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SiO_2-B_2O_3 xerogels: The problem of boron leaching

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ABSTRACT

Borosilicate materials are of interest for many technological applications. Whereas sol-gel techniques are well suited for the preparation of these materials, the nominal concentration of boron is often not maintained, and a considerable amount of boron is lost during the preparation procedure. In this work we deal with the synthesis of borosilicate systems in order to analyse the problem of the boron loss. Different sol-gel precursors of B_2O_3 were explored and organically modified silicon alkoxide were tested, in addition P_2O_5 co-doping was proposed. IR spectroscopy, differential Scanning Calorimetry, Thermogravimetry and ICP-OES analyses were performed. Sol-gel synthesis of SiO_2-B_2O_3 xerogels with a high boron content (>18 wt.%) was successfully obtained by employing trimethoxyboroxine and 3-aminopropyltriethoxysilane.

1. Introduction

Borosilicate glasses and glass-ceramics have historically found many applications as thermal and acoustic insulators, textile fibres for reinforcement of polymers, glassware for laboratory, cookware, LCD technology and other optoelectronics devices [1,2]. In addition, in these last 40 years research on borosilicate materials focussed on a possible application as immobilizer for radioactive wastes due to the great chemical and thermal resistance of these glasses, [3,4]. More recently, boron-based glass nanoparticles were proposed for cancer treatment *via* Boron Neutron Capture Therapy (BNCT) [5].

Sol–gel methods are well suited for the synthesis of many inorganic oxides, including ceramics, glasses, porous glasses (xerogels) and aerogels. In the recent years, the development of the sol–gel knowledge has led to a great increase of interest in the method, which is now applied for the production of a very large number of advanced materials [6]. The reasons at the basis of this interest are different: i) the chemical conditions are mild and the temperatures required for all the stages apart from densification are normally near to room temperature (r.t.); ii) the precursors employed are metal alkoxides and mixed alkyl/alkoxides, that are usually volatile and easily purified to very high levels; iii) the organometallic precursors are frequently miscible, and a degree of homogeneity better than that obtained by melt quenching can be obtained. Moreover, sol–gel methods can produce highly and controlled porous materials by appropriate chemical modifications of the precursors and/or the use of template agents in the sol [7].

Despite of all these advantages, sol–gel methods present some limitations. The precursors are expensive and often sensitive to moisture, the number of the parameters to control can be large, and the process could also be time-consuming, particularly when careful ageing and drying procedures are required, as in the production of xerogel bulks. In addition, for binary or ternary glasses, it is not always possible to extend, or even maintain, the glass formation region obtained by the traditional melt-quenching methods.

The SiO_2-B_2O_3 glassy system was prepared for the first time using a sol–gel method by R. Jabra et al. in 1980 [8]. These authors followed two strategies: the first one was based on the gelification of an aqueous colloidal SiO_2 and $(NH_4)_2B_4O_7 \bullet 4H_2O$ solution; the second one on the classic organometallic route employing $Si(OCH_2CH_3)_4$ (TEOS) and $B(OCH_3)_3$ (TMB). In both cases the dried xerogel powders were densified by hot pressing, and neither the structure nor the actual composition were carefully investigated. In 1982 Nogami and Moriya [9] prepared different compositions of a borosilicate glass starting from $Si(OCH_2CH_3)_4$ and $B(OCH_3)_3$ and treating the obtained xerogels at 800 °C. Their study showed that for the sample containing more than 20 mol% B_2O_3, a large amount of boron (about 25%) was lost during the gel synthesis and not during the densification step of the xerogel. The problem of the Si–O–B bond formation was analysed by Irwin and coworkers [10,11] for samples obtained from TEOS or $Si(OCH_3)_4$ (TMOS) and TMB. By means of ^{29}Si and ^{11}B MAS NMR spectroscopy they demonstrated that the majority of boron in the gels dried at room temperature was in the form of boric acid hydrogen-bonded to the silica network, whereas there was only a small amount of B–O–Si groups. Although water was added in stoichiometric amounts, this result could be explained by considering that water resulting by sol condensation can easily hydrolyse the B–O–Si bonds. They concluded that the leaching

