

## Thermal and structural study on densification of rare-earth-doped PbO–SiO<sub>2</sub> aerogels

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### Abstract

An attempt to prepare Ce- and La-doped SiO<sub>2</sub>–PbO glasses for applications as scintillators was realised via aerogel route. The synthesis has been optimised in order to obtain large massive samples required for this application. The effect of Pb in the silica matrix as a co-dopant for rare-earths atoms is discussed: in particular, an increase of rare-earth solubility has been observed. Both <sup>207</sup>Pb and <sup>29</sup>Si magic angle spinning (MAS) NMR were used to investigate local order and connectivity. The densification of aerogels, investigated by means of DSC, TGA, and X-ray powder diffraction (XRPD), led to glass–ceramic samples because concurrent crystallisation occurred.

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### 1. Introduction

The possible application of scintillating materials in biomedicine and nuclear physics makes these materials of great interest. For this reason, a number of studies are devoted to obtain new solid-state scintillators. Among them, SiO<sub>2</sub>-based glasses can successfully replace more traditional materials such as (a) liquids, like pseudocumene; (b) organic materials, like naphthalene or anthracene trapped in a polymeric matrix; (c) single crystals as NaI or CsI. The most important drawbacks presented by these materials are low versatility (in case of liquids), bad chemical stability (as hygroscopicity of inorganic materials), low resolution (for the organic ones) and very long scintillating times.

It is known from literature that rare-earths-doped SiO<sub>2</sub> glasses exhibit scintillating properties [1,2]. The possibility to build up silica-doped scintillators would, therefore, offer some advantages as high matrix stability, relatively low cost, and good optical properties. However, the solubility of rare-earths in silica is a well known problem in optics and optoelectronics [3–9], where it is necessary to have

a large amount of the dopant (>1 mass%) homogeneously distributed in the glassy matrix without clustering or crystallisation. This problem seems to be independent from both the rare-earth used and the synthesis procedure. Concerning the latter aspect, one of the most convenient methods for producing amorphous silica is represented by sol–gel route. Despite the number of advantages presented by this approach, the main limitations in its applications are due to the low reproducibility in absence of a careful control of experimental parameters, and the difficulty to produce quite large (decimetre scale) crack-free objects. A possible way to overcome such problems consists in following an aerogel route. Regarding the former problem, it is well recognised that, whatever the method of synthesis, a solubility increase of rare-earths in the silica matrix is promoted by the insertion of another element called co-dopant. The more used co-dopants are phosphorus and aluminium, while germanium was mentioned more recently [6]. Unfortunately, Al can easily yield devitrification, P makes the glass hygroscopic, and Ge is useful only in large quantities. In this work lead was chosen, since it seems to be a good candidate for scintillators, also because of its large cross-section for radiation, which increases the energy-transfer process. However, lead might cause sample crystallisation as well.

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The aim of the present paper is two-fold. From one side, the bias of Pb to act as a co-dopant for rare-earths in silica glasses has been investigated by varying its content, and by keeping the amount of Ce or La fixed. The connectivity of both lead and silicon was also studied by solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) on  $^{207}\text{Pb}$  and  $^{29}\text{Si}$ , respectively. On the other side, the effect of Pb in inducing devitrification during the complex densification process of aerogels was investigated by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray powder diffraction (XRPD).

