

The Valance Determination of Cerium Ions in α -SiAlON by Electron Energy Loss Spectroscopy Analysis

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SiAlON ceramics have found applications in many different areas due to their excellent engineering properties such as high hardness, fracture toughness, good thermal shock and oxidation resistance. SiAlON exist mainly in two different polymorphs: α ($M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$; M: metal and rare earth cations, $x \approx 0,35$ and $n \leq 1,35$) and β (β - $Si_{6-z}Al_zO_zN_{8-z}$; $0 \leq z \leq 4$). In general, stable alpha and beta phases separately as well as in combination of α and β are obtained by incorporation of metal and rare earth cations as sintering additives. The metal cations such as Li, Mg, Ca, Y, and most lanthanide cations with the exception of La, Ce, Pr and Eu are able to stabilise α -SiAlON structure. Ekstrom et al 1991 [1] found that cerium can not occupy interstitial sites in α -SiAlON structure due to the fact that ionic radius of Ce^{3+} (0.103 nm) is too large, whereas ionic radius of Ce^{4+} (0.080 nm) is too small to stabilise α -SiAlON structure. After this work, several studies carried out to incorporate cerium cations into α -SiAlON structure [2-4]. It was shown that cerium cation alone can be incorporated into α -SiAlON if the samples are either fast cooled after sintering [2], or when the samples are spark plasma sintered [4]. On the other hand, cerium can also be incorporated into the α -SiAlON structure when it is used as a sintering additive together with a smaller α -SiAlON stabiliser cation such as Yb or Ca [3]. Similar results were observed in other multi-cation doped SiAlONS that non α -SiAlON stabiliser cations like Sr^{2+} (0.112 nm) and La^{3+} (0.106 nm) are able to stabilise α -SiAlON when used together with α -SiAlON stabiliser cations such as Ca or Yb [5-6]. Although it was shown that cerium existed in mixed valance state at domain boundaries in Ce-doped and spark plasma sintered α -SiAlON [7], there is no work on the valance determination of cerium in sintered α -SiAlON which has no domain boundaries. Therefore, in this study; it was aimed to incorporate cerium into α -SiAlON structure by combining with Yb^{3+} and the determination of possible cerium valance states (Ce^{3+}/Ce^{4+}) in both α -SiAlON grains and secondary phases.

For this purpose, SiAlON pellets were prepared by using equal molar CeO_2 - Yb_2O_3 sintering additives and then pre-sintered by gas pressure sintering (GPS) at $1800^\circ C$ for an hour under 22 bar nitrogen pressure. Electron transparent samples for analytical transmission electron microscopy (TEM) investigations were prepared by cutting, polishing, dimpling and finally ion beam thinning (Baltec RES 101). The prepared samples after coating (Baltec MED 020) with a thin carbon film were characterised by using 200 kV field emission transmission electron microscope (JEOL 2100F) attached with an energy filter (GATAN GIF TRIDIEM), parallel electron energy loss spectrometer (PEELS), a high angle annular dark field scanning transmission electron microscope (STEM-HAADF) detector and an energy dispersive x-ray (EDX) spectrometer (JEOL JED-2300T).

The STEM-HAADF image of pre-sintered α/β -SiAlON with CeO_2 - Yb_2O_3 additives is shown in figure 1 (a). EDX analysis were collected from different regions in figure 1 (b) showing that black regions are β -SiAlON grains which do not contain any sintering additives whereas grey and white regions contain different amount of sintering additives which are respectively α -SiAlON and secondary phases formed during sintering.

In order to find out the cerium valence states, the PEELS analysis was carried out on secondary phases, α -SiAlON grains and on the CeO₂ powder used as a sintering additive to see whether it is changing its valence after sintering. Ce M_{4,5} and N_{4,5} edges were acquired from alpha grains, triple junctions and reference CeO₂ powder grains are shown in figure 2 (a-f). The Ce N_{4,5} (110-115 eV) edges were not used for further analysis to avoid overlapping problems since their electron energy loss values are close to Si L_{2,3} (99 eV) edge values.