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of the boron from the gel system was due both to this reason and to the high volatility of TMB. A thermal treatment performed at about 500 °C was able to transform the boric acid hydrogen-bonded to the silica matrix into a real borosiloxane network. In 1984 Woigner et al. [12] prepared SiO_2-B_2O_3 aerogels starting from TMOS and TMB but nothing was reported about the leaching of boron. The authors also prepared the ternary systems SiO_2-B_2O_3-P_2O_5, by employing $PO(OCH_3)_3$ as the precursor for P_2O_5. Kan-Sen Chou [13] prepared the same ternary system by employing as starting materials boric acid and phosphoric acid instead of boron and phosphorus alkoxides. In that work a negligible leaching of both B and P was reported, however the overall amount of B_2O_3 and P_2O_5 introduced in the silica network was very low (max 12 wt.%). Later in 2002 Li et al. [14], starting from the same precursors, reported the synthesis and characterization of the system SiO_2-B_2O_3-P_2O_5 with different molar ratios. Here the loss of boron was hypothesized but not quantified. In a more recent work [15] C. Zhang and coworkers reported a Pechini-type sol–gel process to obtain samples of the $BPO_4 \times SiO_2$ system, and employed a 50 mol% excess of H_3BO_4 in order to compensate for the high-temperature B evaporation. Soraru and coworkers [16,17] found that the synthesis of SiO_2-B_2O_3 gels is favoured by employing organo-modified silicon alkoxides, which retain boron in the xerogels by means of the creation of a high number of borosiloxane bonds. Nonetheless, when the boron content was actually verified by elemental analysis [16], the loss of boron was found to be significant (>50%). A very recent work [18] proposed a particular sol–gel synthesis of borosilicate nanoparticles (100–500 nm) by exothermic phase separation, but the true boron content was not checked.

From this short literature review it clearly appears that the problem of boron leaching in sol–gel preparation of SiO_2-B_2O_3 glasses and glass/ceramics is far from being solved. Of course, this problem is really relevant when considering BNCT applications were the boron content must be as high as possible. Aim of present work is to prepare and study SiO_2-B_2O_3 xerogels differing in composition and in sol–gel preparation methods. In particular, three different boron precursors have been employed not only to study the boron loss from the network but also to find the optimized conditions for boron-rich silicates by sol–gel synthesis. Modified silicon alkoxides as aminopropyltriethoxysilane, and P_2O_5 co-doping were also employed.

2. Experimental

2.1. Preparation of borosilicate xerogels

A first attempt was carried out in accordance with the procedure of Nogami and Moriya [9] but for the hydrolysis of TEOS and TMB that was performed at r.t. (25 °C). Then sol was poured in 2 different closed containers: the first one was kept in an oven at 50°, the other was kept at r.t. Gelation occurred within 2 days and then containers were opened and gels left to dry for about three weeks in air and in the oven. Samples were mentioned as REF0_RT and REF0_oven. Since this preparation was not satisfactory, three kinds of different recipes were developed in order to test different boron precursors. The first type of sol–gel synthesis employed H_3BO_3 dissolved in 70 ml of distilled water with about 2 ml of NH_4OH 5 M and the following addition of TMOS. After gelation (in closed containers) xerogels were dried for about 2–3 weeks at 50 °C. The second type of synthesis employed TMB mixed in methanol (MeOH) and a small amount of H_2O, after 1 h of stirring TMOS was added. Then mixture was stirred for about 4 h and sol was made to gel in closed containers and then dried as synthesis of type 1. In the third type of synthesis TMOS was mixed to MeOH and a small amount of H_2O and stirred for half an hour, then trimethoxyboroxine (TMBX) were quickly added and the sol was stirred for an hour. In this case two different conditions of gelation were studied in closed containers: the first one was kept in an oven at 50 °C and the second one was kept at room temperature. After gelation both the containers were opened and gels were dried for about 2–3 weeks in air. Obtained samples were mentioned: 1SiB; 2SiB; 3SiB_RT; 3SiB_oven. These preparation methods were employed for the system $2SiO_2$-B_2O_3, afterwards two different changes were tried: i) introduction of P_2O_3; ii) utilization of the precursor APTES (3-aminopropyltriethoxysilane) for 25% mol of the total Si.

