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Boron Oxide Glasses and Nanocomposites: Synthetic, Structural and Statistical Approach

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Three different precursors of boron-aqua and glycerol solutions of boric acid and ethanol solution of trimethyl borate were used for the preparation of organic–inorganic advanced materials. The films and bulk materials samples were heat treated at 100, 400, 800 °C for 2 h. The hybrid samples were stable and transparent until 100 °C. The further increase of temperature to 400 °C led to destruction of samples, and at 800 °C they were molten. The structural changes during the pyrolysis were studied by Fourier transform infrared spectroscopy, differential thermal analysis, and X-ray diffraction. Details of surface morphology were observed by scanning electron microscopy. The obtained BO_3 and BO_4 groups were identified in the molten materials after pyrolysis. The quantities and order of borate structural units as well as residual carbon in the networks depended on boron precursor type. PVA/PEG/B_2O_3 hybrid materials were proved to be appropriate precursors for synthesizing borate and carboborate glass and carbon/borate glass nanocomposites. To access the impact of the experimental conditions on the structural changes of the nanocomposites, cluster analysis of the IR-spectral data was used as a classification method.

1. Introduction

Pure borate glass is made up of a random network including boroxol rings (B_3O_6) and threefold coordinate boron (BO_3). The addition of modifiers, such as alkaline, supports the formation of BO_4 groups in the glass structure. The structuring role of the network modifier is determined by its size, charge and network forming agent of the glass. Through sol-gel processing, homogeneous, high-purity inorganic oxide glasses can be made at ambient temperatures rather than at very high temperatures as required in conventional approaches. The sol-gel process is a useful technique for processing a large number of technologically important glasses, glass-ceramics and crystalline ceramics, mainly because of its ability to generate stoichiometric materials with good control over final amount of compositions.

Significantly, less number of borate compositions is modified by low-temperature sol-gel technology. Special attention has been given to the effect of the ionic conductivity of alkali-borate glasses, especially of lithium-borate, and possibility of applications for solid state batteries and energy storage devices[1–3]. The hybrid borate hydrogel materials obtained by sol-gel technology with a combination of aqua soluble polymers, like polyvinyl alcohol (PVA) and polyethylene glycol (PEG), may have potential applications. Such materials are hybrids of borate esters applied as an electrolyte in lithium-ion batteries[4–8] and materials for medical and biotechnological applications[9–11]. Incorporations of boron in the polymer backbone are used for reinforcing carbon/carbon composite materials. As a result, carbon active sites are blocked because boron generates an oxygen diffusion barrier on the surface of the materials, preventing oxygen from reaching the carbon surface[12–15]. Ceramic fiber[16], boron carbide[17–20] and boron nitride ceramics[21] are produced using only PVA-B_2O_3 hybrid precursors. For borate glasses, data exist only for the cases of metal counterions for anions borate units' compensation. In this work, PVA/PEG/B_2O_3 precursors for boron doped carbon, materials are provided. The polymer pyrolysis is a simple processing route to produce multicomponent nanostructured materials. According to this method, organic–inorganic materials are converted to the borate and carboborate glass and carbon/borate glass nanocomposites.

The objective of the present study is to probe the structure of the hybrid borate hydrogel materials. The crosslinking is achieved by a combination of PVA and PEG in different solutions of borate species. The study is relevant because the new findings will provide information about the basic units forming this multicomponent glass

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structure. Additionally, multivariate statistical interpretation of infrared spectral data (hierarchical cluster analysis) was used to determine specific experimental conditions impacting the procedure of synthesis.

2. Experimental

By the sol-gel process at ambient temperature, homogeneous and transparent organic–inorganic gel materials were obtained with PVA/PEG/B_2O_3 mass ratio of 10/7/1 by the method referred to in the literature[22–24]. All chemicals were used without any further purification: polyvinyl alcohol 72000 (PVA) 98% hydrolyzed, polyethylene glycol 400 (PEG), trimethyl borate $(CH_3O)_3B$, boric acid (H_3BO_3) from Sigma-Aldrich Chemie, Germany. A stock solution of 4 wt% PVA was prepared by dissolving PVA in distilled water by heating. Three precursor solutions of boron are used: 4 wt% H_3BO_3 in distilled water, 4 wt% H_3BO_3 prepared in glycerol and 4 wt% $(CH_3O)_3B$ in ethanol.

The hybrid gels were made by initially mixing and homogenizing PEG and different stock boron solutions. After that, the blended solution was added to the PVA under constant stirring. To obtain self-standing films, and bulk material samples, the hybrid gels were cast onto a glass plate or in a beaker for producing two types of samples for the next steps. The obtained films with 40 μm in thickness and bulk material samples were dried at ambient temperature for one week. The next phase in the experimental procedure was heat treatment at 100, 400, 800 °C for 2 h. Structural changes during the pyrolysis were studied by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer SPECTRUM 1000), differential thermal analysis (TG/DTA, SETRAM LABYS TG/DTA), X-ray diffraction (XRD, DRON-UN CuK_α). The surface morphology was observed by scanning electron microscopy (SEM, JEOL JSM 5300).

Cluster analysis (CA) a is well-known and widely used data mining approach for various purposes with its hierarchical and non-hierarchical algorithms[25,26]. Experimental samples (objects) could be characterized by a set of variables and cluster analysis allows to determine their similarity and to define cluster objects both for objects and variables. A preliminary step of data scaling is necessary (auto scaling or z-transform) for normalized dimensionless numbers replacing the real data values. Thus, important differences in absolute values could be reduced to close numbers. Then, the similarity (or more strictly, the distance) between the objects in the variable space has to be determined. Very often the Euclidean distance was used for clustering purposes. Another approach of measuring similarity is the calculation of the correlation coefficient between the objects. Thus, from the input matrix (raw data) a similarity matrix could be constructed. There is a wide variety of hierarchical algorithms of object linkages, but the typical ones include the single linkage, the complete linkage, and the average linkage methods. The Ward's linkage method was used. The representation of the results of the cluster analysis was performed by a tree-like scheme called dendrogram comprising a hierarchical structure (large groups are divided into small ones).

