

Influence of Type of Cations on Intergranular Phase Crystallisation of SiAlON Ceramics

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Abstract. 25 α :75 β SiAlON composition was designed with different cations and at different molar ratios. Effect of the type of cations both on the composition and the type of intergranular phase investigated after gas pressure sintering and further post sintering heat treatment.

Introduction

Recently, there has been considerable amount of work in the relevant literature on tailoring microstructure of silicon nitride ceramics by using different type of cations such as Lu, La, Yb and others [1-5]. However, the effects of the cations on development of microstructure and the resultant mechanical properties have not been clearly understood yet.

It is generally accepted that, grain growth anisotropy and fracture toughness increase with increasing cation size due to preferred segregation of large cations on the prism plane of grains. Various experimental studies have already been carried out to establish a correlation between the ionic size of cations and grain growth aspect ratio. In order not all the data satisfied the expectations [4]. According to the previous studies [6,7], La³⁺ tends to go to prism plane surface of Si₃N₄ grains and causes the formation of elongated grains and nitrogen rich weak interfaces. As a result, La-containing Si₃N₄ ceramics show high fracture toughness. Contrary to the case with large cations, oxygen rich intergranular phase with strong bonding to Si₃N₄ is obtained by using small ionic size cations such as Lu³⁺ or Yb³⁺ [4,6,7]. Besides, since small cations have lower tendency for segregation to grain surface, low aspect ratio grains were obtained.

In SiAlON ceramics, the effect of cations on the interfacial properties is rather different than Si₃N₄ since some Al³⁺ cations enter into the crystal structure and/or remain in the intergranular phase. Taking this into account, the main aim of this study is to investigate the effect of cation types and cation molar ratios on composition and type of intergranular phase and development of microstructure and hence mechanical properties of SiAlON.

Experimental Procedures

Compositional design was carried out by assuming that Yb³⁺ should go into intergranular phase (triple junctions) due to its small ionic size (0.858 Å) whereas Sm³⁺ (0.964 Å) and Ce³⁺ (1.03 Å) should tend to go into grain boundaries and grain surfaces due to their large size [4,6,7].

Designed SiAlON compositions with single (Yb^{3+} or Ce^{3+}), and multi cation systems with different molar ratio ($1\text{Yb}^{3+}:1\text{Ce}^{3+}$, $3\text{Yb}^{3+}:1\text{Ce}^{3+}$, $3\text{Yb}^{3+}:1\text{Sm}^{3+}$, $9\text{Yb}^{3+}:1\text{Ce}^{3+}$ and $9\text{Yb}^{3+}:1\text{Sm}^{3+}$) were prepared by wet milling in isopropyl alcohol using Si_3N_4 media. The slurries were then dried in a rotary evaporator and sieved down to 250 μm . The powders were uniaxially pressed under 25 MPa and subsequently cold isostatically pressed at 150 MPa to improve green density. The pellets were sintered under 22 bar nitrogen gas pressure, followed by post sintering heat treatments at different times and temperatures. The type and composition of the intergranular phases were determined by x-ray diffraction (XRD) analyses.

Results and Discussions

Fig. 1 shows phase analyses of the SiAlON designed with Yb^{3+} , Ce^{3+} and equimolar Yb^{3+} and Ce^{3+} . Regarding to Yb^{3+} containing SiAlON, silicate phase crystallisation within intergranular phase was observed after sintering. This result verifies that Yb^{3+} cation goes into the intergranular phase and also enter into the crystal structure of α -SiAlON to stabilize it. On the other hand, when Ce^{3+} cation was used, no crystalline phase formation was detected. In addition no α -SiAlON phase was obtained due to large cation size of Ce^{3+} (1.03 Å). Using equimolar $\text{Yb}^{3+}:\text{Ce}^{3+}$ cations, designed $\alpha:\beta$ phase ratio was obtained, but no crystalline phase formation was achieved. Ce^{3+} cations expected to enter into α -SiAlON structure when its incorporated with Yb^{3+} , but a substantial amount should also exist in the grain boundary phase as it inhibit silicate phase crystallisation.