Regarding the first alteration, precursor of phosphorous $P(OCH_3)_3$ (TMPI), was mixed before the addition of TMOS for synthesis of type 1, together to TMB for synthesis of type 2 and before the addition of TMBX for synthesis of type 3. Trimethylphosphite was chosen instead of trimethylphosphate since phosphate esters are not easily hydrolysable, and phosphoric acid reacts too rapidly leading to precipitation rather than gelation [10]. Obtained samples were mentioned: 1PSiB; 2PSiB; 3PSiB_RT; 3PSiB_oven.

Regarding the second alteration, precursor APTES was prehydrolysed in about 10 ml of ethanol and 1.35 ml of H_2O and then slowly added to the final sol, due to its basicity after mixing, gelation occurred more rapidly for each type of synthesis than without APTES. Obtained samples were mentioned: 1SiBNH2; 2SiBNH2; 3SiBNH2_RT; 3SiBNH2_oven. After these three different series of samples, in order to raise the amount of boron, the most promising precursor (TMBX) and the relative utilization of APTES were considered to prepare the systems SiO_2-B_2O_3 and $2SiO_2$-B_2O_3 obtaining samples 3Si2B_RT; 3Si2B_oven; 3Si2BNH2_RT; 3Si2BNH2_oven; 3Si4B_RT; 3Si4B_oven; 3Si4BNH2_RT; 3Si4BNH2_oven .

Details of each synthesis are reported in Table 1.

2.2. Infrared spectroscopy

IR reflectivity spectra were obtained between 600 and 4000 cm^{-1} by using a FT-IR 410 JASCO spectrometer. The samples were ground and finely mixed with KBr (about 5 wt.% of sample), and the spectra were obtained by subtracting the pure KBr spectrum. The signals were averaged over 512 scans, with a resolution of 2 cm^{-1} and a scan velocity of 2 mm/s. The spectra were reported in transmittance mode.

2.3. Thermal analysis

Preliminary thermogravimetric scans were performed by a TGA 2950 (TA Instruments) under dry N_2 purge, at a heating rate of 5 °C/min, from r.t. up to 800 °C. More accurate TGA analyses were then accomplished by first heating the samples up to 150 °C, holding in isothermal for 2 h and finally heating at a rate of 5 °C/min up to 800 °C.

TGA weight loss taken from thermogram are affected by an error within 1%.

Differential scanning calorimetry measurements were carried out by means of a 2910 DSC (TA Instruments) under N_2 purge at 5 °C/min from r.t. up to 500 °C. The upper limited temperature was chosen to prevent cell contamination during sample decomposition.

2.4. ICP-OES analysis

About 60 mg (exactly weighed) of each sample, was digested overnight at r.t. with 0.2 ml 40% HF and 0.2 ml 65% HNO_3 in a closed PET vessel and then diluted with milliQ water to 50 ml. The boron concentration in the digested samples, diluted 1:10, was measured by inductively coupled plasma spectroscopy (ICP-OES). An ICP-OES Perkin Elmer Optima 3300 DV was used for all the measurements, following the operating conditions suggested by the manufacturers (in radial view). A linear relationship between the signal intensity and boron concentration (0.030–20 mg L^{-1}) was obtained by using standard solutions daily prepared from a 1.001 mg mL^{-1} stock solution. LOD = 10 μg L^{-1}, LOQ = 30 μg L^{-1}. Data have an error within. All data were corrected in order to take into account the humidity of the sample. The water content was determined by TGA analysis.