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Transmittance improvement of Dy–α-SiAlON in infrared range by post hot-isostatic-pressing

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Abstract

At present stage, the transmittance improvement is still a thorny problem in SiAlON ceramics due to their complex composition and processing. In the present research, Dy–α-SiAlON ceramics were selected to be translucent in the medium infrared range. The samples had a higher densification value by using hot-pressing (HP) sintering method at 1650–1700 °C with or without LiF additive. The as-sintered specimens experienced the post-hot-isostatic-pressing (PHIP) treatment at 1650–1700 °C for 30–90 min in either N_2 or Ar environment to increase the optical transmittance. A significant optical transparency improvement has been found in Dy–α-SiAlON, with or without LiF co-doping, undergone a PHIP at 1700 °C for 30 min under an Argon gas pressure of 180 MPa. The improved transmittance attributes to a fully developed α-SiAlON crystalline phase, a uniform grain size, a denser grain arrangement, and a clean grain boundary, based on the X-ray diffraction analysis, SEM and TEM microstructure observation, and optical transmittance measurement.

Keywords: α-SiAlON; Hot pressing sintering; Hot isostatic pressing; Transmittance; Infrared range

1. Introduction

SiAlONs, as the solid solution of Si_3N_4 with the substitution of Al and O for Si and N, are well-developed advanced engineering ceramic materials for their excellent combination of mechanical strength, toughness, hardness and thermal shock resistance. And it has also been interesting in the controllable properties of SiAlONs by chemical composition design and processing adjusting. In recent twenty years, the translucent SiAlONs attracted considerable attention for their potential applications as optical window or dome materials in a wide range from visible to medium infrared wavelengths, facing an increased requirement for some applications in the extreme harsh environment, for example, under higher temperature or supersonic working conditions. Many material scientists have successfully prepared different translucent SiAlONs with varied element doping or substitution of Al and O for Si and N. In 1981, Mitomo with his colleagues reported a translucent β-SiAlON using the hot-pressing sintering technique, with a composition of $z = 2$–4, but the transmittance was not very high in the infrared region.[1] Later, Karunaratne reported that Y^{3+}-doped SiAlON could be optical translucent ceramics, just using a pressureless sintering method.[2] In the following years, a serial colorful and translucent SiAlONs were obtained by a wider selection of elements doping from alkali earth cations Ca^{2+}, Mg^{2+} to many rear earth cations, where most of the prepared ceramics were α-SiAlONs. In 1997, Shen's group designed and sintered a series of $Nd3^{+}$, Tb^{3+}, Er^{3+}, Sm^{3+}, and Y^{3+}-doped translucent SiAlONs by hot-pressing method.[3] Then, Mandal's group reported the single-phase α-SiAlONs with a wider optical transmission range by hot-isostatic-pressing sintering.[4] Jones with his colleagues prepared Lu–α-SiAlONs with a higher transmission of 70% in the visible region and a dual phase mixture of α/β-SiAlONs having a higher toughness, in 2003 and 2004 respectively.[5,6] Su and Chen shown us some good results of higher transmission in the infrared range of 3–5 μm obtained in Dy–SiAlON by spark plasma sintering and Gd–SiAlON by hot pressing method in 2004 and 2005.[7,8] Recently, Xiong's group published their research work on the translucent Mg–SiAlON using spark plasma sintering.[9] In the same year, Xue of our group reported the lower temperature sintering of translucent Dy–SiAlON with LiF as additive.[10] Furthermore, Ye with his

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group published their new results about Y^{3+}/Yb^{3+} dual-doped α-SiAlONs having a higher infrared transmission and toughened Sc^{3+}/Lu^{3+} doped α-SiAlONs by an in situ growth of elongated grains in 2008 and 2009 respectively.[11,12]

Now it is clear that a higher optical transmission, without a bigger victim of mechanical properties, is the aim that all SiAlONs researchers pursued for. Therefore many efforts have been made to reach the aim by accurately adjusting of chemical composition and purity, and using post-heat-treatment. While the post-heat-treatment after sintering process was considered to be effective to increase transmission by increasing the uniformity of grain size, minimizing the pores in the bulks, and reducing the amounts of residual glassy phase or grain boundary phase. It is the microstructural inhomogeneity (pores, grain boundary, anisotropy of grains, etc.) in the polycrystalline ceramics that causes the internal light scattering with a resultant of optical opaque.