## 2. Experimental

### 2.1. Samples preparation

1.  $\text{SiO}_2$  samples: 0.5 mol of tetraethylortosilicate (TEOS) were added to 200 ml of HCl 0.01 M and mixed with 50 ml of ethanol (EtOH). The mixture was stirred for 15 min to obtain a sol mainly containing hydrolysed TEOS. In order to complete the hydrolysis step, the ethanol was removed by distillation. After the addition of 100 ml of *N,N*-dimethyl formamide (DMF) [10], a solution of  $\text{NH}_4\text{OH}$  0.05 M was slowly added to the sol to raise the pH from 2 to 4. The final sol was poured in the moulds and gelation occurred in about 20 h.
2.  $\text{SiO}_2$  samples with 1% mol of La or Ce: the procedure was similar to the above one with the addition of the rare-earths salt ( $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  or  $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ) before raising the pH. In this case gelation occurred in about 30 h.
3.  $\text{SiO}_2$ -PbO samples with 1% mol of La or Ce: TEOS was added to an aqueous solution of  $\text{CH}_3\text{COOH}$  with a pH of 2 and mixed with EtOH. The mixture was stirred for 5 min to obtain a sol containing chiefly hydrolysed TEOS. In order to complete the hydrolysis step, EtOH was removed by distillation. At this stage,  $(\text{CH}_3\text{COO})_2\text{Pb}$ , DMF, and the stoichiometric amount of the rare-earths salt ( $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  or  $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ) were added. Then, the solutions were poured in the moulds and gelation occurred in hours.

The amounts of reagents and the gelation times are reported in Table 1. After gelation, all the samples were washed with acetone to allow gel ageing and water evacuation from the gel pores. This step is also needed to have a good supercritical drying process. Since this part of the

synthesis is very critical for decimetre scale bulks, a method starting from aqueous acetone that progressively becomes more anhydrous, was employed. The washing was prolonged for 5 days in case of small samples and for about 10 days for the bigger ones. Afterwards, the samples were dipped in ethyl acetate for 1 day and placed in autoclave for the supercritical drying process. The critical point of this solvent is  $T_c = 250^\circ\text{C}$  and  $P_c = 39\text{ atm}$  and the employed process refers to a patent [11].

The aerogels were densified with the following thermal treatment: samples were heated at a rate of  $0.2^\circ\text{C}/\text{min}$  up to  $400^\circ\text{C}$  and held at this temperature for 3 h to calcinate all organic residues. Then, the heating rate of  $0.6^\circ\text{C}/\text{min}$  was used up to  $800^\circ\text{C}$  and the one of  $1.2^\circ\text{C}/\text{min}$  up to  $1200^\circ\text{C}$ . This last temperature was held for 45 min and, finally, the samples were cooled down to room temperature by switching the oven off. The purging gases were  $\text{N}_2$  (0.4 l/min) and  $\text{O}_2$  (0.2 l/min) up to  $800^\circ\text{C}$  and, above this temperature, He (0.4 l/min).

### 2.2. Measurements

The quantitative determinations of Pb, La and Ce were performed by inductively coupled plasma mass spectroscopy (ICP-MS) by the ELAN 5000 instrument. The sensitivity of this technique can be estimated in the range of few ppb, and the error is  $\sim 5\%$  of the absolute value. Each sample was dissolved in HF ( $\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$ ) and then the solution was completely dried in order to remove gaseous  $\text{SiF}_4$ . The residue was dissolved in ultra pure  $\text{HNO}_3$  and then injected in the plasma torch.

$^{207}\text{Pb}$  solid-state NMR spectra were acquired on freshly crushed samples with a AMX400WB spectrometer (Bruker, Germany) at the frequency of 83.7 MHz (magnetic field of 9.4 T). A 7 mm cross polarisation magic angle spinning (CP-MAS) probe (Bruker) was used, but no differences were observed between the spectra acquired with sample rotation (up to 7 kHz) and the static ones. Crystalline  $\text{PbSO}_4$  was used as a secondary chemical shift reference ( $-3613\text{ ppm}$  from  $\text{Pb}(\text{CH}_3)_4$ ). The spectra were acquired with a Hahn echo sequence ( $8\ \mu\text{s}$  for the  $90^\circ$  pulse) and averaged over 512 acquisitions. A spectral width of 1 MHz was used.

