

## Accepted Manuscript

Title: Pr<sup>3+</sup> surface fraction in CePr mixed oxides determined by XPS analysis

Authors: Eduardo Poggio-Fraccari, Graciela Baronetti, Fernando Mariño



PII: S0368-2048(17)30203-7  
DOI: <https://doi.org/10.1016/j.elspec.2017.11.003>  
Reference: ELSPEC 46718

To appear in: *Journal of Electron Spectroscopy and Related Phenomena*

Received date: 20-9-2017  
Revised date: 17-11-2017  
Accepted date: 18-11-2017

Please cite this article as: Eduardo Poggio-Fraccari, Graciela Baronetti, Fernando Mariño, Pr<sup>3+</sup> surface fraction in CePr mixed oxides determined by XPS analysis, *Journal of Electron Spectroscopy and Related Phenomena* <https://doi.org/10.1016/j.elspec.2017.11.003>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Pr<sup>3+</sup> surface fraction in CePr mixed oxides determined by XPS analysis

Eduardo Poggio-Fraccari\*, Graciela Baronetti, Fernando Mariño

ITHES, UBA-CONICET, Pabellón de Industrias, Ciudad Universitaria. (1428) Ciudad Autónoma de Buenos Aires, Argentina.

\*eduardoaristidespf@di.fcen.uba.ar

## Highlights

- Pr 3d XPS spectra of CePr samples were submitted to a deconvolution procedure
- By considering a previous peak assignment, the Pr<sup>3+</sup> surface fraction was obtained
- Pr<sup>3+</sup> surface fraction was higher than Ce<sup>3+</sup>, as it was suspected in previous work

## Abstract

CePr mixed oxides were previously studied as supports for Water Gas Shift catalysts, considering their promising textural and redox properties arising from the presence of a non-stoichiometric oxide. A very small Ce<sup>3+</sup> fraction was observed on those oxides, suggesting that Pr<sup>3+</sup> ion could be responsible for the enhanced activity. Therefore, in-depth XPS analysis is conducted in the present work in order to determine the Pr<sup>3+</sup> fraction by fitting the XPS Pr 3d region. Much higher values of reduced Pr ions than Ce ions were observed, confirming the promoter role of the former.

Keywords: Pr, XPS, oxidation state

## 1. Introduction

Previous studies of CePr mixed oxides for the Water Gas Shift reaction showed an enhanced catalytic activity in samples promoted with Pr, due to a combination of higher surface area and better reducibility [1]. In fact, even a small Pr addition improved sample reducibility and oxygen storage capacity (OSC), both features that are related to the presence of Ce<sup>4+</sup>/Ce<sup>3+</sup> and Pr<sup>4+</sup>/Pr<sup>3+</sup> redox couples. XRD patterns showed that Pr addition expanded the fluorite lattice, by inducing reduction of tetravalent ions, although it was not possible to distinguish between Ce<sup>3+</sup> and Pr<sup>3+</sup>. In line with this observation, Raman spectroscopy and OSC presented evidence of higher concentration of oxygen vacancies in Pr-doped samples. Finally, the theoretical study of density functional theory with Hubbard parameter (DFT+U) suggested that reduction of Pr<sup>4+</sup> was easier than Ce<sup>4+</sup> in these samples [2].

In previous works, XPS spectra of CePr mixed oxides samples were also analyzed. Pr surface content, Ce<sup>4+</sup>/Ce<sup>3+</sup> ratio and a depth analysis were conducted. It was observed that Pr concentration was higher than the expected value, implying surface enrichment in these samples; moreover, the effect was more noticeable as Pr addition increased. Ce<sup>3+</sup> fraction was calculated by fitting the Ce 3d spectrum. It was found that the fraction of cerium reduced ions decreased with Pr content. Besides an angle-variation analysis were also carried out for a bare ceria sample, in order to estimate the Ce<sup>3+</sup> presence depth in CeO<sub>2</sub>. It was concluded that Ce<sup>3+</sup> ions would tend to occupy the first monolayer, suggesting that they are more stable on the surface of the sample. In CePr samples, the promoter surface enrichment displaced Ce ions from the surface to subsurface sites, explaining the lower Ce<sup>3+</sup> ions fraction observed with Pr addition [2]. This suggest that Pr<sup>4+</sup>/Pr<sup>3+</sup> redox couple would be the main factor responsible of surface enhanced redox properties. In contrast to Ce 3d spectrum, which is well known, the Pr spectrum was less studied, which encourage a further analysis.

