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Preparation and thermal properties of samarium doped silica xerogels

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ABSTRACT

Samarium doped silica xerogels with different content of Sm^{3+} up to 0.5 Sm/Si are prepared using a sol–gel method based on acid-catalysed hydrolysation of tetraethylorthosilicate (TEOS) and gelation. The prepared xerogels are investigated by SEM, X-ray diffraction, TG/FTIR, differential scanning calorimetry (DSC) and thermogravimetry (TG). It is proved that triclinic microcrystallites of $Sm(NO_3)_3{\cdot}6H_2O$ are formed at high Sm contents. Detailed thermal analysis up to 500 °C demonstrates a strong effect of Sm content on the thermal properties of doped xerogels. A peculiar sharp endotherm is observed in the vicinity of 80 °C which position, unexpectedly, shifts to higher temperatures by decreasing of the heating rate. Other two wide endotherms are observed depending on both Sm amount and heating rate. Two different activation energies related to these endotherms are evaluated for the lower- and higher temperature effects: E_a = 38 kJ/mol, and E_a = 210 kJ/mol, respectively. They characterize the corresponding processes of xerogels dehydratation and chemical decomposition of $Sm(NO_3)_3{\cdot}6H_2O$. This finding is also in accordance with TG/FTIR analysis of Sm-doped silica xerogels.

1. Introduction

The sol–gel process is a promising way for synthesizing and developing of new materials [1–3]. Sol–gel chemistry offers a possibility for the preparation of transparent ceramic materials like xerogels or layers doped with rare-earth ions. In the same way a wide range of important ceramic materials like ZrO_2, SnO_2, SiO_2, and Al_2O_3 can be easily prepared. In this way essential functional optical materials, containing co-activators or organic molecules in gels, can be prepared [4–9]. Recently we described the sol–gel incorporation of high amounts of rare-earth ions using tetraethoxysilane (TEOS) and nitrate solutions of rare-earth ions [4–9]. The monoliths obtained in our recent papers display interesting optical properties, coming from f–f transitions of Tb^{3+} or Ho^{3+} ions, where in terbium doped samples Ge → Tb and Ce → Tb energy transfer take place [5,6]. Sol–gel glasses doped with rare-earth ions are important kind of materials for laser applications or antireflection layers in silicon solar cells. The optical spectroscopy of rare-earth ions is also informative for characterization of glasses [10–13]. The thermal behavior of doped silica xerogels, however, is not detailed investigated at this time.

The aim of the present paper is to describe detailed the thermal behavior of silica xerogels, containing different amounts of Sm^{3+} and to find correlations between rare-earth content, phase composition and thermal properties of the gels. To the best of our knowledge, there is a lack of information in the literature about thermal properties of Sm-doped xerogels and samarium salts, as well.

2. Experimental details

The Sm^{3+} doped xerogels were prepared at room-temperature by the acid-catalysed hydrolysation of tetraethylorthosilicate (TEOS), which was dissolved in ethanol (EtOH) and hydrolysed with HCl at pH = 2, followed by gelation and a subsequent drying at 50 °C (Boeco dry block). Before hydrolysis a 0.55 M $Sm(NO_3)_3$ solution prepared from Sm_2O_3 and HNO_3 was added to the TEOS/EtOH solution. The initial molar composition for all samples were $TEOS/H_2O$ = 1/4, with Sm/Si contents n_{Sm}/n_{Si} of 0.01, 0.05, 0.1, 0.2 and 0.5, respectively, and a starting amount of 5 ml TEOS. The duration of the different sol–gel steps was 1 h for room-temperature hydrolysis, 48 h for gelation and 100 h for drying at 50 °C.

The samples were investigated by X-ray diffraction using a standard powder diffractometer Philips PW 1050. Scanning electron microscope (SEM) investigations were performed on a JEOL 5510 microscope.

The chemical composition and thermogravimetrical behavior of the xerogels are checked by TG/FTIR investigations (NETZSCH TG

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209 F1 IRIS and the FTIR spectrometer Brucker TENSOR 27™ unit). The sample to be investigated is transferred into a crucible that is made from alumina or platinum. Typical sample masses are within a range of 5–100 mg. The sample carrier is designed in a way that allows admitting the sample with controlled temperature treatments. Isothermal or dynamic heating and cooling cycles are possible between room-temperature and to 1000 °C. With this technique it is possible to quantify the amount of gases that are released temperature- and/or time-dependent. Beyond the information about the temperature-dependent mass loss, identification of the released gases can be achieved by combining the thermobalance with spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR). The coupling facility has to be designed in a way that condensation of the gaseous compounds is excluded. The exhaust of the furnace of the thermobalance is therefore connected with a heated transfer line that guides the released gases into a heated gas detection cell of the infrared spectrometer. Small total volume of the thermobalance furnace, the transfer line and the gas cell guaranty a fast gas transport (typically 30 s) by employing a purge gas flow of only 30 ml/min. The efficiency of fast and complete gas transportation in combination with a small purge gas flow rate is an important precondition for a high concentration of the released gases inside the gas detection cell of the spectrometer.

The thermal properties of samarium doped silica xerogels were studied systematically by differential scanning calorimetry (DSC) and thermogravimetry (TG), using a Mettler TA 3000 system. All experiments were carried out in the temperature range from 25 to 500 °C with samples amount ca. 10 mg in aluminium pans. Different heating rates were applied for both DSC and TG studies: 3, 5, 8, 10, 15, 20, 25, 30, 40 and 50 K/min. From endothermal effects on DSC curves the temperature of peaks maxima and enthalpy changes ΔH are determined. Activation energies of the observed endothermal processes are also evaluated. The weight losses, temperature intervals of weight losses and corresponding temperature maxima are estimated from TG curves.