$^{29}\text{Si}$  MAS-NMR data were collected with the same spectrometer at a Larmor frequency of 79.46 MHz. The spectra were acquired on freshly crushed powders, by using a 7 mm probehead equipped with cylindrical zirconia rotors and a boron nitride stator. The samples were spun at 5 kHz and the data were averaged over 1000–3000 acquisitions using

Table 1  
 $\text{SiO}_2$ -PbO recipe details

Pb (mol%)	TEOS (mol)	EtOH (ml)	$\text{CH}_3\text{COOH}$ (ml)	$(\text{CH}_3\text{COO})_2\text{Pb}$ (g)	DMF	Gelation time (h)
10	0.45	51	206	18.97	103	4
5	0.475	54	217	9.48	108	12
2	0.49	57	223	3.79	112	20

Table 2  
SiO<sub>2</sub>–PbO aerogels doped with La

Pb mol% (nominal)	Pb mass% (nominal)	Pb mass% (experimental)	La mol% (nominal)	La mass% (nominal)	La mass% (experimental)
0	0	0.49 ± 0.02	1	1.79	0.062 ± 0.003
2	6.55	0.79 ± 0.04	1	1.79	0.306 ± 0.015
5	15.20	0.72 ± 0.04	1	1.79	0.116 ± 0.006
10	27.15	1.90 ± 0.09	1	1.79	0.266 ± 0.013

a single-pulse sequence, with a 30° pulse of 3 μs and a recycle time of 30 s. The spectra were referenced to tetramethylsilane (TMS).

Both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out by means of a simultaneous SDT 2960 (TA Instruments, USA) at a rate of 10 °C/min under nitrogen purge. In order to reduce moisture contamination, all specimens were freshly cut into small disks fitting the pans (6 mm in diameter).

### 3. Results

#### 3.1. Actual sample composition

Both nominal and experimental contents of Pb, La and Ce are reported in Tables 2 and 3, respectively. It can be noticed that also pure silica samples are contaminated by Pb, probably because all the specimens were hypercritically

dried in the same environment. In the co-doped samples, the actual Pb content is lower than the nominal amount, likely due to the washing procedure. Similarly, Ce and La losses are also observed. The actual ratios between Pb and rare-earths (Pb:Ce = 14 and Pb:La = 9.6) are consistent with the data reported in Refs. [8,9,12–14].

#### 3.2. NMR evidences

Fig. 1 shows the <sup>207</sup>Pb magic angle spinning (MAS) NMR spectrum of a typical aerogel. Three features can be detected: (I) one above 1000 ppm; (II) one around 0 ppm; (III) one below –1000 ppm. The chemical shift tensor of <sup>207</sup>Pb in crystalline and glassy compounds has been recently investigated by Fayon et al. [15,16]. On the basis of their assignments, feature (I) can attribute to Pb in a coordination resembling that of PbO, with the spectrum enlarged by the anisotropic part of the chemical shift (c.s.) tensor. The other two features (II and III) may be assigned to Pb at the apex of

Table 3  
SiO<sub>2</sub>–PbO aerogels doped with Ce

Pb mol% (nominal)	Pb mass% (nominal)	Pb mass% (experimental)	Ce mol% (nominal)	Ce mass% (nominal)	Ce mass% (experimental)
0	0	0.58 ± 0.03	1	1.8	0.057 ± 0.003
2	6.55	0.88 ± 0.04	1	1.8	0.189 ± 0.01
5	15.20	0.80 ± 0.04	1	1.8	0.082 ± 0.004
10	27.15	2.83 ± 0.14	1	1.8	0.265 ± 0.01

