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Valence and Localization of Praseodymium in Pr-Doped Zircon

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The valence and localization of the praseodymium species in the zircon matrix of Pr-doped zircon powders obtained by calcination of the metal oxides in the presence of fluxes are analyzed through the use of X-ray diffraction and XAS (XANES and EXAFS) spectroscopy. It is concluded that the Pr cations present a tetravalent state and form a solid solution with the zircon lattice, in which they occupy the triangular dodecahedral positions of Zr. An enrichment of Pr(IV) ions in the outer layers of the pigment particles was also observed by XPS, indicating that they are heterogeneously distributed inside the zircon grains. © **1998 Academic Press**

INTRODUCTION

Pr-doped zircon (Pr-$ZrSiO_4$) powders find important applications in the ceramic industry as a yellow pigment (1, 2), which is one of the market leaders in the high temperature color range because of its high tinctorial strength and superior chemical stability during firing. Since its discovery in the late 1950s, much work has been conducted to improve the optical properties of this pigment (2–5); however, little progress has been made to increase the knowledge of the nature and localization of the praseodymium species in the zircon matrix. Thus, although it has been traditionally assumed that the Pr cations form a solid solution with the zircon lattice, which was recently confirmed by measurements of the zircon unit cell parameters (6), their valence (3+ or 4+) has not been well established (6, 7). The position that these Pr ions occupy in the zircon lattice has not been clarified, either. In general, it has been postulated that Pr is located at the dodecahedral positions of Zr (6, 8). However, recent theoretical studies based on lattice energy calculations have reported that the substitution at the tetrahedral position of Si is also energetically favored (7).

The aim of this work is to investigate the oxidation state and the localization of the Pr species in Pr-doped zircon pigments mainly through the use of X-ray absorption (XANES and EXAFS) spectroscopy, which affords structural and electronic information on a selected atom, even in the absence of large-range order. X-ray photoelectron spectroscopy (XPS) was also used to gain additional information on the distribution of the Pr ions inside the Pr-doped zircon particles. In a recent paper we have shown that these techniques are suitable to determine the environment of other doping cations in similar systems such as V-doped zircon (9).

EXPERIMENTAL

The Pr-doped zircon sample was prepared by heating at 1020°C for 3 h an equimolecular mixture of ZrO_2 and SiO_2 in the presence of Pr_6O_{11} (Pr/Zr atomic ratio = 0.04) and alkaline halides (NaF and NaCl) used as fluxing agents (10). Chemical analysis of this powder carried out by ICP gave a Si/Zr atomic ratio of 0.96 and a Pr/$ZrSiO_4$ mole ratio of 0.04. According to X-ray diffraction data (not shown), this sample mainly consisted of zircon. The only additional phase detected was a small amount of monoclinic ZrO_2 due, at least in part, to the little excess of Zr revealed by the measured Si/Zr ratio, which was slightly lower than that required for stoichiometric zircon.

The measurement of the unit cell parameters of zircon in the Pr-$ZrSiO_4$ sample was carried out by a Rietveld analysis of the X-ray diffraction data, using the method and the experimental conditions described in Ref. (11).

In order to analyze the XAS spectra, Pr(III) acetate and Pr_6O_{11} were used as reference compounds for the trivalent and tetravalent state of Pr, respectively. Notice that in the latter, two different oxidation states of Pr (3+ and 4+) are actually present, although it contains a higher amount ($\sim$67%) of Pr^{4+}. XAS spectra were collected at the LURE synchrotron facility in Orsay, using synchrotron radiation from the DCI storage ring running at 1.85 GeV with an average current of 250 mA. The XAS data were taken at room temperature in the transmission mode using two ion chambers containing a He–Ne mixture as detectors. Monochromatization of the light was done with a double-crystal monochromator [Si(111)]. For measurements, the Pr-doped

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zircon sample and the references, Pr(III) acetate and Pr_6O_{11}, were dispersed in boron nitride in order to optimize the absorptions. Three or four scans were collected for each sample and averaged. The spectra were analyzed with the software package developed by Bonin *et al.* (12). Because of the presence of the Pr L_{II} edge over 6410 eV, only the EXAFS data between 3 and 10 $Å^{-1}$ were extracted and analyzed. These data were k^3 weighted and Fourier transformed over a Kaiser window. The coordination numbers (*CN*), interatomic distances (*R*), and Debye–Waller values ($\Delta\sigma$) were extracted by a least-squares fitting procedure that make use of the theoretical phases and amplitudes determined with the program FEFF6 (13), which were previously tested with the Pr(III) acetate reference, where the Pr coordination is well known.