Ce M₄ (3d_{3/2}→4f_{5/2}) and Ce M₅ (3d_{5/2}→4f_{7/2}) edges can be observed respectively at 908.9 eV and 890.8 eV as sharp white lines on the reference CeO₂ powder in figure 2 (b). Ce⁴⁺ were distinguished from Ce³⁺ primarily by the appearance of extra peaks 5 eV higher in energy than the main Ce M_{4,5} peaks [7]. These extra peaks in 896.0 eV and 913.7 eV corresponding to Ce⁴⁺ could be seen clearly in the PEELS spectra of CeO₂ reference powder in figure 2 (b). In previous studies [7-8], the intensity ratio of cerium M₅ and M₄ edges was found to be 0.796 and 1.107 for Ce⁴⁺ and Ce³⁺ valence states, respectively. In this study, the intensity ratio of cerium M₅ and M₄ edges was calculated to be 0.785 for CeO₂ powder indicating that cerium was in quadrivalent (Ce⁴⁺) state in the reference CeO₂ powder which is used as a sintering additive in this study. Ce M_{4,5} edges from secondary phase in figure 2 (d) showed that Ce M₄ and Ce M₅ edges were respectively at 903.3 eV, 885.9 eV. It was also realised that Ce M_{4,5} edges were shifted towards the left in comparison to Ce M_{4,5} edges in CeO₂ powder. The intensity ratios of cerium M₅ and M₄ edges in secondary phase was calculated to be 1.185 which is indicating that Ce exist in trivalent (Ce³⁺) state transformed from Ce⁴⁺ used as a sintering additive. This is in line with the previous result [1] that Ce⁴⁺ was found to be unstable in silicon nitride at elevated temperatures during sintering process because a redox reaction takes place in which the Ce⁴⁺ was reduced to Ce³⁺ with outgoing nitrogen gas. Ce M_{4,5} edges from α -SiAlON grain in figure 2 (f) showed that Ce M₄ and Ce M₅ edges were at 902.9 eV and 885.7 eV, respectively in addition to small visible satellite edges. Similar to the spectra from the secondary phase, Ce M_{4,5} were shifted towards the left. The intensity ratio of cerium M₅ and M₄ edges in α -SiAlON grain was calculated to be 1.071. From this calculation, it can be deduced that cerium was in the mixed valence (Ce³⁺/Ce⁴⁺) state in α -SiAlON grains. This is confirming the results obtained from the domain boundaries of spark plasma sintered Ce doped α -SiAlON [7].

In conclusion, it is found that cerium could indeed be incorporated into α -SiAlON structure if it was used together with Yb³⁺ which acts as α -SiAlON stabiliser and cerium was existed in mixed valence (Ce³⁺/Ce⁴⁺) states in α -SiAlON structure whilst it was in trivalent valence (Ce³⁺) state in the secondary phases.

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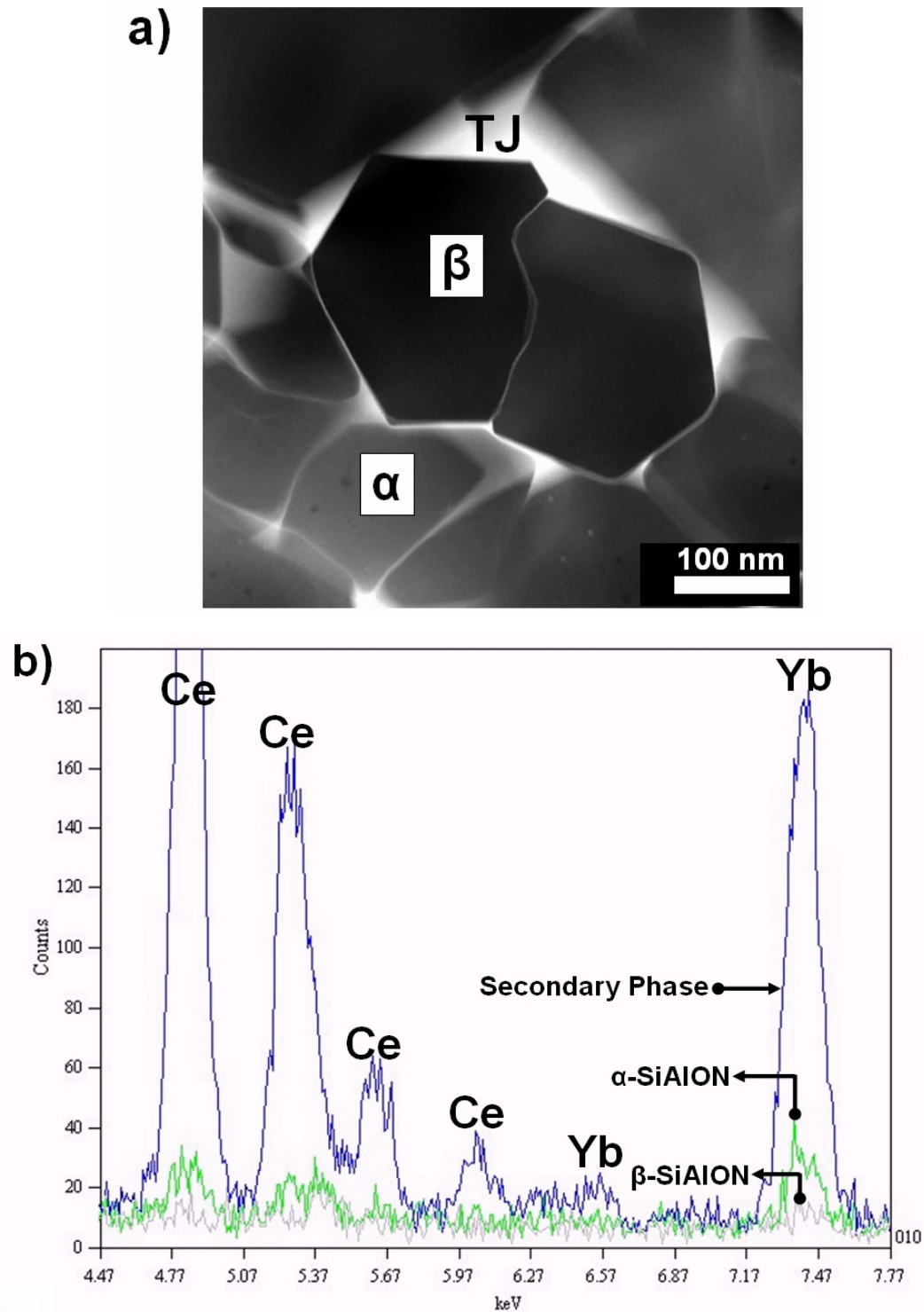


