

Effect of annealing on the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio measured by XPS in luminescent $\text{SiO}_2:\text{Ce}$

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Abstract. Ce doped silica was prepared by the sol gel method and annealed in air or reduced with hydrogen, both at 1000°C . The reduced sample exhibited strong luminescence while the sample annealed in air did not, which has been attributed to Ce taking the tetravalent form which is non-luminescent in the latter case. In order to test this, x-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation state of the Ce ion. The obtained spectra were fitted with 10 Gaussian peaks. The fitted parameters showed the existence of the Ce^{3+} ion is about 20% and 73% in annealed and reduced sample respectively, confirming the increased luminescence is associated with reduction of the Ce. This is in contrast to other published results where samples subjected to rapid thermal annealing using an oxidising oxygen-hydrogen flame exhibited an increase in luminescence despite indications that the Ce^{4+} concentration had increased. Photoluminescence (PL) and UV-vis spectroscopy were done on the reduced and annealed samples of this study and the results are consistent with the XPS measurements.

1. Introduction

Ce doped silica has potential applications as a luminescent material as phosphors for cathodoluminescence, scintillators and detectors [1]. Ce ions can occur in a trivalent or a tetravalent state: only the trivalent Ce^{3+} state with a single 4f electron is optically active, while the tetravalent Ce^{4+} ion is non-luminescent. X-ray photoelectron spectroscopy (XPS) is a suitable technique to investigate the oxidation states of Ce in cerium oxides and such studies have been carried out because of the importance of $\text{CeO}_2/\text{Ce}_2\text{O}_3$ conversion in automotive exhaust catalysts [2]. However, the XPS Ce3d spectrum of cerium oxide is rather complex as it contains ten closely spaced and overlapping peaks on a strong background. The main challenge is to obtain accurate fits to experimental data while still maintaining a good physical basis for the fitting parameters [3]. The analysis of Ce in $\text{SiO}_2:\text{Ce}$ is even more challenging since the Ce concentration for luminescent samples is only in the region of 1 mol%. Although it has been experimentally shown that to improve the luminescence efficiency of Ce doped silica it can be useful to anneal the glass in a reducing atmosphere [4], with the implication that this increases the concentration of Ce^{3+} luminescent ions, the authors are not aware of XPS measurements that correlate the relative concentrations of the Ce^{3+} and Ce^{4+} ions to the luminescent properties. In this work, cerium doped silica was prepared by the sol-gel method. The effect of annealing atmosphere on the luminescent properties is correlated to XPS measurements of the oxidation state of Ce in the samples.

2. Experimental

Ce-doped SiO₂ glass was prepared by the sol–gel method using tetraethylorthosilicate (TEOS), water, ethanol (C₂H₅OH) and Ce(NO₃)₃ as starting materials and nitric acid (HNO₃) as a catalyst. The molar ratio of TEOS:H₂O:C₂H₅OH was 1:5:10, and the HNO₃ concentration was 0.015 M in water. TEOS was mixed with ethanol and stirred for 30 minutes after which the acidified water was added and stirring continued for another 30 minutes. After that Ce(NO₃)₃ was dissolved in a little ethanol and added to the mixture, which was stirred for a further 4 h. Then the mixture was stored in a closed container and transferred to a water bath at 50°C until a gel was formed. The gel was dried, crushed and divided into two parts, one part annealed in air at 1000°C for 2 h, and the other part annealed at flowing 4% hydrogen in argon atmosphere for the same time and temperature. XPS measurement were made using two different spectrometers, PHI 5400 ESCA and PHI 5000 Versaprobe both using Al x-rays. The powder sample was deposited onto a conductive carbon tape stuck to the sample holder. Charging shifts of the spectra were corrected using the known values of the C1s and/or Si2p peaks. Photoluminescence was measured at room temperature with a Cary Eclipse fluorescence spectrophotometer equipped with a xenon lamp. Diffuse reflectance spectra were recorded using a Lambda 950 UV–vis spectrophotometer with an integrating sphere.