The XPS spectrum was measured with a VG Escalab 210 model using the Mg$K\alpha$ excitation source. Calibration of the spectra was done at the C 1*s* peak of surface contamination taken at 284.6 eV. Atomic percentages of the elements were calculated from the peaks areas after background subtraction (Shirley background). The areas were referred to the sensitivity factors of the elements as supplied by the instrument manufacturers.

RESULTS AND DISCUSSION

The unit cell parameters of zircon in the Pr-$ZrSiO_4$ sample showed a cell expansion when compared with undoped zircon (Table 1) indicating the formation of a Pr/zircon solid solution in agreement with previous reported results (6).

The valence of the Pr cations was determined from the analysis of the L_{III} edge XANES spectrum of the sample, which is shown in Fig. 1 along with those obtained for Pr(III) acetate and Pr_6O_{11} chosen for comparison. As can be seen, while Pr(III) acetate presents a single white line maximum (A) at 5954 eV, due to a $2p \rightarrow 6d$ transition (9), two white lines (at 5954 (B) and at 5965 eV (C)) are detected for the Pr-doped zircon sample. As previously reported by Bianconi *et al.* (14), these two peaks are characteristic of Pr(IV) cations and have been explained as a configuration interaction due to a large mixing between localized 4*f* levels of Pr and more delocalized O 2*p* levels. The appearance of the same peaks in the XANES spectrum of Pr_6O_{11} (Fig. 1) is consistent with the presence of ~67 % of Pr^{4+} in this oxide. In this case, the line at 5954 eV has contribution from the Pr^{4+} ions as well as from the Pr^{3+} ions, whereas the line at 5965 eV is only due to Pr^{4+}. It should be noted that the intensity of the two white lines also depends on the metal–ligand bonding. Therefore, the presence of a certain amount of Pr^{3+} in the Pr-doped zircon sample cannot be excluded from the direct comparison between the relative intensity of these two features observed in the XANES spectra of this sample and Pr_6O_{11}. Nevertheless, the low relative intensity of the line at 5954 eV observed for the Pr-doped zircon powder suggests that a high amount of Pr ions in this sample is in the tetravalent state.

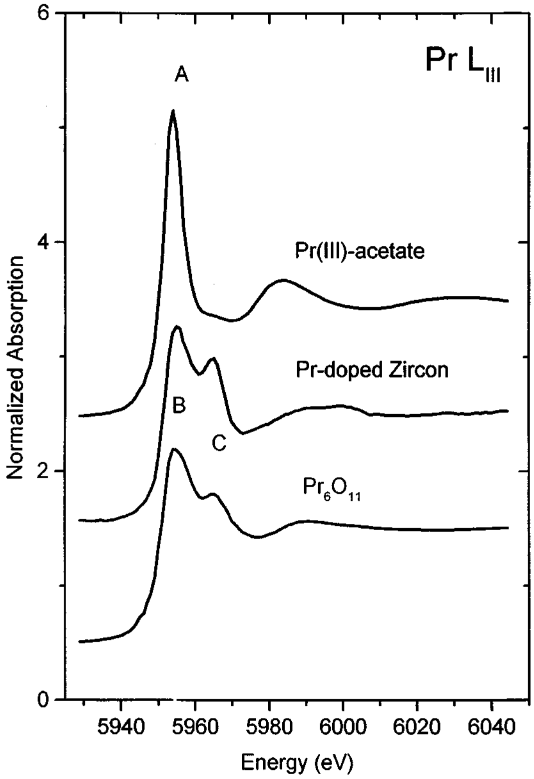

FIG. 1. Pr L_{III} edge XANES spectra of the Pr-doped zircon sample, Pr(III) acetate, and Pr_6O_{11}.