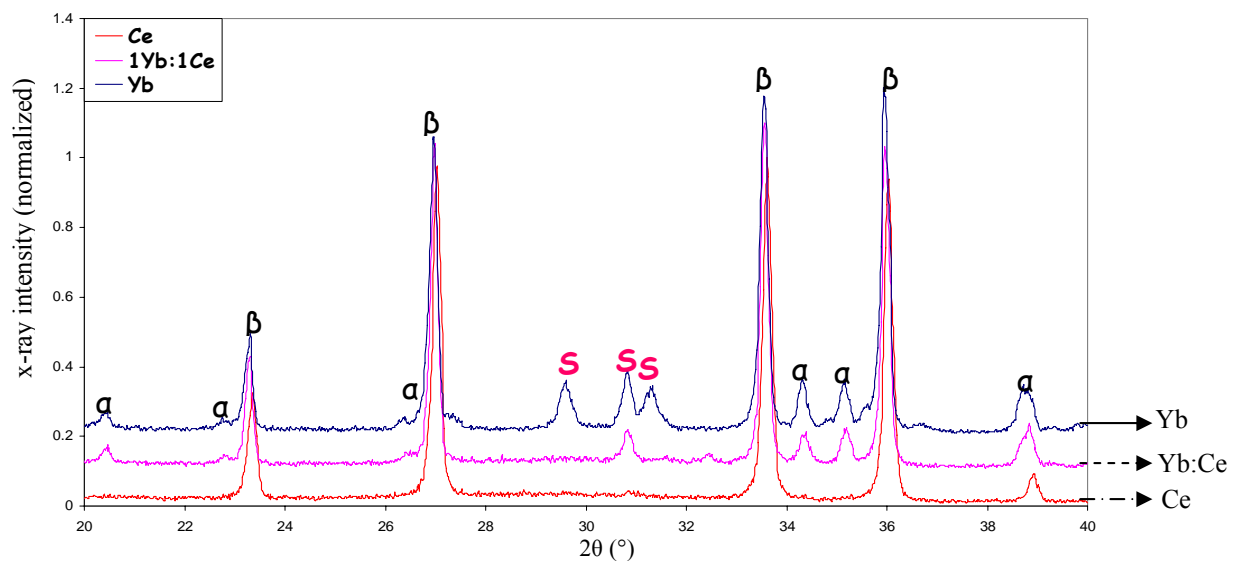


Fig.1. Comparison of the phases in Yb^{3+} , Ce^{3+} and equimolar $\text{Yb}^{3+}:\text{Ce}^{3+}$ cation systems after sintering (β :beta SiAlON phase, α :alpha SiAlON phase, S:silicate phase ($\text{Ln}_2\text{Si}_2\text{O}_7$))

Increasing the molar ratio of Yb:Ce up to 9:1 and also changing Ce^{3+} with a smaller size cation of Sm^{3+} also caused ... secondary phase crystallisation after sintering α and β SiAlONs were obtained as designed in both cation systems (Fig 2). Despite the fact that silicate type grain boundary phase really crystallise in Yb system presence of only a small amount of Ce or sm was encourage to or inhibit the crystallisation of silicate type grain boundary phase.