Early works on XPS spectra of lanthanide compounds (particularly La, Ce and Pr oxides) were focused in many-electron satellite structure for the 3d and 4d ionizations. Burroughs et al reported one of the first XPS spectrum of a praseodymium oxide, the 3d region of  $\text{Pr}_2\text{O}_3$  sample [3]. Afterwards, Sarma and Rao reported an analysis carried out over a series of lanthanide oxides, including  $\text{Pr}_2\text{O}_3$ , and  $\text{PrO}_2$  [4]. Both oxides showed similar spectra, with shoulders at the low energy side of the  $3d_{5/2}$  peaks centered at 935.0 for  $\text{PrO}_2$  and at 932.9 eV for  $\text{Pr}_2\text{O}_3$ . These authors also reported the magnitude of spin-orbit splitting, being 17.8 for  $\text{PrO}_2$  and 20.7 eV for  $\text{Pr}_2\text{O}_3$ . Indeed, both oxides presented very similar features making very complex the identification of peaks corresponding to Pr cations, in case of the simultaneous presence of  $\text{PrO}_2$  and  $\text{Pr}_2\text{O}_3$  in the same sample.

Bianconi et al. conducted a deep analysis of 3d region of some lanthanide oxides, including  $\text{PrO}_2$  [5]. By spectral fitting, in the Pr 3d region (920-970 eV) these authors found three doublets, a shoulder close to 966 eV in the high-energy tail of O 1s Auger peak, and they reported a spin-orbit-splitting energy close to 20.6 eV between  $3d_{5/2}$  and  $3d_{3/2}$  lines [6]. Ogasawara et al. reduced a  $\text{Pr}_6\text{O}_{11}$  compound at 850°C for 20 h in order to obtain a reliable  $\text{Pr}_2\text{O}_3$  sample. In the 3d region two main peaks were observed, at 925 and 945 eV, with two satellites centered at the low energy side of peaks (920 and 940 eV), which were related to  $3d_{5/2}$  and  $3d_{3/2}$  lines respectively [7]. In summary, only a few peak positions are unequivocally accepted, making complex the calculation of  $\text{Pr}^{3+}/\text{Pr}^{4+}$  ratio in the oxides. In fact, the fraction of  $\text{Pr}^{3+}$  ions is seldom estimated and usually Pr reduced ion quantification is performed from the ratio of only one isolated peak to the whole spectrum. An analogue procedure is often employed to determine  $\text{Ce}^{3+}$  fraction, but this method is only recommended if the fraction of reduced ions is higher than 35% [8].

In the present work, an approach to quantify the fraction of  $\text{Pr}^{3+}$  ions by considering all the peaks involved in XPS spectrum is proposed.

## 2. Experimental

CePr mixed oxides samples were the same previously studied in ref. 2, obtained by urea co-precipitation and annealed at 450 °C [2]. Mixed oxides were called CePrX, where X is the percentage atomic ratio (at %) between [Pr] and ([Pr] + [Ce]). XPS measurements were carried out with a multi-technical system (SPECS) equipped with a dual X-ray source of Mg/Al and a hemispheric synthesizer PHOIBOS 150. Spectra were acquired using Al- $K\alpha$  radiation operated at 200 W and 12 kV. The pressure of the chamber was lower than  $10^{-9}$  mbar. The analyzed region was Pr 3d, between 920-990 eV. The binding energies were calibrated using the  $\text{Ce}^{4+}$  ( $u'''$ ) signal at a 916.7 eV as a reference [9]. Background subtraction (Shirley) and peak fitting were performed using a commercial software CasaXPS® v2.3.15.