Among the post-heat treatment techniques, the hot-isostatic-pressing (HIP) or post-hot-isostatic pressing (PHIP) were proved to be an important way to further densify the powder compacts, then to provide the improvement of mechanical and optical properties. Ekstrom et al. reported the Yttrium-doped α-SiAlON HIP-ed and PHIP-ed with less residual grain boundary glass phases.[13] It was the reduced residual grain boundary glass phases that played a positive role in raising the optical transmittance of materials.

Motivated by the research activities mentioned above, in the present study, hot-pressing sintering (HP) and post-hot-isostatic-pressing technique were combined to fabricate and enhance the Dy–α-SiAlONs with a higher transmission in medium infrared region of 3–5 μm, because Dy–α-SiAlONs are excellent candidates for optical window materials, not only for their stability of crystal phase but also for the economical consideration.

2. Experimental

According to the phase equilibrium relationship of the complex SiAlONs and the formula of $M_{m/v}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, the α-SiAlON ceramics reported here has a nominal composition $Dy_{0.66}Si_{9.0}Al_{3.0}O_{1.0}N_{15.0}$ (noted as Dy–SiAlON, where M = Dy, $m = 2n = 2.0$, $v = 3$). High-purity powders of α-Si_3N_4 (SN-E10, Ube, Japan), AlN (Grade A, Starck, Germany), Dy_2O_3 (Yaolong Chemical Plant, Shanghai, China), Al_2O_3 (Yaolong Chemical Plant, Shanghai, China), and LiF (Sinopharm Chemical Reagent Co., Ltd, Beijing, China) were mixed in ethanol, milled using Si_3N_4 balls in a Si_3N_4 jar. After milling, the powder slurry was dried at 80 °C and sieved. And then a charge of 6.0 g each was loaded directly into a graphite die of 25 mm in diameter. The samples were hot pressed at 1650–1700 °C under a 30 MPa pressure for 60 min in a flowing nitrogen atmosphere of 0.1 MPa. After HP sintering, the compacted samples were put into the HIP furnace for a further PHIP heat treatment at 1650–1700 °C for 30–90 min under a 120 MPa pressure of N_2 or a 180 MPa pressure of Ar atmosphere. The HP-sintered and PHIP-treated samples were sliced with the surface perpendicular to the hot-pressing direction, and then polished or thinned to different thickness for the microstructure observation and optical transmission measurement.

Bulk density of specimens was measured by Archimedes principle. The phase analysis was performed using the X-ray diffractionmeter (D8, Advance X-ray Diffractionmeter, Bruker, Germany). Microstructure observation was carried out under an electron probe microanalyzer (JXA-8100, JEOL, Japan) and transmission electron microscope (JEM-2010/200CX/2100F, JEOL, Japan). Optical transmission of the translucent samples in wavelength of 2.5–6.5 μm was measured using a Fourier Transform Infrared Spectrometer (EQUINOX55, Bruker, USA).

3. Results and discussion

Table 1 lists the results obtained from all samples HP-sintered and PHIP-treated, in which it clearly shows the effects of temperature, soaking time, or atmosphere of PHIP treatment on phase purity and optical transmittance of the resultant bulks.

Based on the previous researches by other scientists and ourselves,[10,14–16] additional and optimal 0.1 wt% LiF was added to reduce the HP-sintering temperature, decrease the grain size, and then increase the optical transmittance to some extent. LiF was considered to be an important sintering additive for preparing ceramics at lower temperatures by causing the formation of intermediate phase. Presumably, LiF "film", or a film of complex composition formed by reaction with SiO_2 on Si_3N_4 powders, or Al_2O_3 on AlN powders, or grain boundary phases, could act as an "eutectic activated layer" or "pathway" through which an enhanced grain boundary sliding, or particle rearrangement, or interface diffusivity could occur, with an increasing sintering rate and grain growth. Comparatively, Dy–SiAlON without 0.1 wt% LiF additive should be sintered at a higher

Table 1
Results obtained from all samples HP-sintered and PHIP-treated.

