Spain, 1992) 39.