## 3. Results and Discussion

As it was mentioned above, the surface fraction  $\text{Ce}^{3+}$  ions decreased with Pr incorporation in samples, suggesting that  $\text{Pr}^{3+}$  cations should be responsible for the enhanced redox properties. In order to quantify  $\text{Pr}^{3+}$  fraction in CePr mixed oxides samples, XPS Pr 3d spectra are now analyzed.

Usual reported approaches involve the ratio between one solely isolated peak and the whole spectra. Pajaczkowska et al. determined the presence of trivalent ions in their mixed Sr-Pr-Ga oxide spectra, by the distinct feature presented by  $\text{Pr}^{4+}$  close to 965 eV [10]. Often, this peak is used to identify the  $\text{Pr}^{4+}$  oxidation state [11], in a similar way as  $u'''$  character is used to quantify  $\text{Ce}^{3+}$  fraction [12]. However, some authors reported that the 965 eV peak might be partially overlapped with the oxygen

KLL Auger peak hindering the determination [6,13]. As an alternative, Aragón et al. proposed the application of the intensities of the main peaks of  $\text{Pr}_2\text{O}_3$  and  $\text{PrO}_2$  compounds in  $3d_{5/2}$  lines between 933.2-933.9 eV and 935-936 eV respectively [13]. Sinev et al. reported a fit of Pr 3d spectrum including seven peaks, but only two of them were used to determine  $\text{Pr}^{3+}$  surface fraction [14]. Borchert et al. followed the latter method for several samples, including one of  $\text{Pr}_6\text{O}_{11}$ , and found a good agreement with the theoretical composition ( $\text{PrO}_{1.875}$  stoichiometry was experimentally obtained, instead of the theoretical  $\text{PrO}_{1.833}$ ) [15]. However, to the best of our knowledge, a quantification of  $\text{Pr}^{3+}$  fitting all peaks as is usually carried out for the determination of  $\text{Ce}^{3+}$  in pure ceria samples was not previously attempted [2,16]. This is probably due to the similarity of the features of both Pr oxides ( $\text{PrO}_2$  and  $\text{Pr}_2\text{O}_3$ ), the closeness of peaks, and doublet splitting [4,11,17]. In fact, some authors limited their analysis to the comparison of Pr 3d spectra of several samples in order to estimate  $\text{Pr}^{3+}/\text{Pr}^{4+}$  presence [18,19].

A two-step procedure is proposed: first, we identify  $\text{Pr}^{4+}$  and  $\text{Pr}^{3+}$  peaks; and second, we fit the whole spectrum considering the simultaneous presence of both ions. Afterwards, we calculate  $\text{Pr}^{3+}$  surface fraction from the ratio of their characteristic peaks intensities to the whole spectrum. By the inspection of several published works, it arises that only a few characteristics peaks (listed in Table 1) are reported.

Table 1: summary of peak assignment for  $\text{Pr}^{3+}$  and  $\text{Pr}^{4+}$  ions in Pr-containing samples

$\text{Pr}^{4+}$ peaks (eV)		$\text{Pr}^{3+}$ peaks (eV)		Peak positions references
$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	
	935.0		932.9	[4]
966	929; 933; 946	940; 945	920; 925	[6] <sup>a</sup> [7] <sup>a</sup>
967	935-936		933.2-933.9	[13]
966.1-966.8	945.8-946.4			[15]
953.5; 966.9	933.9	949.8; 973.2	929.5	[18]
	935.5		929.1; 933.4	[19]
953.5; 966.4	933.9	949.8; 973.2	929.5	[20]
		955	935	[21]
966-968		953	933	[22]
		953.85	933.75	[23]
967				[24]

<sup>a</sup>: values read from figures

There is a consensus that the peak close to 966 eV, and its spin-orbit partner close to 946 eV, are related to  $\text{Pr}^{4+}$  ion [6,15,18,20,22,24]. Moreover according to some authors, the peak centered between 934-936 eV is associated to  $\text{Pr}^{4+}$  [6,13,18,20]. Peak located between 933 and 934 eV is associated to the presence of  $\text{Pr}^{3+}$  [13,19,22-23], as its partner reported at 953-954 eV [22-23]. Finally, the peak usually observed at the lower end of the binding energy of 3d spectra, close to 929 eV, is associated to  $\text{Pr}^{3+}$  ion [18-20]. Besides, in this binding energy range 928-931 eV, it was also reported the presence of a  $\text{Pr}^{4+}$  peak [6] which was taken into account in the spectrum fitting procedure.