Sample	HP condition	PHIP condition	Phase analysis	Transmittance
Dy–SiAlON	1700 °C/60 min/N_2	–	α′ + minor M′	Translucent
		1650 °C/90 min/N_2 (120MPa)	α′ + more M′	Opaque
		1680 °C/60 min/N_2 (120MPa)	α′ + more M′	Opaque
		1700 °C/30 min/Ar (180MPa)	α′ + minor M′	Translucent
0.1 wt%LiF–Dy–SiAlON	1650 °C/60 min/N_2	–	α′ + minor M′	Translucent
		1650 °C/90 min/N_2 (120MPa)	α′ + more M′	Opaque
		1680 °C/60 min/N_2 (120MPa)	α′ + more M′	Opaque
		1700 °C/30 min/Ar (180MPa)	α′ + minor M′	Translucent

α′-Dy–α-SiAlON, M′-Dy–melilite solid solution ($Dy_2Si_{3-x}Al_xO_{3+x}N_{4-x}$).

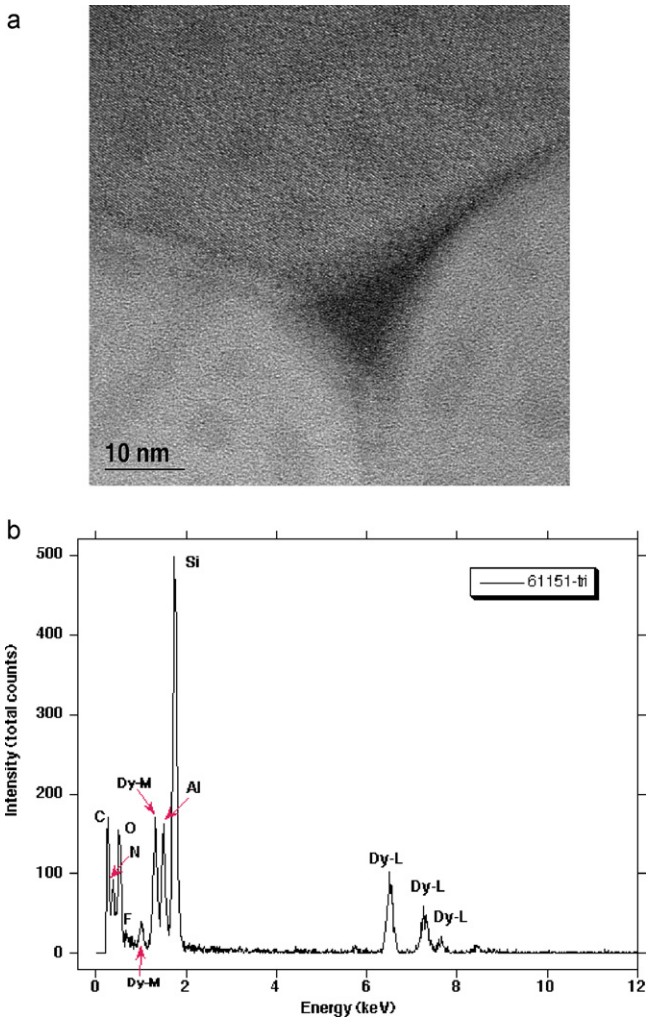

Fig. 1. HRTEM micrograph (a) and EDAX analysis (b) of a triple junction by three grains in 0.1LiF-doped Dy–α-SiAlON sample, HP-sintered at1650 °C/60 min/N_2.

temperature level (1700 °C) to reach a full density. Therefore, there were no significant differences in grain size, morphology, grain boundary phases, and even density between LiF-doped and undoped Dy–SiAlON. Fig. 1 shows a HRTEM micrograph and EDAX analysis of the triple junction by three grains in the 0.1 wt%LiF–Dy–SiAlON HP-sintered at 1650 °C for 60 min in N_2 gas. The elemental analysis of the grain boundary phase indicates the complex composition of Dy–Si–Al–O–N with a trace of F existence.