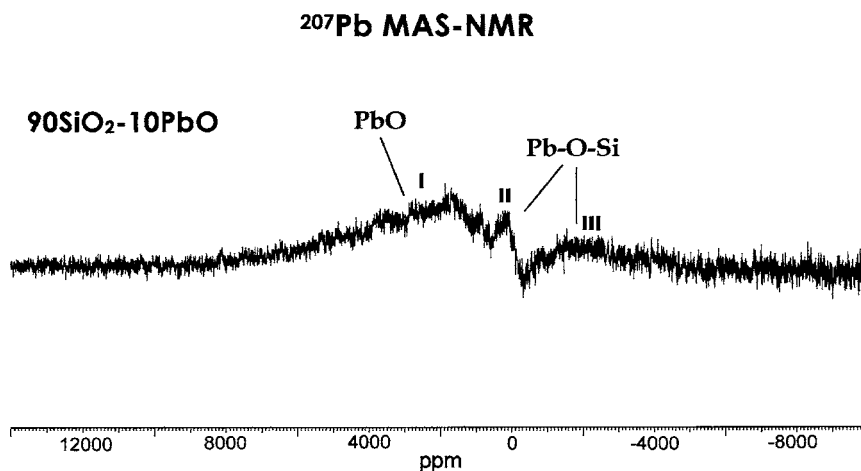


Fig. 1. <sup>207</sup>Pb MAS–NMR of the 90SiO<sub>2</sub>–10PbO<sub>2</sub> aerogel sample: peak (I) Pb in PbO-like coordination; peak (II) Pb at the apex of trigonal pyramids; peak (III) Pb at the apex of tetrahedral pyramids.

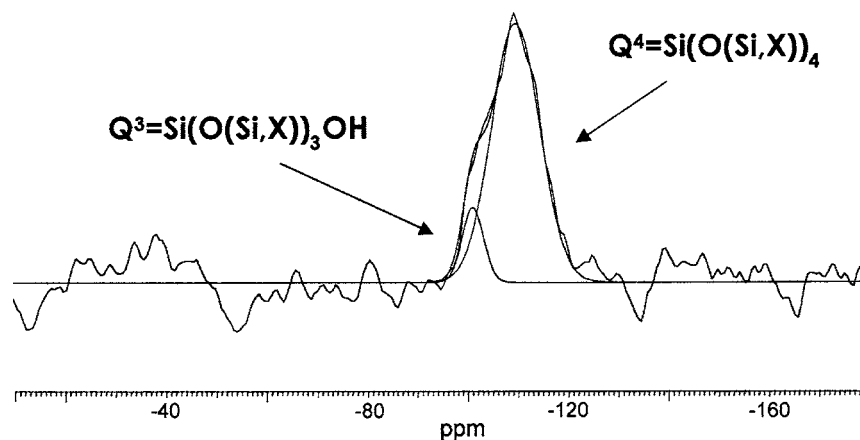


Fig. 2. Typical  $^{29}\text{Si}$  MAS–NMR of a  $\text{SiO}_2\text{:PbO}$  aerogel sample: the peaks represent a tentative gaussian deconvolution.

trigonal  $\text{PbO}_3$  and tetrahedral  $\text{PbO}_4$  pyramids, respectively, which are typical of  $\text{PbO-SiO}_2$  glasses [17]. Therefore, it seems that Pb is partially clustered to form a  $\text{PbO}$ -like structure, and partially inserted into the silica matrix.

Fig. 2 shows the  $^{29}\text{Si}$  NMR spectrum of a typical  $\text{SiO}_2\text{:PbO}$  aerogel sample. Following a standard procedure [18], the spectrum can be deconvolved into Gaussians giving the fractions of the  $Q^n$  units, where  $n = 3, 4$  is the number of Si–O bonds bridging towards others  $M = \text{Si, Pb}$  atoms.

The deconvolution data are reported in Table 4. The most interesting point is that the full width at half height of the  $Q^4$  peak increases of  $\sim 30\%$  when lead is added to the matrix, irrespective from the addition of the rare-earth. This seems to confirm that lead enters the silica matrix by forming Si–O–Pb bonds. Readers should be warned that the amounts of  $Q^3$  are affected by the formation of Si–OH groups during crushing in ambient atmosphere.