3. Results and Discussion

3.1. FTIR spectra

All obtained hybrid materials were transparent and thermally stable up to 100 °C, and over 400 °C they were converted into black powder. The final pyrolyzed products were obtained at 800 °C as transparent borate glasses, or black melt carbon/borate glass nanocomposites. Structural changes, which are visually observed, were gained as a function of the borate solutions type. Figs. 1–4 show the FTIR spectra for hybrid precursors during pyrolysis for PVA/PEG/B_2O_3.

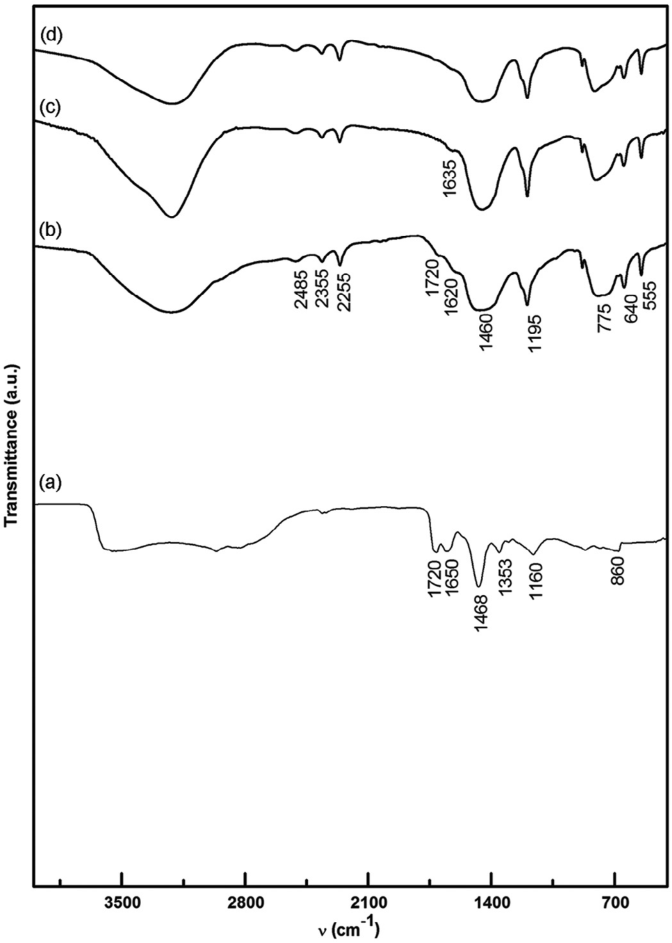

Fig. 1. Fourier transform infrared (FTIR) spectra (spectra are vertically shifted) of pyrolyzed hybrid precursor PVA/B_2O_3: (a) 100 °C, (b) 400 °C, (c) 800 °C, (d) H_3BO_3 molten of 800 °C.

The absorption bands presented at 100 °C are assigned to: 3700–3100 cm^{-1} (ν_sH—OH, ν_sC—OH, ν_sB—OH, hydrogen bonds), 2940–2870 cm^{-1} (ν_sC—H of CH_2, CH_3), 2300–1900 cm^{-1} (δ hydrogen bonds), 1720–1710 cm^{-1} (ν_sC═O), 1650–1640 cm^{-1} (O—H of H_2O, C—C), 1460–1425 cm^{-1} (ν_{as}O—H, δC—H of CH_2 and C—C), 1370–1350 cm^{-1} ($\delta_{as}CH_3$ and C—C), 1370–1220 cm^{-1} (δC—OH, νO—C—C), 1120–1080 cm^{-1} (νC—OH of secondary alcohol PVA, Glycerol), 1065–1020 cm^{-1} (νC—OH of primary alcohol PEG, Glycerol), 1100–1000 cm^{-1} (δC—O—C of esters), 1200–970 cm^{-1} (δC—O), 940–920 cm^{-1} (γC—OH and δC—C), 700–670 cm^{-1} (δC—H and C—C)[16–21,27,28]. The bands in region 1500–1200 cm^{-1} are allied to (νB—O of BO_3), 1200–850 cm^{-1} to (νB—O of BO_4) and 800–600 cm^{-1} (bending vibrations for various borate segments)[29,30]. The characteristic frequency for B—O—C bond occurred at 1030 cm^{-1}[16–19].

The major changes of vibration frequencies for O—H and C-OH (3700–3100 cm^{-1}) and C—H (2940–2870 cm^{-1}) bonds are observed in FTIR spectra at 400 °C. The effects of water evaporation and burning of polymers lead to decrease of widths and intensities of these bands[31]. The spectral changes depicted in Figs. 1 and 2 are connected to the simultaneous disappearance of the absorptions bands in the regions of 2940–2870 cm^{-1} and 1720 cm^{-1}. The presence of new bands at 700 cm^{-1}, 460 cm^{-1}, 550 cm^{-1} indicates the presence of BO_3 groups[16,19,29,30]. The network of the PVA-H_3BO_3 hybrid precursor at 400 °C is destroyed, and typical bands of BO_3 group in boric acid are observed in Fig. 1(b). FTIR spectrum

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