The XRD data for the series samples either HP-sintered or PHIP-treated ones showed that the crystalline phase in the HP-sintered bulks was primarily α-SiAlON with minor Dy–melilite solid solution Dy–melilite solid solution ($Dy_2Si_{3-x}Al_xO_{3+x}N_{4-x}$, abbreviated as M′) or as main grain boundary phase, but the samples undergone a PHIP-treatment in N_2 atmosphere contained more Dy–mellilite solid solution phase. It is reasonable to consider the co-existence of α-SiAlON with $Dy_2Si_{3-x}Al_xO_{3+x}N_{4-x}$ phase, according to the subsolidus phase relationships in the systems R–Si–Al–O–N (R = Nd, Sm, Dy) and also the calculation results of multicomponent systems,[17,18] where R-melilite solid solution was thought

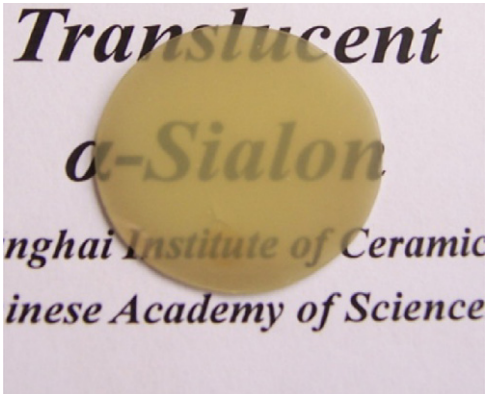

Fig. 2. Translucent LiF-doped Dy–α-SiAlON sample HP-sintered (0.5 mm in thickness).

to be the only stable compound which is compatible with α- or β-SiAlON in the complex system of R_2O_3–Si_3N_4–AlN–Al_2O_3. It should emphasize that the percentages of Dy–melilite solid solution increase gradually with the increase of temperature and Al substitute in a following N_2 atmosphere. In our present experiment, when PHIP-treated in N_2 atmosphere, the Dy–SiAlON experienced the second run of heating and soaking at higher temperature in a N_2 atmosphere. As a consequence, the solution–precipitation–recrystallization process might occur during the longer PHIP stage at the interface between $Dy_2Si_{3-x}Al_xO_{3+x}N_{4-x}$ and α-SiAlON phase. And more $Dy_2Si_{3-x}Al_xO_{3+x}N_{4-x}$ phase too could develop because its lower viscosity and higher mobility of reaction than those of Dy–SiAlON.

The most striking feature in the experimental result was the big difference in optical transmittance between the HP-sintered and PHIP-treated samples. The HP-sintered ones, with or without LiF addition, were all translucent in a wide range from visible to medium infrared wavelength, seen in Fig. 2, showing a translucent LiF–Dy–α-SiAlON sample after HP-sintered.

Contrarily, the samples PHIP-treated in the N_2 atmosphere were all opaque, with more grain boundary phase contents contained, as mentioned above. The increased grain boundary phase was thought to be formed at the interface or triple junctions of grains under a higher PHIP temperature, a longer soaking time, but a rather lower N_2 pressure (120 MPa) condition. That might be related to a solution–precipitation–recrystallization process of SiAlON grains, reacted with grain boundary phase Dy–melilite solid solution during the PHIP step under a rather lower pressure of N_2 gas, since the PHIP-treatment was generally carried out under a much higher gas pressure than 180 MPa to restrict the “solution” of crystalline grains. Fig. 3 gives a strong evidence to support the explanation, which illustrates the surface micrograph of the sample Dy–SiAlON PHIP-treated at 1650 °C/90 min/N_2 (120 MPa), where it can be seen that the round α′ grains are surrounded by grain boundary phases, that is indentified to be the chemical composition rich in N and Si contents according to EDAX elemental analysis. And a heavier C contamination (about 5 wt%) was also detected in the same sample.