### 3.3. Thermal behaviour

Fig. 3 reports (a) DSC and (b) TGA traces of the as-prepared aerogel samples. All specimens exhibit very similar thermal behaviours: the first endothermic peaks recorded below  $200^\circ\text{C}$  (see Fig. 3a) is associated to the mass losses observed in Fig. 3b) in the same temperature range and can be easily ascribed to the loss of water and residual solvents. The larger and smoothed out endotherms starting from  $400^\circ\text{C}$ , correspond to the remarkable mass losses taking place between 400 and  $1000^\circ\text{C}$  and is due to

the removal of bonded water as well as ethoxy and –OH groups from the aerogel network. Above  $1000^\circ\text{C}$ , in the  $90\text{SiO}_2\text{--}10\text{PbO}$  aerogel sample (solid line) no further mass change is seen, whereas both La-doped (long dash) and Ce-doped (short dash) samples exhibit little mass losses ( $<2\%$ ). In such a region the DSC signals keep decreasing up to  $\sim 1100^\circ\text{C}$  where exothermic features related to structural rearrangements, do start off.

Fig. 4 reports (a) DSC and (b) TGA thermo-analytical curves of the Ce–Pb co-doped aerogel samples thermally treated at 1000 and  $1100^\circ\text{C}$ . The DSC signals of Fig. 4a) look somewhat different. It is apparent that the sample heated at  $1000^\circ\text{C}$  (solid line) shows a broad endotherm starting from  $400^\circ\text{C}$  due to the loss of residual bonded water, followed by an exothermic peak above  $1050^\circ\text{C}$  probably related to a crystallisation, whilst the sample treated at  $1100^\circ\text{C}$  (dashed line) presents only a tiny exotherm for  $T > 1050^\circ\text{C}$ . In the TGA traces of Fig. 4b) a total mass loss  $\approx 2\%$  is recorded for the sample treated at  $1000^\circ\text{C}$  (solid line), whereas a little mass decrease ( $<1\%$ ) is observed at high temperatures for the sample treated at  $1100^\circ\text{C}$  (dashed line).

## 4. Discussion

From Tables 2 and 3 one can see that the addition of lead as a co-dopant does enhance the solubility of rare-earths in silica aerogels. Unfortunately, preliminary densification

Table 4  
 $^{29}\text{Si}$  MAS–NMR data

Sample	$Q^4$			$Q^3$		
	c.s. (ppm)	Area (%)	FWHH (Hz)	c.s. (ppm)	Area (%)	FWHH (Hz)
$\text{SiO}_2$	110.8	51	660	102.0	49	400
$90\text{SiO}_2\text{--}10\text{PbO}$	119.6	78	900	101.0	22	400
$\text{SiO}_2\text{--PbO--La 1\%}$	110.5	78	900	101.1	22	400
$\text{SiO}_2\text{--PbO--Ce 1\%}$	109.9	75	850	101.9	25	400