It is worth to mention that  $3d_{5/2}$  spectra for  $\text{CeO}_2$  and  $\text{PrO}_2$  present similar features. Bianconi et al. proposed to assign the peaks identified in Pr  $3d_{5/2}$  core level spectrum of  $\text{PrO}_2$  to the same electronic configuration found for peaks in Ce  $3d_{5/2}$  of ceria, which was confirmed by the analysis of Pr  $3d_{5/2}$

XAS spectrum. Similar conclusions were obtained by the comparison of the spectra of Pr  $3d_{3/2}$  and Ce  $3d_{3/2}$  core levels [5,6]. Therefore, data presented in Table 1 and the mentioned similarity between CeO<sub>2</sub> and PrO<sub>2</sub> 3d spectra would suggest that three doublets (six peaks) are expected for Pr<sup>4+</sup> (hereafter called a'''-b''', a''-b'', a-b), and two doublets (four peaks) are expected for Pr<sup>3+</sup> (hereafter named a'-b', a<sub>o</sub>-b<sub>o</sub>).

Several features were taken into account in Pr 3d spectra fitting procedure for the three samples studied. The peaks intensities in same doublet were fitted in order to satisfy a 2:3 ratio corresponding to  $3d_{3/2}:3d_{5/2}$  signals respectively. It was considered a similar FWHM for peaks belonging to the same doublet, with values constrained to a difference lower than 15%. Besides, the peaks positions along samples were fitted to be the same in a 0.3 eV gap. In case of a'''-b''' doublet, it were allowed larger constrains due to a''' was mounted on low BE side of the strong O KLL Auger peak, hindering the fitting procedure [15]. Then, a maximum difference in FWHM close to 30 % was allowed, and the peak positions (a''' and b''') along samples, were constrained to be same with 0.6 eV range.

From the fitting procedure, doublet splitting close to the values reported in literature for PrO<sub>2</sub> [6] and Pr<sub>2</sub>O<sub>3</sub> [5] were found. Results for CePr50, CePr15 and CePr5 samples are shown in Tables 2, 3 and 4, respectively. As it can be seen, similar peak features are observed for CePr50 and CePr15 mixed oxides. Pr 3d spectrum for CePr5 sample was quite noisy due to the low promoter content, hindering the fitting procedure and this result should be taken as a roughly approximation.