3. Results and Discussions

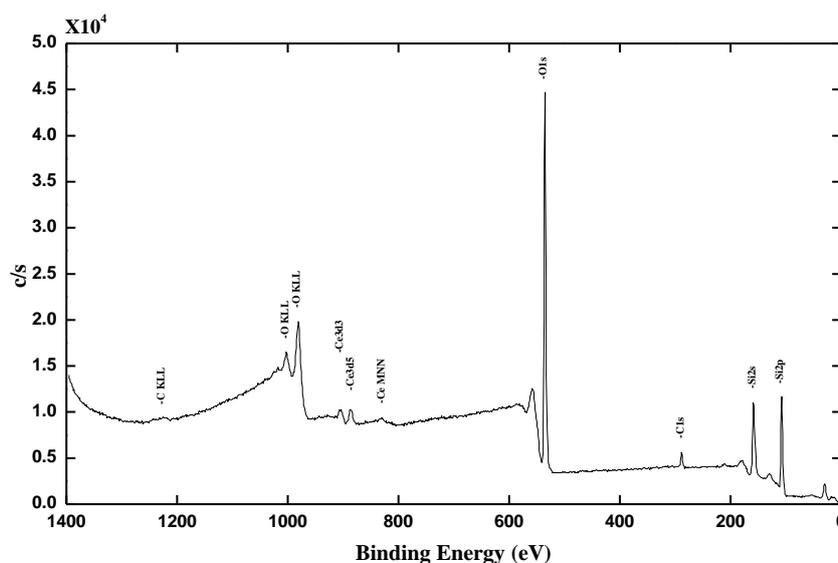


Figure 1. XPS survey scan spectrum of the reduced sample

3.1. XPS

For XPS analysis a higher dopant concentration (4 mol%) was used than what is required for good luminescence (0.5 mol%) to obtain a reasonable Ce3d signal. Figure 1 shows the full range survey scan spectrum of the reduced sample. The spectrum is dominated by four photoelectron peaks, corresponding to electrons originating in the 2p orbital of the Si, 1s orbitals of the C and O and 3d orbital of the Ce atoms in the sample surface. The existence of the C atoms on the sample surface can be ascribed to three possible reasons: from adventitious hydrocarbon nearly always present, or from the precursors, or from the carbon tape used to stick the powder to the sample holder. Multipak version 8.2c software was used to fit the Ce3d pattern. The spectrum was fitted with 10 Gaussian peaks, two doublet peaks of the spin–orbit split 5/2;3/2 components attributed to the final states of Ce³⁺ and three doublet peaks of the spin–orbit split 5/2;3/2 components attributed to the final states of Ce⁴⁺ (see Tables 1 and 2). Peak position, spin–orbit splitting, area ratio and FWHM, are fitting

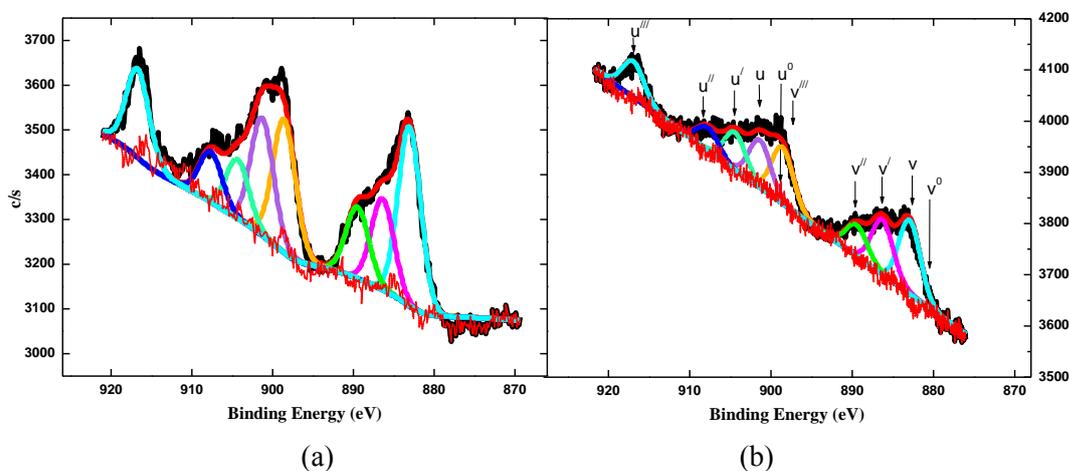


Figure 2. Ce3d XPS spectra of the annealed sample obtained by (a) PHI 5000 (b) PHI 5400.