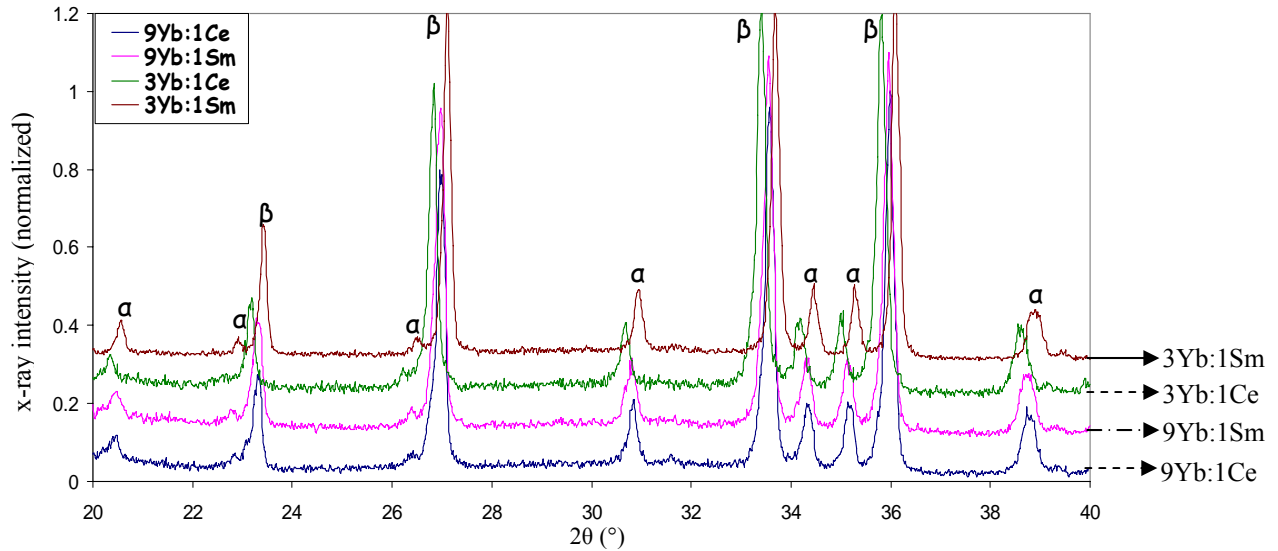


Fig. 2. Comparison of the phases in $3\text{Yb}^{3+}:\text{1Ce}^{3+}$, $3\text{Yb}^{3+}:\text{1Sm}^{3+}$, $9\text{Yb}^{3+}:\text{1Ce}^{3+}$ and $9\text{Yb}^{3+}:\text{1Sm}^{3+}$ cation systems after sintering (β : beta SiAlON phase, α : alpha SiAlON phase)

After the post sintering heat treatment, crystalline silicate phase evolution was observed for Yb^{3+} containing SiAlON composition (Fig. 3). Regarding Ce^{3+} composition, nitrogen rich melilite ($\text{Ln}_2\text{Si}_{3-x}\text{Al}_x\text{O}_{3+x}\text{N}_{4-x}$) phase was detected. Also, equimolar $\text{Yb}^{3+}:\text{Ce}^{3+}$ cations gave rise to melilite phase crystallisation. This result proved that Ce^{3+} cation is the dominant to form crystalline phase after the post sintering heat treatment. Namely, Ce^{3+} cations segregate to grain surface to give elongated grains and also could go into intergranular phase.

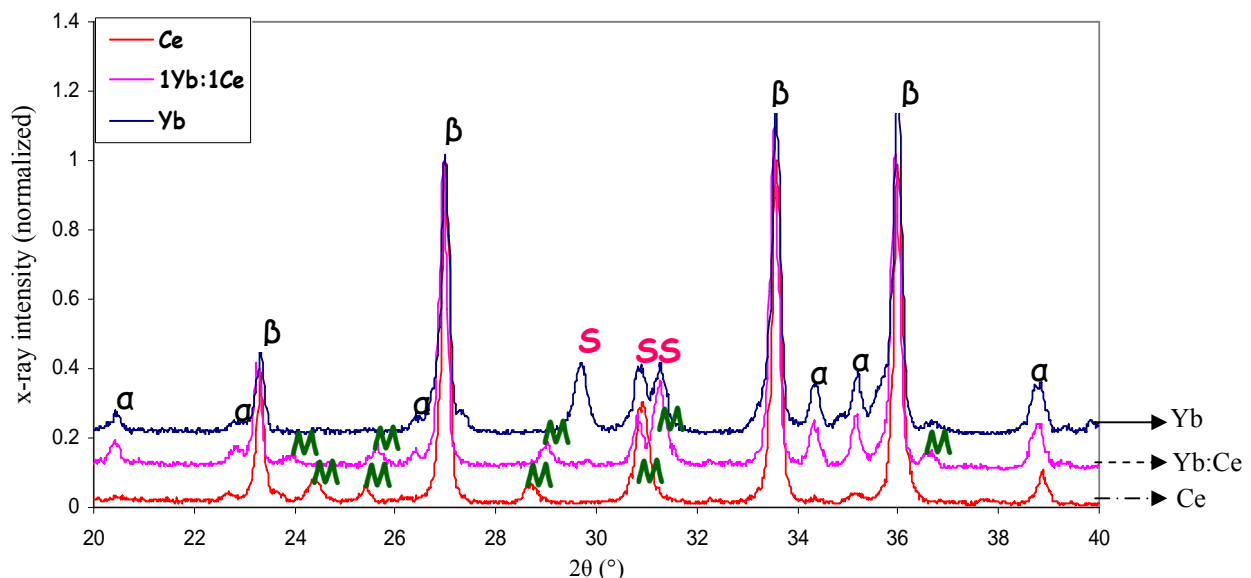


Fig. 3. Comparison of the phases in Yb^{3+} , Ce^{3+} and $\text{Yb}^{3+}:\text{Ce}^{3+}$ compositions after post sintering heat treatment (β :beta SiAlON phase, α :alpha SiAlON phase, S :silicate phase ($\text{Ln}_2\text{Si}_2\text{O}_7$), M :melilite phase ($\text{Ln}_2\text{Si}_{3-x}\text{Al}_x\text{O}_{3+x}\text{N}_{4-x}$)).