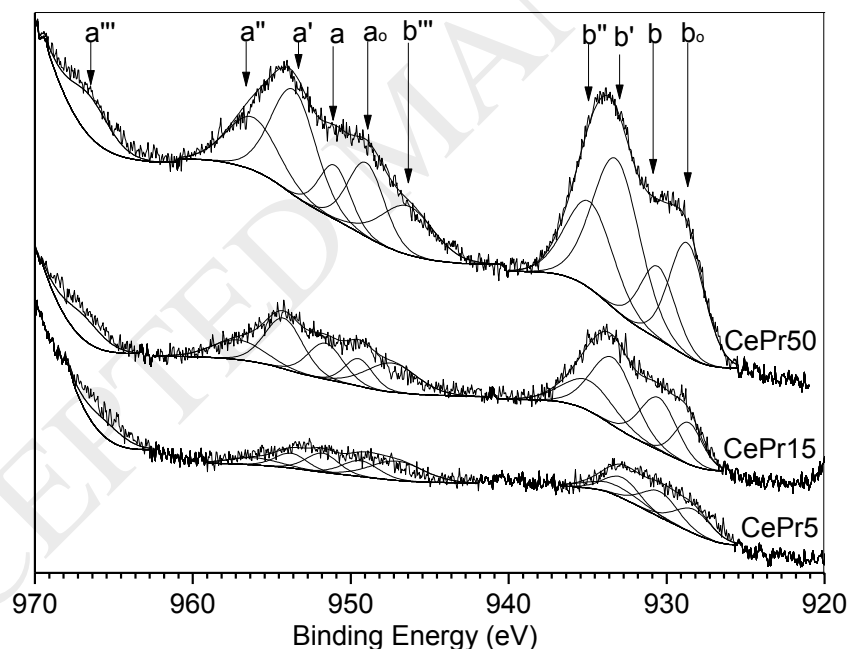


Figure 1: Pr 3d region fitted spectra of CePr mixed oxides.

Table 2: Peaks fitting features of CePr50 (doublets a'-b' and a<sub>o</sub>-b<sub>o</sub> were assigned to Pr<sup>3+</sup>)

Peak	Position (eV)	FWHM (eV)	Intensity (a.u.)	Doublet splitting (eV)	Ref.
a'''	966.7	3.0	59	20.5	[6,15,18,20,22,24]
b'''	946.3	3.9	89		[6,15]

a''	956.0	3.8	94	21.1	This work [6,13,18,20]
b''	934.9	3.5	141		
a'	953.6	3.2	164	20.4	[21-23] [13,19,22-24]
b'	933.2	3.5	246		
a	951.0	2.3	58	20.5	This work [5]
b	930.6	2.6	87		
ao	949.0	2.7	93	20.3	This work [18-20]
bo	928.7	2.7	140		

Table 3: Peaks fitting features of CePr15 (doublets a'-b' and ao-bo were assigned to Pr<sup>3+</sup>)

Peak	Position (eV)	FWHM (eV)	Intensity (a.u.)	Doublet splitting (eV)	Ref.
a'''	966.9	3.1	36	20.0	[6,15,18,20,22,24]
b'''	946.9	3.8	54		
a''	955.7	3.8	33	20.9	This work [6,13,18,20]
b''	934.8	3.5	50		
a'	953.8	2.8	61	20.6	[21-23] [13,19,22-24]
b'	933.2	2.9	91		
a	951.1	2.6	41	20.5	This work [5]
b	930.6	2.7	62		
ao	949.1	2.1	30	20.5	This work [18-20]
bo	928.6	2.1	45		

Table 4: Peaks fitting features of CePr5 (doublets a'-b' and ao-bo were assigned to Pr<sup>3+</sup>)

Peak	Position (eV)	FWHM (eV)	Intensity (a.u.)	Doublet splitting (eV)	Ref.
a'''	965.7	3.0	24	19.8	[6,15,18,20,22,24]
b'''	946.6	3.9	36		
a''	958.8	3.7	15	22.0	This work [6,13,18,20]
b''	933.8	4.0	22		
a'	953.6	2.3	20	20.6	[21-23] [13,19,22-24]
b'	933.0	2.8	30		
a	951.3	2.4	21	20.8	This work [5]
b	930.5	2.7	31		
ao	949.1	2.6	19	20.4	This work

Results of the fitting procedure are summarized in Table 5 where it can be readily seen that the  $\text{Pr}^{3+}$  surface fraction increases with promoter content, with the  $\text{Pr}^{3+}$  values much higher than those of  $\text{Ce}^{3+}$  calculated for these samples [2]. This finding is in agreement with the previously observed Pr surface enrichment in CePr mixed oxides, where promoter addition displace Ce ions to the bulk.

