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X-ray Photoelectron Spectroscopy Determination of the Ce(III)/Ce(IV) Ratio in Cerium Compounds

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Cerium is the second and most reactive member of the lanthanide series. It is highly electropositive and has a predominantly ionic character due to the low ionization potential for the removal of its three most weakly bound electrons [1]. Ce exhibits two stable oxidation states, the Ce^{3+} and Ce^{4+} ions. The addition of cerium oxide has been found to increase the toughness of ceramic compounds such as zirconium oxide [2]. The Ce(III) to Ce(IV) ratio in the ceramic appears to be of vital importance to the mechanical properties of these materials.

X-ray photoelectron spectroscopy (XPS) is a technique that can be used to measure the oxidation states of species in compounds. For cerium, however, the binding energy shift between Ce(III) and Ce(IV) is too small to be experimentally resolved [3–5]. For this reason, other means of determining the Ce(III)/Ce(IV) ratio from XPS spectra were investigated.

Experimental

$Ce(NO_3)_3 \cdot 6H_2O$ and CeO_2 (anhydrous) were ground to fine powders and mechanically mixed to obtain samples containing mole fractions of 0.0, 0.1, 0.25, 0.4, 0.5, 0.6, 0.75, 0.9 and 1.0 Ce(IV) to Ce(III).

The XPS spectra were recorded using a VG ESCALAB Mk II. Non-monochromatic Mg Kα (1253.6 eV) radiation was sourced from an X-ray gun operated at 15 kV and 20 mA. The base pressure in the analyser was better than 7×10^{-11} mbar, with the samples being cooled to liquid nitrogen temperatures. Spectra were recorded using a constant analyser energy of 50 eV. No electrostatic charge corrections were undertaken as the interpretation did not require accurate peak positions. Linear background subtraction and least-squares fitting procedures were used for the determination of line widths and peak areas.

Results and Discussion

The Ce 3d Peaks

It has been shown that the Ce(III) and Ce(IV) satellite structures are due to shake-down (energy-gain), rather then shake-up (energy-loss) processes, and are derived mainly from ligand-to-metal charge-transfer transitions [3]. Nakano *et al.* [4] reported two pairs of peaks in the 3d spectrum for Ce_2O_3, due to the mixed $4f^1$ and $4f^2$ configurations. They also reported three doublets for CeO_2: one due to the $4f^0$ configuration and the other two due to mixed $4f^1$ and $4f^2$ configurations. Kaindl *et al.* [5] reported three doublets for the qualitatively similar CeF_4 compound. Stronger satellite structures in certain cerium compounds indicate a stronger covalency of the compound. In a detailed study of the XPS 3d satellite structures for the lanthanoid oxides, Burroughs *et al.* [3] indicated the existence of four CeO_2 doublets.

The Ce 3d spectra for CeO_2 obtained in this study (see Fig. 1) show remarkable similarity to those of

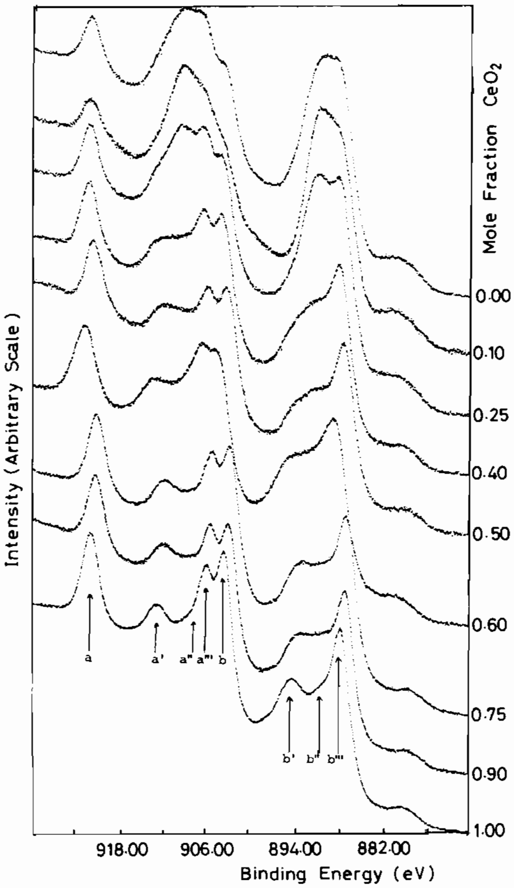

Fig. 1. Ce 3d XPS spectra for the different Ce(III)/Ce(IV) compounds.

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Burroughs. They reported a Ce 3d multiplet splitting of 18.7 eV, compared to the 18.5 eV found in this study. In Fig. 1 the $3d_{5/2}$ peak is designated by a, and its satellites by a′, a″, and a‴. Similarly b, b′, b″ and b‴ are used for the $3d_{3/2}$ peaks.

The two sets of weaker peaks, a′, a″ and b′, b″ are believed to arise either from 3d–4f coupling in the Ce^{4+} ($3d^{-1}$ $4f^1$) final state, or from the production of excited states of the ionized system such as Ce^{4+} ($3d^{-1}$ $5d^1$). The a‴ and b‴ satellites represent the Pr^{V}-like excited state [3].