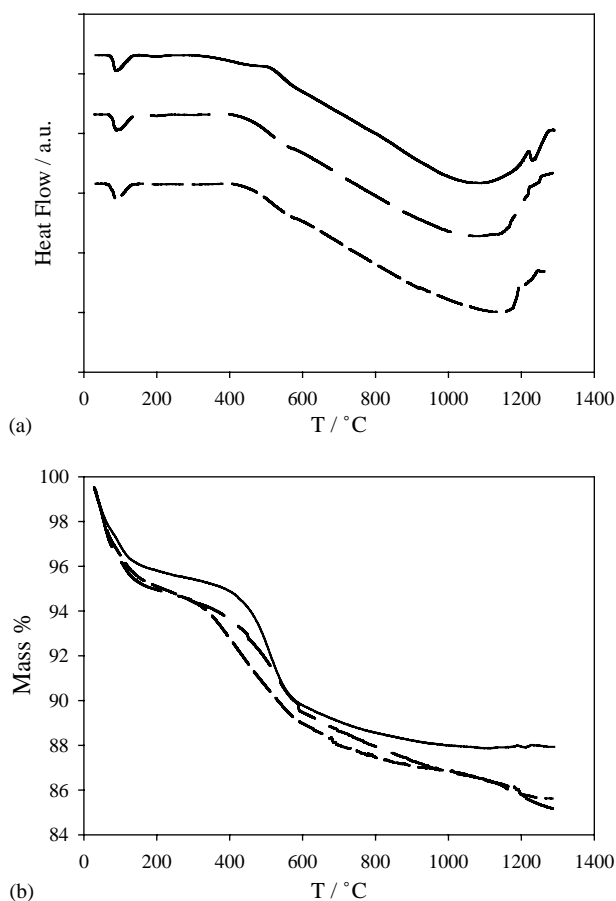


Fig. 3. (a) DSC and (b) TGA traces of the as-prepared aerogels samples: 90SiO<sub>2</sub>–10PbO<sub>2</sub> sample (solid line); La-doped sample (long dash); Ce-doped sample (short dash).

studies on Pb-containing aerogels showed that sample devitrification occurred during thermal treatments up to 1200 °C. Moreover, as can be evinced by <sup>209</sup>Pb NMR spectra (see Fig. 1), even in as-prepared aerogels lead tends to partially segregate by forming PbO clusters.

It is known that one of the most important features required to rare-earth-doped-silica to make solid-state scintillators is the absence of crystalline phases. For the above reason, it is of great importance to shed light on the possibility to drive the aerogel densification without promoting sample crystallisation. The combined use of DSC, TGA and X-ray diffraction can hence, help in monitoring the formation of crystalline phases during the thermal densification. Unfortunately, the heating rates adopted in the aerogel thermal treatment (see Section 2.1) are too small to produce significant DSC signals. Though the standard rate of 10 °C/min chosen for the DSC/TGA scans (one order of magnitude higher than the densification rate) allow to better appreciate all thermal phenomena, it can also significantly affect the devitrification kinetics.

A possible compromise between the need of a relatively high heating rate in the DSC runs, and the requirement of following structural changes above 1000 °C during the slow

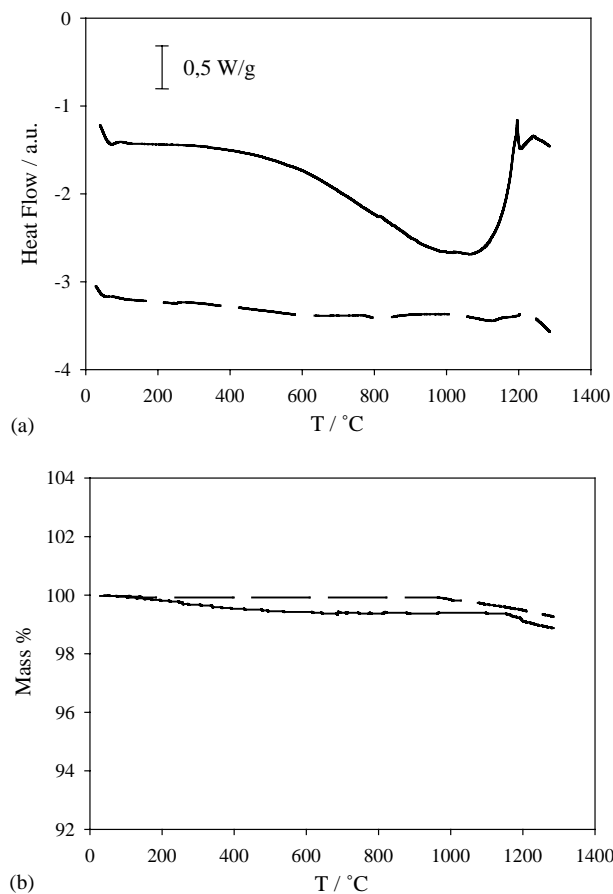


Fig. 4. (a) DSC and (b) TGA traces of the Ce–Pb co-doped aerogel samples: treated at 1000 °C (solid line); treated at 1100 °C (long dash).

densification process, consists in performing slow thermal treatments up to selected temperatures (1000 and 1100 °C), and then analyse the obtained samples by thermal analysis. This is the case of Ce–Pb co-doped samples reported in Fig. 4. The exothermic effect recorded above 1100 °C, much larger in the case of samples treated at 1000 °C than that in samples heated at 1100 °C, suggests that most crystallisation takes place in this temperature range.