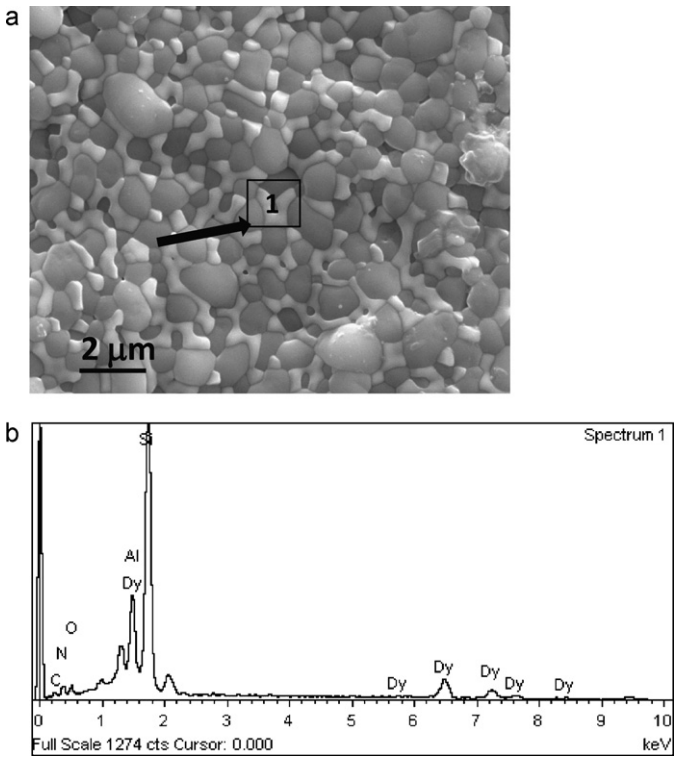

Fig. 3. Surface micrograph and EDAX spectrum of grain boundary phase (marked in arrow) in the sample Dy–SiAlON PHIP-treated at 1650 °C/90 min/N_2 (120 MPa).

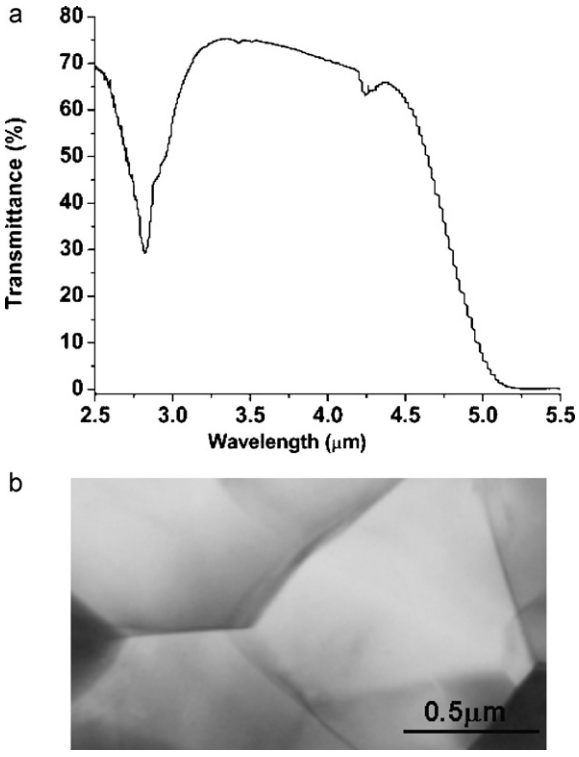

Fig. 4. Optical transmittance spectrum and micrograph of 0.1LiF-doped Dy–α-SiAlON sample (PHIP-treated in Ar gas, thickness 0.5 mm).