Table 1. Fit parameter of the annealed sample.

ion	3d _{5/2} /3d _{3/2}	pos	final state	%area	%total
Ce⁴⁺	v/u	882.3/901.0	Ce 3d ⁹ 4f ² O 2p ⁴	36	80
	v''/u''	888.9/907.5	Ce 3d ⁹ 4f ¹ O 2p ⁵	16	
	v'''/u'''	898.2/916.8	Ce 3d ⁹ 4f ⁰ O 2p ⁶	28	
Ce³⁺	v ⁰ /u ⁰	880.5/898.8	Ce 3d ⁹ 4f ² O 2p ⁵	0	20
	v'/u'	885.7/904.1	Ce 3d ⁹ 4f ¹ O 2p ⁶	20	

parameters that need to be controlled in order to perform good fits with physically meaningful parameters. Figure 2(a) and (b) show the detailed Ce3d XPS spectra of the sample annealed at 1000°C obtained by PHI 5000 and PHI 5400 respectively. The spectra were fitted with 10 peaks and the FWHM of all the peaks was kept the same for each fit. The peaks positions and the spin-orbit splitting agree well with the literature [5] and the intensity ratio between 3d_{5/2} and 3d_{3/2} was taken as 3:2 [6]. Six peaks labelled as v/u, v''/u'' and v'''/u''' referring to three doublets of the spin-orbit split components are attributed to Ce⁴⁺ final states. The high binding energy doublet v'''/u''' at 898.2 and 916.8 eV are attributed to the final state of Ce 3d⁹4f⁰ O 2p⁶, doublet v''/u'' at 888.9 and 907.5 eV are attributed to the state of Ce 3d⁹4f¹ O 2p⁵, and doublet v/u at 882.3 and 901.0 eV correspond to the state of Ce 3d⁹4f² O 2p⁴. The other four peaks labelled as v⁰/u⁰ and v'/u' referring to two doublets of the spin-orbit split components are attributed to Ce³⁺ final states. The doublet v'/u' at 885.7 and 904.1 eV are corresponding to the final state of Ce 3d⁹4f¹ O 2p⁶ and the doublet v⁰/u⁰ at 880.5 and 898.8 eV are corresponding to the final state of Ce 3d⁹4f² O 2p⁵. Table 1 lists the fit parameters obtained from the spectra of the PHI 5000. The peak area percentage can be used to determine the relative concentrations [6]. From the table the relative total concentration of the Ce⁴⁺ is 80% while that of the Ce³⁺ is 20%. From the PHI 5400 spectrometer, the calculated relative concentrations of Ce⁴⁺ and Ce³⁺ are 75% and 25% respectively. The different values given by the two spectrometers can be taken as an indication of the accuracy of the technique. Figure 3(a) and (b) shows the Ce3d XPS spectra of the reduced sample obtained by the PHI 5000 and PHI 5400 respectively. The Ce⁴⁺ u''' characteristic peak has almost disappeared indicating that the sample contains less Ce⁴⁺. The spectra can be fitted with the

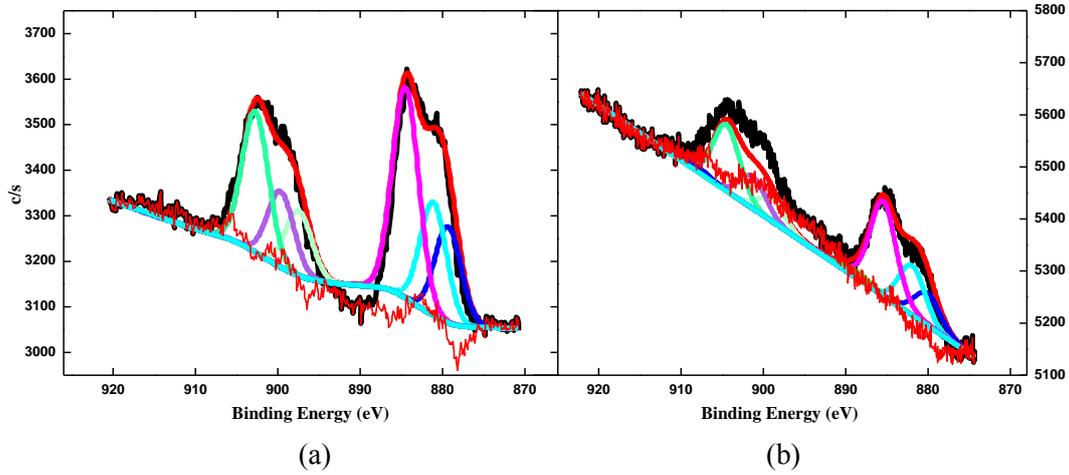


Figure 3. Ce3d XPS spectra of the reduced sample obtained with the (a) PHI 5000 and (b) PHI 5400 XPS systems.