3. Results and discussion

3.1. Characterization of the microstructure and chemical composition of Sm-doped xerogels

The drying procedure results in the formation of monoliths with typical sizes bellow 1 cm. Samples with low samarium content and un-doped gels are transparent, with increasing Sm content the gels become translucent. The as prepared gels have a light yellow colour, coming from the Sm^{3+} f–f transitions [9]. Detailed investigations of the optical properties of transparent Sm-doped gels prepared by gelation at pH = 6–7 and controlled room-temperature drying are summarized in a separate contribution [13].

X-ray diffraction results showed that un-doped gels and samples with low samarium content (Sm/Si up to 0.1) are amorphous, displaying the typical for SiO_2 – gels halo (Fig. 1). It can be concluded that at low Sm contents the rare-earth ions are randomly distributed in the amorphous silica network. All samples containing higher amount of Sm (Sm/Si = 0.2 and 0.5) display small diffraction peaks besides the amorphous halo of SiO_2. Obviously, they are due to crystalline structures co-existing with the amorphous material. An analysis of the X-ray diffraction patterns of gels containing 0.2 and 0.5 Sm/Si confirmed the existence of triclinic $Sm(NO_3)_3{\cdot}6H_2O$, PDF 35–950. The X-ray diffraction results were proved by SEM investigations, displaying needle's like microcrystallites, co-existing with amorphous sections (Fig. 2). Xerogels with low Sm content are transparent and smoothly.

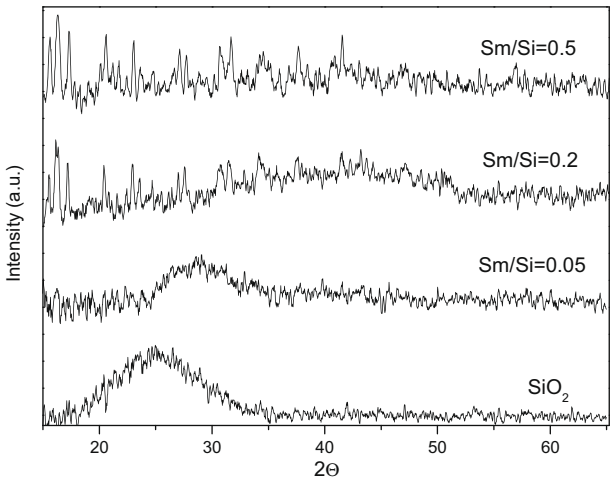

Fig. 1. X-ray diffraction patterns of silica gels. The peaks at high samarium doping are from triclinic $Sm(NO_3)_3{\cdot}6H_2O$, PDF 35–950.

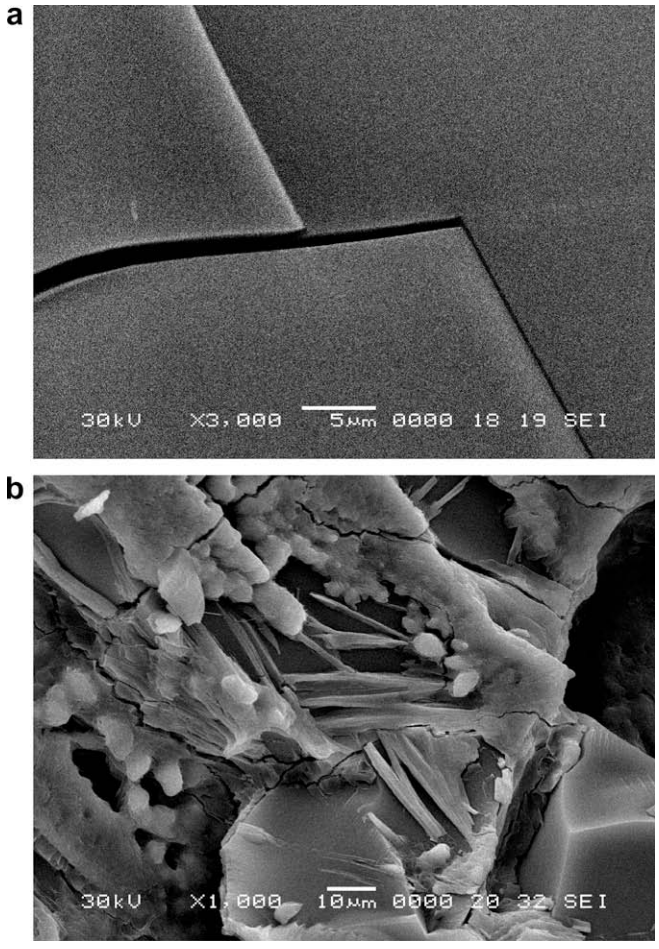

Fig. 2. SEM investigations of xerogels with Sm/Si = 0.01 (a) and Sm/Si = 0.2 (b). The dense spaced sections are typical for amorphous xerogels, the needles are expected to be from $Sm(NO_3)_3{\cdot}6H_2O$.

The X-ray results are supported by TG/FTIR observations. Samples containing 0.05 Sm/Si, 0.2 Sm/Si as well as un-doped silica gels are investigated. Typical results from the FTIR study are shown in Fig. 3 for a sample with 0.2 Sm/Si. They unambiguously prove that the gas products of heated Sm-doped gels contain NO_x products.