Comparatively, the samples, that were PHIP-treated at much higher temperature of 1700 °C but in an inert Ar environment, showed a higher transmittance than that of the original HP-sintered ones. There was only a minor M′ phase existence in the PHIP-treated sample around an inert Ar gas, since a much higher inert gas pressure was very effective to restrict the "solution" of crystalline grains. The highest value of transmittance was obtained in the sample 0.1LiF-doped Dy–α-SiAlON experienced a PHIP history at 1700 °C/30 min/Ar (180 MPa) after HP-sintering at 1650 °C/60 min/N_2. Fig. 4 shows the optical transmittance spectrum and a TEM micrograph of the investigated PHIP-ed (in Ar gas) sample, 0.1LiF-doped Dy–α-SiAlON with a thickness of 0.5 mm for transmittance measurement. The sample has a higher optical transmittance in the medium infrared region and the transmittance value is over 70%, possessing a maximum value of 73%. As a comparison, the maximum transmittance value of the original HP-ed 0.1LiF-doped Dy–α-SiAlON sample was only 62%. The specimen PHIP-treated at 1700 °C/30 min/Ar (180 MPa) was chosen for electron microscope observation to find some answers about the transparency improvement in the view of microstructure. The micrograph in Fig. 4 reveals a denser grains arrangement, an equiaxed grain morphology, and less grain boundary phases remaining at the interface or triple junctions in the PHIP-treated specimen. As expected, the PHIP treatment provided an important role in enhancing plastic yielding, creep, and diffusion of grains during the heating under a higher gas pressure applied. It is the denser grain arrangement and less grain boundary phases that attribute the transmittance improvement by reducing the light scattering from the inhomogeneous microstructure feature in the polycrystalline ceramics.

As the parallel or reference experimental, the samples without additive of LiF were also investigated on their optical property and microstructure feature. The sample Dy–α-SiAlON needed to be HP-sintered at a higher temperature of 1700 °C owning less M′ grain boundary phase at interface or triple conjunctions of grain boundary. Therefore, the sample was also translucent in the visible and medium infrared region as well. The highest value of transmittance was obtained in the sample Dy–α-SiAlON experienced a post-HIP history at 1700 °C/30 min/Ar (180 MPa) after HP-sintering at 1700 °C/60 min/N_2. Fig. 5 shows the optical transmittance spectrum and a micrograph of the investigated Dy–α-SiAlON sample, with a thickness of 1.0 mm for transmittance measurement. The sample has a higher optical transmittance in the medium infrared region and the transmittance value is over 60%, having a maximum value of 64%. As a comparison, the maximum transmittance value of the original HP-ed Dy–α-SiAlON sample was only 58%. Electron microscope observation shows no significant grain growth after experienced a PHIP step. Fig. 4 reveals a uniform grains size distribution in the PHIP-ed sample. Similarly, it is the well-grown grain size, denser grain arrangement, and less residual intergranular phases that result in the transmittance improvement in PHIP-ed Dy–α-SiAlON by weakening the light scattering from the inhomogeneous microstructure feature in the ceramics.

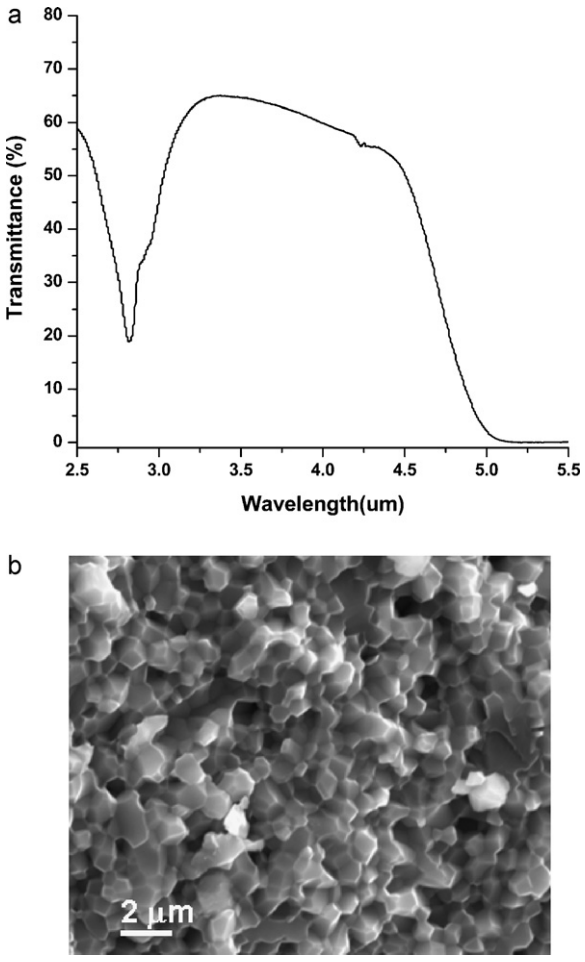

Fig. 5. Optical transmittance spectrum and micrograph of Dy–α-SiAlON sample (PHIP-ed in Ar gas, thickness 1.0 mm).