The 3d spectra of the Ce(III) compounds are not as well resolved as those of the Ce(IV) compounds [3, 4]; however, the core level peaks and satellites compare qualitatively. Quantitative analysis involves peak-fitting routines, the results of which are subjectively influenced.

The Auger Parameter

The modified Auger parameter (α') is defined as the sum of the binding energy of the major photoelectron peak (Ce $3d_{5/2}$) and the kinetic energy of the major Auger peak (Ce_{MNN}) [6]. The broad but well-defined Ce_{MNN} Auger peaks appear at approximately 595 eV binding energy for all the cerium compounds. Due to the fact that the Ce $3d_{5/2}$ peak overlaps with the Ce $3d_{3/2}$ satellites, it was decided to introduce another modification to the Auger parmeter (α'') using the well-resolved Ce $3d_{3/2}$ peak.

$$\alpha'' = KE\,(\text{Auger MNN}) + BE\,(\text{Ce } 3d_{3/2})$$

Figure 2 represents the correlation between the α'' value and Ce(III)/Ce(IV) ratio. A decreasing α'' value with increasing Ce(IV) content is observed.

The Ce 4d Peaks

The satellite structures in the Ce 4d XPS spectra are also due to charge-transfer processes in the final states [3]. CeO_2 shows six bands in its 4d spectrum. Although the satellite structures are complex, the detail for CeO_2 appears parallel to that observed for the 3d spectra [3]. The spectra for CeO_2 obtained in this study closely resemble that observed by Burroughs *et al.* [3]. They concluded that the 4d spectrum consists of four doublets, with an overlap of two pairs of bands. A multiplet splitting of approximately 3.2 eV was reported, while the value observed in this study is 3.25 eV. From Fig. 3 it is clear that the area of the $4d_{3/2}$ increases, whereas that of the $4d_{5/2}$ decreases with increasing Ce(III) content. The

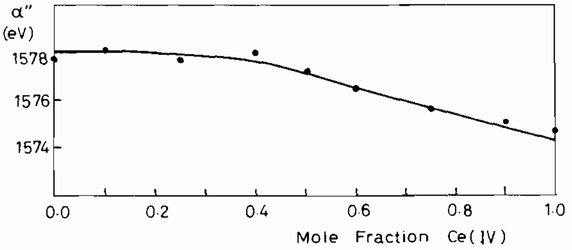

Fig. 2. The modified Auger parameter α'' as a function of the Ce(III)/Ce(IV) ratio.

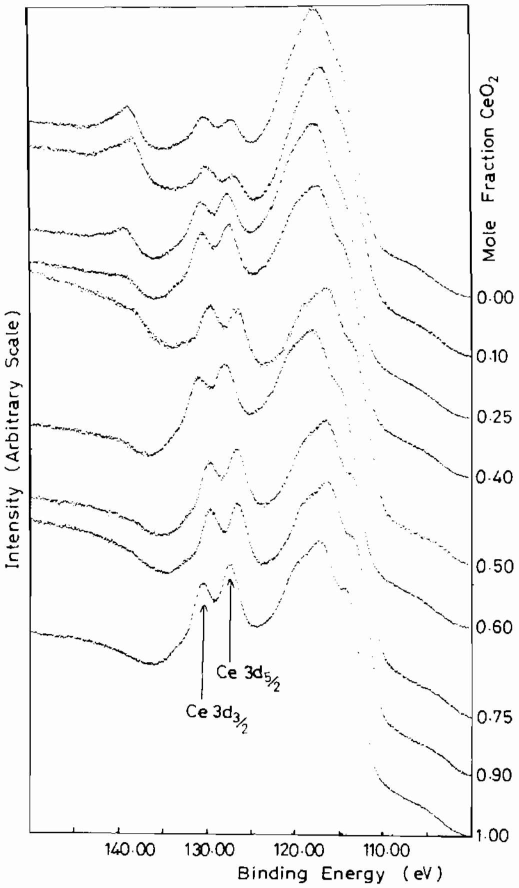

Fig. 3. Ce 4d XPS spectra for the different Ce(III)/Ce(IV) compounds.

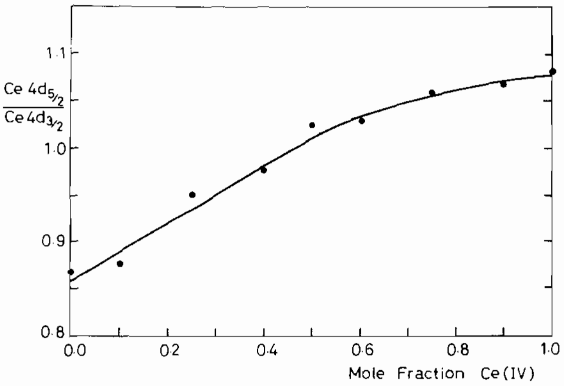

Fig. 4. The Ce $4d_{5/2}/4d_{3/2}$ peak area ratio as a function of the Ce(III)/Ce(IV) ratio.

correlation between the Ce(III)/Ce(IV) ratio and the $4d_{5/2}/4d_{3/2}$ peak area is given in Fig. 4.

It appears that the combined application of the modified Auger parameter and the $4d_{5/2}/4d_{3/2}$ peak area ratio may be used as an indication of the Ce(III)/Ce(IV) ratio.

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