For $3\text{Yb}^{3+}:\text{1Sm}^{3+}$ and $9\text{Yb}^{3+}:\text{1Sm}^{3+}$ cation system, melilite phase crystallisation was observed after post sintering heat treatment although amorphous phase was detected in assintered samples (Fig. 4). Increase in Sm molar ratio results in enhancing melilite phase crystallization. Therefore, Sm^{3+} cation presumably diffuses to intergranular phase and also segregates to grain surface to

enhance the grain anisotropy. Ce^{3+} cation has an effect to prevent crystallisation of intergranular phase in Yb^{3+} containing SiAlON composition.

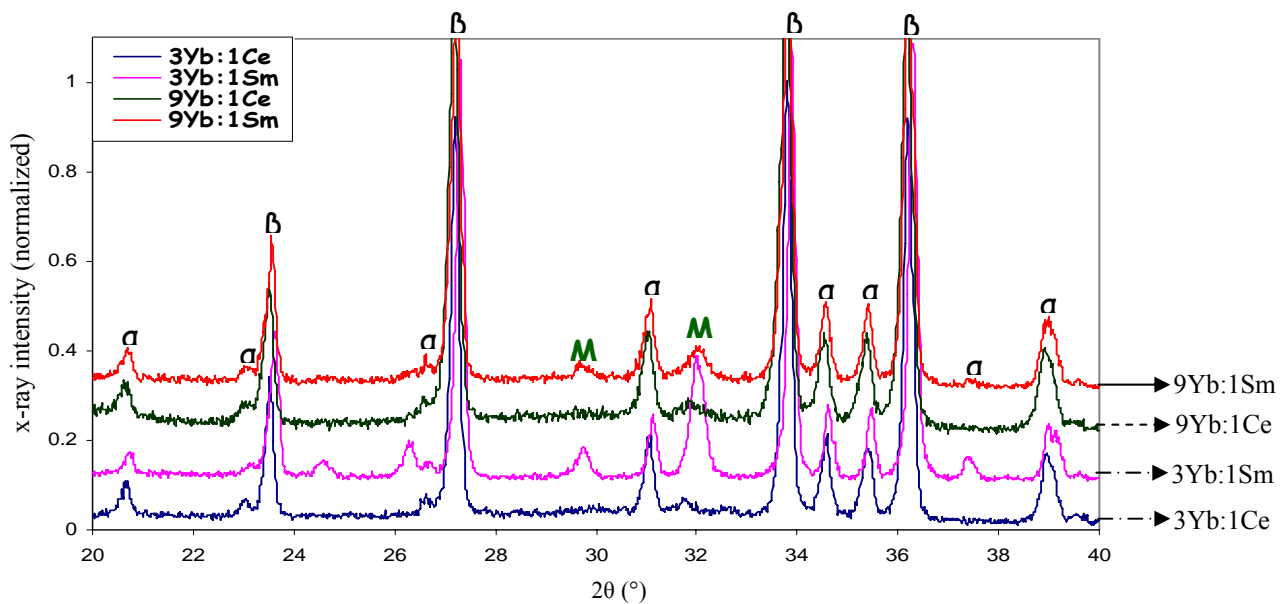


Fig. 4. Comparison of the phases in $3Yb^{3+}:1Ce^{3+}$, $3Yb^{3+}:1Sm^{3+}$, $9Yb^{3+}:1Ce^{3+}$ and $9Yb^{3+}:1Sm^{3+}$ compositions after post sintering heat treatment (β :beta SiAlON phase, α :alpha SiAlON phase, M:melilite phase ($Ln_2Si_{3-x}Al_xO_{3+x}N_{4-x}$)).

Conclusion

In this study, SiAlON ceramics with a high refractory crystalline intergranular phase were obtained by using different type of cations and different molar ratios. Yb^{3+} cation provides silicate phase formation regardless of after sintering or post sintering heat treatment. Ce^{3+} is the dominant cation to determine the type and composition of intergranular phase. Ce^{3+} cation generally contributes to amorphous or melilite intergranular phase formation, which is related to heat treatment schedule. Sm^{3+} cation yields amorphous or melilite phases which depends on other cations in the system and post sintering heat treatment conditions. Consequently, heat treatment schedule is believed to be very important parameter on composition and type of intergranular phase.

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