TABLE 1

Unit Cell Parameters (a, c), Unit Cell Volume (V), Residual Structure Factor (R_f), and Residual Bragg Factor (R_b) Measured for the Pr-Doped Zircon Sample and for a Zircon Blank[a]

Sample	a (Å)	c (Å)	V ($Å^3$)	R_f	R_b
Zircon	6.6046 (6) 5.4308 (3)[b]	5.9798 (5)	260.84 (7)	5.01 4.57[b]	11.3 5.94[b]
Pr-zircon	6.616 (2) 5.4314 (8)[b]	5.987 (2)	262.1 (2)	10.2 10.1[b]	17.3 14.4[b]

[a] Parameters measured for a silicon standard added to the samples are also included. Errors are given in parentheses.

[b] Data referred to the silicon standard having an a parameter of 5.4309 Å.

The elucidation of the position occupied by the Pr cations into the zircon lattice was carried out by the analysis of the EXAFS region of the XAS spectra. The Fourier transform functions for the Pr-doped zircon sample, Pr(III) acetate, and Pr_6O_{11} are presented in Fig. 2. In the case of Pr_6O_{11}, the Pr^{3+} and Pr^{4+} cations have a very heterogeneous and distorted environment (15) with a first coordination shell of

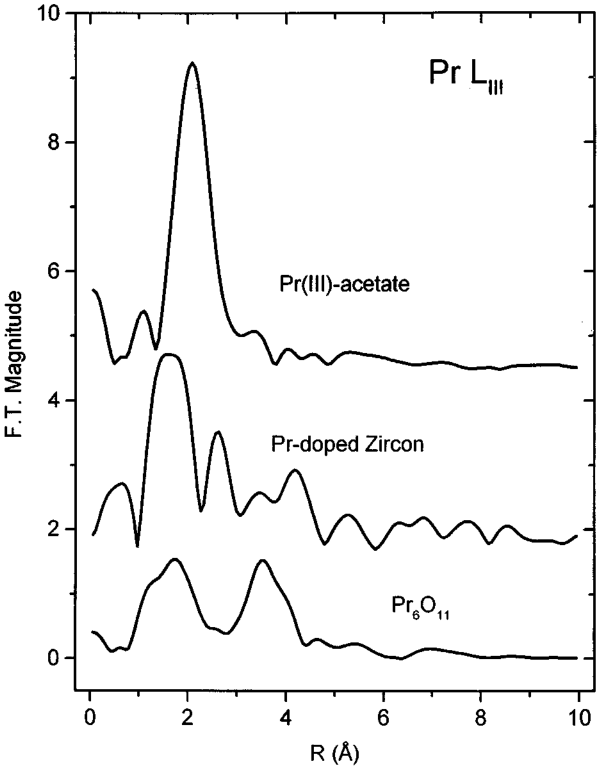

FIG. 2. FT functions obtained from the Pr L_{III} EXAFS oscillations for the Pr-doped zircon sample, Pr(III) acetate, and Pr_6O_{11}.

6–7 oxygen atoms at distances ranging from 2.19 to 2.59 Å. In agreement, the first peak of the FT is broad and has a low intensity, likely due to a self-cancellation between the different Pr–O contributions to the peak. In the Pr(III) acetate (16), the Pr^{3+} are coordinated with eight oxygen atoms at distances between 2.40 and 2.60 Å, for which the peak is better defined and has a higher intensity than in Pr_6O_{11}. In any case, owing to the complex crystalline structure of these compounds, the quantitative analysis of the atomic environment is not straightforward. In the case of the Pr-doped zircon sample in which according to X-ray diffraction a solid solution between the Pr cations and the zircon lattice is present, the quantitative analysis of the EXAFS spectrum was carried out by initially considering two possible environments for the Pr cations, the tetrahedral positions of Si^{4+} (coordination number = 4, with Si–O distances of 1.622 Å) and the triangular dodecahedral positions of Zr^{4+} (coordination number = 8, with four O atoms at a Zr–O distance of 2.268 Å and four O atoms at 2.131 Å) in the zircon lattice (17). The experimental EXAFS oscillations and the theoretical ones obtained by fitting with the parameters included in Table 2 are shown in Fig. 3. This quantitative analysis, corresponding to peaks in FT between 1.0 and 3.1 Å, gives coordination numbers for Pr similar to those of the Zr^{4+} cations in the zircon network (17), i.e. eight oxygen atoms, four of them at 2.13 Å and the remaining ones at 2.30 Å (at 2.13 and 2.268 Å for Zr), and 1.7 silicon atoms at 2.99 Å (2 atoms at 2.99 for Zr). These results clearly show that there is only one type of Pr cations (Pr^{4+} according to the XANES spectrum) in the Pr-doped zircon sample, being located in the triangular dodecahedral position of the zircon network, substituting for Zr^{4+}. This finding excludes the possible presence of an appreciable amount of Pr^{3+} in the sample which should give rise to additional Pr environments (coordination numbers and Pr–O distances).