Table 5: Surface fraction of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  by XPS spectra fitting

Sample	$\text{Pr}^{3+}$ surface fraction (%)	$\text{Ce}^{3+}$ surface fraction (%)*
CePr50	55	2.2
CePr15	45	3.1
CePr5	39	4.9

\*taken from [2]

#### 4. Conclusions

An in-depth XPS analysis in order to determine the presence of  $\text{Pr}^{3+}$  surface fraction was carried out for CePr mixed oxides. By fitting of Pr 3d spectra in several samples, a much higher surface content of  $\text{Pr}^{3+}$  relative to  $\text{Ce}^{3+}$  ions was observed. This finding is in agreement with observations made in one of our previous papers [2], where it was suggested that surface  $\text{Pr}^{3+}$  ions were the main factor responsible for the enhanced redox properties of cerium oxide samples promoted with praseodymium.

#### 5. Acknowledgments

We thank to UBA and CONICET for their financial support and to ANPCyT for the purchase of the SPECS multitechnique analysis instrument (PME8-2003).

#### 6. References

- [1] E. Poggio-Fraccari, F. Mariño, M. Laborde, G. Baronetti, Copper and nickel catalysts supported on praseodymium-doped ceria (PDC) for the water-gas shift reaction, *Appl. Catal. A: Gen.*, 460 (2013) 15-20.
- [2] E. Poggio-Fraccari, B. Irigoyen, G. Baronetti, F. Mariño, Ce-Pr mixed oxides as active supports for Water-gas Shift reaction: Experimental and density functional theory characterization, *Appl. Catal. A: Gen.*, 485 (2014) 123-132.
- [3] P. Burroughs, A. Hamnett, A. Orchard, G. Thornton, Satellite structure in the X-ray photoelectron spectra of some binary and mixed oxides of lanthanum and Cerium, *J. Chem. Soc. Dalton Trans.*, 17, (1976) 1686-1698.
- [4] D. Sarma, C. Rao, XPS Studies of Oxides of Second- and Third Row Transition Metals Including Rare Earths, *J. Electron Spec. Rel. Phenom.*, 20 (1980) 25-45.
- [5] A. Bianconi, T. Miyahara, A. Kotani, Y. Kitajima, T. Yokoyama, H. Kuroda, H. Kuroda, M. Funabashi, H. Arai, T. Ohta, Correlation satellites in deep metal 3p core x-ray photoemission of tetravalent oxides  $\text{MO}_2$  ( $\text{M} = \text{Ce, Pr, Tb, Hf}$ ) and of  $\text{LaF}_3$ , *Phys. Rev. B*, 39 (1989) 3380-3385.