Figure 1. (a) STEM-HAADF image of SiAlON ceramics sintered with the addition of $\text{CeO}_2\text{-Yb}_2\text{O}_3$ (b) EDX spectrum obtained from secondary phase (TJ), α and β SiAlON grains.

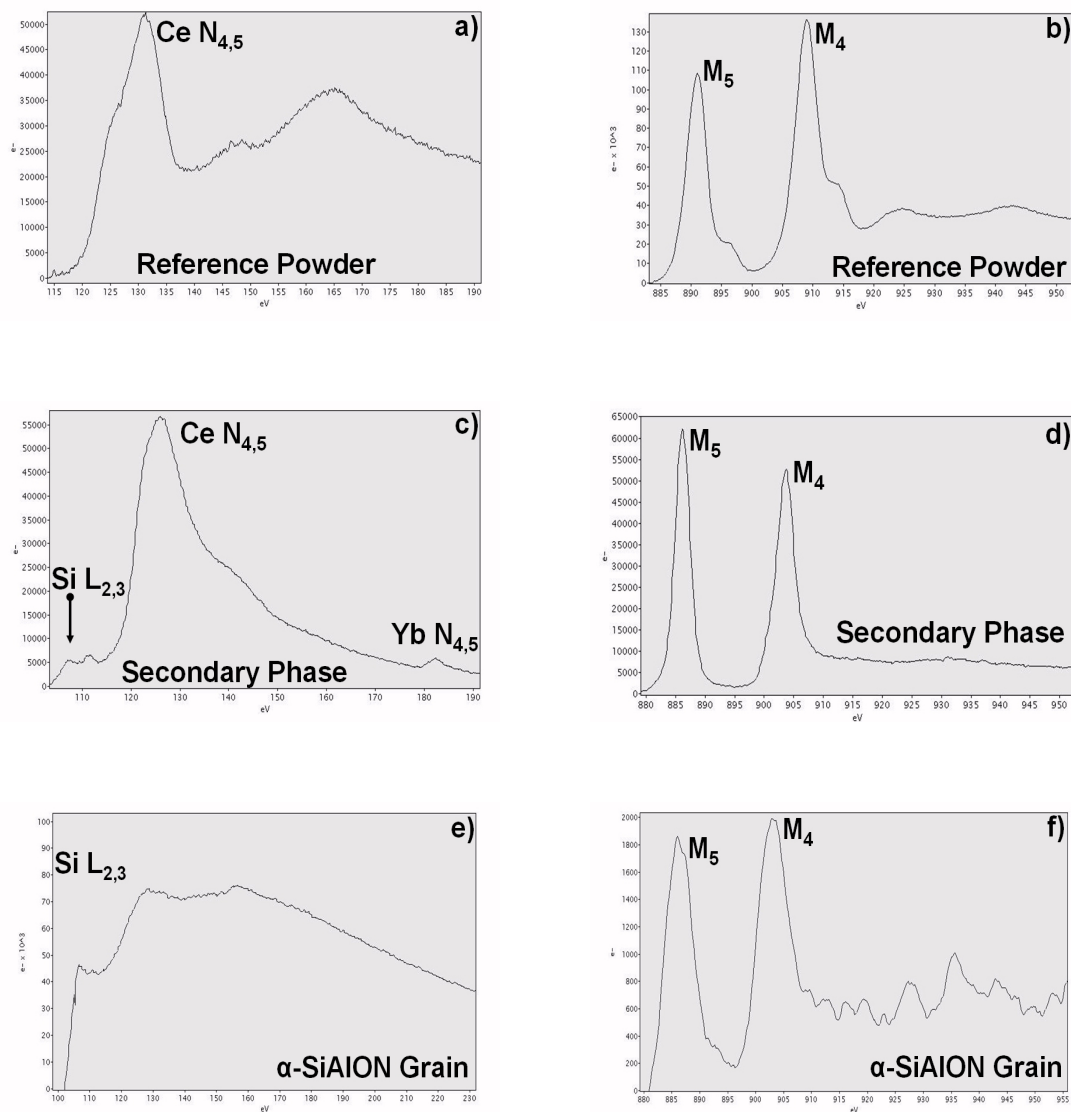


Figure 2. The PEELS spectra obtained from Ce $M_{4,5}$ edges at CeO_2 powder (a, b), secondary phase (c, d) and α -SiAlON grain (e, f). Please note that as a result of very low concentration of the cerium ions in the α -SiAlON grains, the PEELS analysis have been difficult and signals are very weak in comparison to the signals obtained from the reference powder (a, b) and the secondary phases (c, d).