Such a behaviour, common to all the examined samples, can be better understood by analysing the X-ray diffraction patterns of the Ce–Pb co-doped samples reported in Fig. 5. Whilst the XRPD pattern of the sample treated at 1000 °C (curve a) just shows an amorphous hump centred around  $2\theta = 30^\circ$ , as a clear evidence that no crystallisation yet occurred during the thermal cycle, the presence of the reflection peaks of cristobalite in the sample treated at 1100 °C (curve b), confirms that devitrification takes place between 1000 and 1100 °C. On the other hand, by the assessment of geometrical density data reported in Table 5, one can remark that even in samples heated up to 1100 °C, the figures are well below the value of 2.2 g/cm<sup>3</sup> typical of amorphous silica. Hence, it is apparent that sample crystallisation occurs before that thermal densification reaches its completion and, since this happens also for the “pure” silica sample (con-

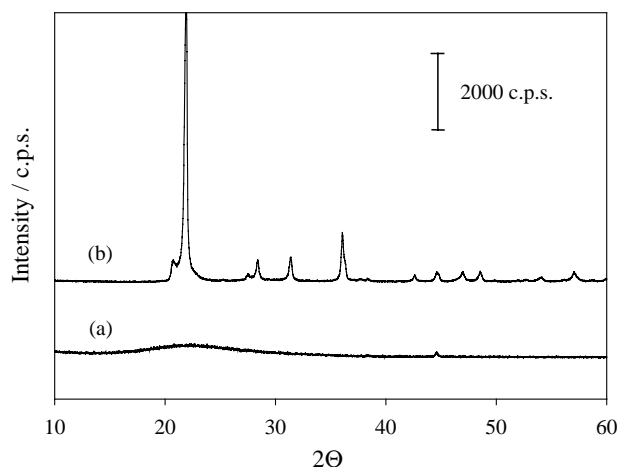


Fig. 5. X-ray diffraction patterns of the Ce–Pb co-doped aerogel samples: (a) treated at 1000 °C; (b) treated at 1100 °C.

Table 5  
Density of samples before and after heat treatments

Sample	Density (g/cm <sup>3</sup> )		
	As prepared	Heated up to 1000 °C	Heated up to 1100 °C
Pb-doped SiO <sub>2</sub>	0.221 ± 0.03	0.375 ± 0.05	0.745 ± 0.06
Pb, La co-doped SiO <sub>2</sub>	0.186 ± 0.03	0.345 ± 0.04	0.717 ± 0.07
Pb, Ce co-doped SiO <sub>2</sub>	0.299 ± 0.03	0.405 ± 0.05	0.770 ± 0.07

taminated by lead), one can likely infer that the growth of the cristobalite phase is promoted by that part of lead atoms which clusterise as PbO (see NMR results).

## 5. Conclusions

In this paper a new route via aerogel for the synthesis of Ce- and La-doped SiO<sub>2</sub>–PbO has been proposed.

The co-doping effect of Pb in silica has been verified although the employed method does not allow to obtain samples having the desired nominal composition.

Solid-state <sup>207</sup>Pb NMR showed that in the aerogel samples, Pb is present both as PbO and as Si–O–Pb groups. Solid-state <sup>29</sup>Si NMR revealed that the silica aerogel structure is more disordered when Pb is inserted, confirming that lead is partially connected to the silica network.

The combined use of thermal analysis and X-ray diffraction showed that Ce- and La-doped SiO<sub>2</sub>–PbO glasses cannot be produced from aerogels according to the proposed route of synthesis, as long as sample crystallisation takes place during the densification process.

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