Table 2. Fit parameter of the reduced sample.

ion	$3d_{5/2}/3d_{3/2}$	pos	final state	%area	%total
Ce^{4+}	v/u	882.3/901.0	Ce $3d^9 4f^2 O 2p^4$	27	27
	v"/u"	888.9/907.5	Ce $3d^9 4f^1 O 2p^5$	0	
	v"/u"	898.2 /916.8	Ce $3d^9 4f^0 O 2p^6$	0	
Ce^{3+}	v ⁰ /u ⁰	880.5/898.8	Ce $3d^9 4f^2 O 2p^5$	23	73
	v'/u'	885.7/904.1	Ce $3d^9 4f^1 O 2p^6$	50	

four peaks v⁰/u⁰ and v'/u' of the Ce³⁺ components, in addition of the doublet v/u peaks of Ce⁴⁺ in the valley between (v⁰ and v') and (u⁰ and u'). Table 2 lists the fit parameters for the spectra obtained by the PHI 5000 from the reduced sample. The total relative concentration of the Ce³⁺ is 73% which compares well with the 71% measured by the PHI 5400. There were some difficulties to fit these spectra. The software can not subtract the background well in the spectra obtained by PHI 5000, using either the Shirley or iterated Shirley algorithms. While the background was subtracted successfully in the spectra obtained by PHI 5400, the two separate bands could not fit well simultaneously without relaxing the physically important constraints. Ce3d XPS spectra and their fitting obviously show that reducing the sample with hydrogen can improve the Ce³⁺ concentration.

3.2. Photoluminescence and UV-vis spectroscopy

Figure 4(a) shows the PL of the reduced and annealed samples. The sample which was annealed in air does not show significant emission, while the reduced one exhibits a high intensity emission. The sample annealed in air may contain more Ce⁴⁺ which is optically inactive [7]. A significant PL emission is observed in the reduced sample which may contain more Ce³⁺ rather than Ce⁴⁺ and significant PL emission observed. These results are consistent with the XPS measurements done on the two samples. Figure 4(b) shows the reflectance spectra done on the annealed and the reduced samples. The optical reflectance profile from the annealed sample exhibits a wide absorption peak which corresponds to Ce⁴⁺ ion absorption due to charge transfer from O²⁻ to Ce⁴⁺ [8]. In the reduced sample an absorption peak appeared at around 338 nm, which corresponds to the 4f to 5d transition of Ce³⁺ [9,10].

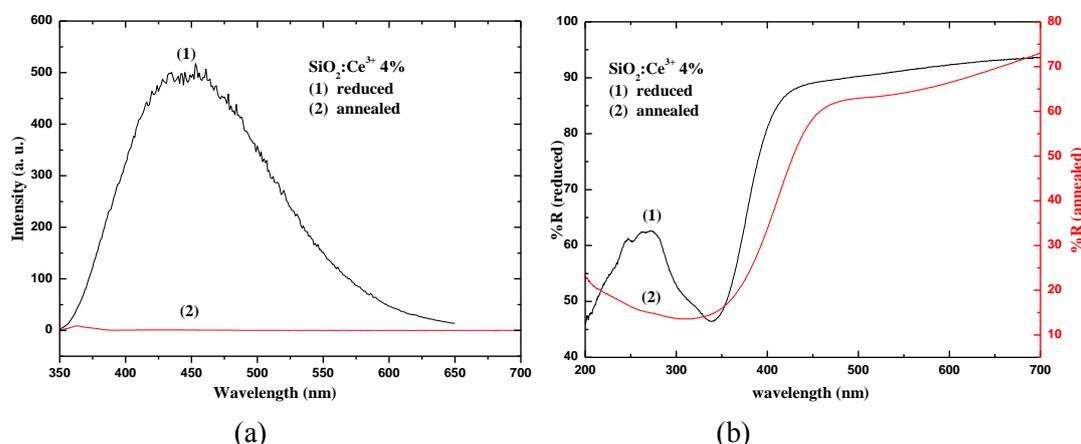


Figure 4. (a) Photoluminescence and (b) diffuse reflectance of reduced and annealed samples

4. Conclusion

Ce ions were successfully incorporated into SiO₂ by the sol-gel process. Ce 3d XPS spectra analysis indicates that the concentration of the Ce³⁺ was increased in the reduced sample. This is in contrast to other published results [10] where samples subjected to rapid thermal annealing using an oxidising oxygen-hydrogen flame exhibited an increase in luminescence despite indications that the Ce⁴⁺ concentration had increased. The reduced sample shows a high intensity PL emission compared to the annealed sample. UV-vis spectroscopy done on the reduced sample shows an absorption peak associated with the Ce³⁺ ion while the annealed samples shows an absorption peak associated with the Ce⁴⁺ ion. The photoluminescence and UV-vis spectroscopy results are consistent with the XPS measurements.

Acknowledgments

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