- [6] A. Bianconi, A. Kotani, K. Okada, R. Giorgi, A. Gargano, A. Marcelli, T. Miyahara, Many-body effects in praseodymium core-level spectroscopies of PrO<sub>2</sub>, *Phys. Rev. B*, 38 (1988) 3433-3437.
- [7] H. Ogasawara, A. Kotani, R. Potze, R. Sawatzky, B. Thole, Praseodymium 3d- and 4d- core photoemission spectra of Pr<sub>2</sub>O<sub>3</sub>, *Phys. Rev. B*, 44 (1991) 5465-5469.
- [8] A. Kotani, T. Jo, J. Parlebas, Many-body effects in core-level spectroscopy of rare-earths compounds, 37 (1988) 37-85.
- [9] M. Romeo, K. Bak, J. El Fallah, F. Le Normand, L. Hilaire, XPS Study of the Reduction of Cerium Dioxide. *Surf. and Int. Sci.*, 20 (1993) 508-512.
- [10] A. Pajaczkowska, A. Novoselov, D Klimm, E Talik, R. Uecker, Does Valency of Pr Ions Influence Color of SrPrGaO<sub>4</sub> Single Crystals? *Cryst. Growth Des.*, 2 (2004) 497-501.
- [11] S. Lutkehoff, M. Neumann, A. Slebarski, 3d and 4d x-ray-photoelectronspectra of Pr under gradual oxidation, *Phys. Rev. B*, 52 (1995) 13808-13811.
- [12] J. Shyu, W. Weber, H. Gandhi, Surface characterization of alumina-supported ceria, *J. Phys. Chem.*, 92 (1988) 4964-4970.
- [13] F. Aragón, I. Gonzalez, J. Coaquira, P. Hidalgo, F. Brito, J. Ardisson, W. Macedo, P. Morais, Structural and Surface Study of Praseodymium-Doped SnO<sub>2</sub> Nanoparticles Prepared by the Polymeric Precursor Method, *J. Phys. Chem. C*, 119 (2015) 8711-8717.
- [14] M. Sinev, G. Graham, L. Haack, M. Shelef, Kinetic and structural studies of oxygen availability of the mixed oxides Pr<sub>1-x</sub>M<sub>x</sub>O<sub>y</sub> (M = Ce, Zr), *J. Mater. Res.*, 11 (1996) 1960-1971.
- [15] H. Borchert, Y. Frolova, V. Kaichev, I. Proskin, A. Sadykov, Electronic and Chemical Properties of Nanostructured Cerium Dioxide Doped with Praseodymium, *J. Phys. Chem. B*, 109 (2005) 5728-5738
- [16] E. Poggio, M. Jobbágy, M. Moreno, M. Laborde, F. Mariño, G. Baronetti, Influence of the calcination temperature on the structure and reducibility of nanoceria obtained from crystalline Ce(OH)CO<sub>3</sub> precursor, *Int. J. Hydrogen Energ.*, 36 (2011) 15899-15905.
- [17] A. Schefer, S. Gevers, V. Zielasek, T. Schroeder, J. Falta, J. Wollschläger, M. Bäumer, Photoemission study of praseodymia in its highest oxidation state: The necessity of in situ plasma treatment. *J. Phys. Chem.* 134 (2011) 54701-54708.
- [18] H. Dai, C. Ng, C. Au, SrCl<sub>2</sub>-Promoted REO<sub>x</sub> (RE = Ce, Pr, Tb) Catalysts for the Selective Oxidation of Ethane: A Study on Performance and Defect Structures for Ethene Formation, *J. Catal.*, 199 (2001) 177-192.
- [19] A. Mekki, K. Ziq, D. Holland, C. McConville, Magnetic properties of praseodymium ions in Na<sub>2</sub>O-Pr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses, *J. Magn. Mater.*, 260 (2003) 60-69.
- [20] H. He, H. Dai, K. Wong, C. Au, RE<sub>0.6</sub>Zr<sub>0.4-x</sub>Y<sub>x</sub>O<sub>2</sub> (RE=Ce, Pr; x=0, 0.05) solid solutions: an investigation on defective structure, oxygen mobility, oxygen storage capacity, and redox properties, *Appl. Catal. A: Gen.*, 251 (2003) 61-74.
- [21] A. Kitamura, Y. Noguchi, M. Miyayama, Polarization properties of praseodymium-modified SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramics and thin films prepared by sol-gel method, *Mat. Lett.* 58 (2004) 1815-1818.
- [22] Z. Song, W. Liu, H. Nishiguchi, A. Takami, K. Nagaoka, Y. Takita, The Pr promotion effect on oxygen storage capacity of Ce-Pr oxides studied using a TAP reactor, *Appl. Catal. A: Gen.*, 329 (2007) 86-92.



[23] Y. Zhang, K. Han, X. Yin, Z. Fang, Z. Xu, W. Zhu, Synthesis and characterization of single-crystalline  $\text{PrCO}_3\text{OH}$  dodecahedral microrods and its thermal conversion to  $\text{Pr}_6\text{O}_{11}$ , *J. Crys. Growth*, 311 (2009) 3383-3888.

[24] C. Narula, L. Haack, W. Chun, W. Jen, W. Graham, Single-Phase  $\text{PrO}_y\text{-ZrO}_2$  Materials and Their Oxygen Storage Capacity: A Comparison with Single-Phase  $\text{CeO}_2\text{-ZrO}_2$ ,  $\text{PrO}_y\text{-CeO}_2$ , and  $\text{PrO}_y\text{-CeO}_2\text{-ZrO}_2$  Materials, *J. Phys. Chem. B*, 103 (1999) 3634-3639.

ACCEPTED MANUSCRIPT