TABLE 2
Best Fitting Parameters of the Pr L_{III} Edge EXAFS Spectrum of the Pr-Doped Zircon Sample[a]

	R (Å)	$\Delta\sigma^2$ ($Å^2 \times 10^{-3}$)	*CN*
$Pr–O_1$	2.12	0.625	4.0
$Pr–O_2$	2.30	0.625	4.0
Pr–Si	2.99	0.00	1.7

[a] *R*, interatomic distance; $\Delta\sigma^2$, difference in the Debye–Waller factor with respect to the Pr(III) acetate reference; *CN*, coordination number.

Additional information on the distribution of the Pr^{4+} cations in the Pr-doped zircon particles was obtained from the XPS spectrum of the sample. As expected, this spectrum (data not shown) showed bands at 101.2, 182.4, 530.4, and

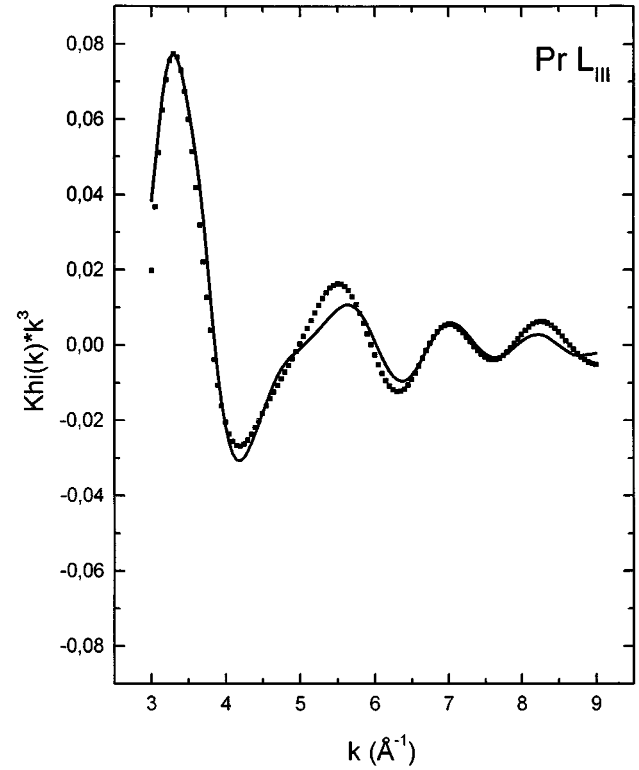

FIG. 3. Inverse Fourier transform (dotted line) and curve obtained by fitting analysis (solid line) of the Pr L_{III} EXAFS spectrum registered for Pr-doped zircon.

933.3 eV corresponding to the Si 2*p*, Zr $3d_{5/2}$, O 1*s*, and Pr $3d_{5/2}$ levels, respectively (18). A band at 1020 eV was also observed due to the 1*s* level of the Na cations associated to the flux agents. The Pr/$ZrSiO_4$ mole ratio obtained from the relative intensity of these bands was much higher (20%) than that of the bulk material (4%) indicating an enrichment of Pr cations in the outer layers of the pigment particles.

In summary, we have unambiguously demonstrated that the Pr cations in Pr-doped zircon pigments present a tetravalent state and form a solid solution with the zircon lattice substituting for Zr at its triangular dodecahedral positions. These cations are not homogeneously distributed in the pigment particles and are preferentially concentrated at their outer layers.

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