4. Conclusion

Post-hot-isostatic-pressing (PHIP) treatment at a higher temperature (1700 °C) and under a higher inert Ar environment pressure (180 MPa) was an effective method for promoting the optical transparency of Dy–α-SiAlON with or without LiF additive, by supplying an extra driving force for sintering. The higher inert Ar gas pressure was very effective to restrict the "solution" of crystalline grains and the formation of grain boundary phase. Microstructure observation reveals that the uniform grain size with an equiaxed grain morphology, denser grain arrangement, and less grain boundary phases attribute the transmittance improvement of the Dy–α-SiAlON or LiF-doped Dy–α-SiAlON ceramics that experienced a PHIP processing in Ar environment. But the PHIP treatment under a rather lower N_2 pressure (120 MPa) showed a negative effect on the transparency increasing, by inducing a higher Dy–mellilite solid solution (M′) grain boundary phase content, resulting in a stronger light scattering. So, the further investigation on the gas pressure, gas type, and temperature of PHIP has to be considered to further promote the transparency of the SiAlONs ceramics.

References

1. Mitomo M, Moriyoshi T, Sakai T, Ohsaka Y, Kobayasgi M. Translucent β-SiAlON Ceramics. *J Mater Sci Lett* 1981;**1**:25–6.
2. Karunaratne BSB, Lumby RJ, Lewis MH. Rear-earth-doped α-SiAlON ceramics with novel optical properties. *J Mater Res* 1996;**11**:2790–4.
3. Shen ZJ, Nygren M, Hslenius U. Absorption spectra of rare-earth-doped α-SiAlON ceramics. *J Mater Sci Lett* 1997;**16**:263–6.
4. Mandal H. New developments in α-SiAlON ceramics. *J Eur Ceram Soc* 1999;**19**:2349–57.
5. Jones MI, Hyuga H, Hirao K. Optical and mechanical properties of α/β-SiAlON composites. *J Am Ceram Soc* 2003;**86**:520–2.
6. Jones MI, Hyuga H, Hyuga K, Yamauch Y. Highly translucent Lu–α-SiAlON. *J Am Ceram Soc* 2004;**87**:714–6.
7. Su XL, Wang PL, Chen WW, Shen ZJ, Nygren M, Cheng YB, et al. Effects of composition and thermal treatment on infrared transmission of Dy–α-SiAlON. *J Eur Ceram Soc* 2004;**24**:2869–77.
8. Chen WW, Su XL, Wang PL, Yan DS. Optical properties of Gd–α-SiAlON ceramics: effect of carbon contamination. *J Am Ceram Soc* 2005;**88**:2304–6.
9. Xiong Y, Fu ZY, Wang H, Wang WM, Zhang JY, Zhang QJ. Translucent Mg–α-SiAlON ceramics prepated by spark plasma sintering. *J Am Ceram Soc* 2007;**90**:1647–9.
10. Xue JM, Liu Q, Gui LH. Lower-temperature hot-pressed Dy–α-SiAlON ceramics with LiF additive. *J Am Ceram Soc* 2007;**90**:1623–5.
11. Ye F, Liu LM, Liu CF, Zhang HJ, Zhou Y, Yu J. High infrared transmission of Y^{3+}–Yb^{3+}-doped-α-SiAlON. *Mater Lett* 2008;**62**:4535–8.
12. Ye F, Liu CF, Liu LM, Zhou Y. Optical properties on in-situ toughened ScLu–α-SiAlON. *Scipta Mater* 2009;**61**:982–4.
13. Bartek A, Ekstrom T, Herbertsson H, Johansson T. Yttrium α-SiAlON ceramics by hot isostatic pressing and post-hot isostatic pressing. *J Am Ceram Soc* 1992;**75**:432–9.
14. Benscke MW, Olson NE, Pask JA. Effect of LiF on hot-pressing of MgO. *J Am Ceram Soc* 1967;**50**:365–8.
15. Guha JP, Anderson HU. Reaction during sintering of barium titanate with lithium fluoride. *J Am Ceram Soc* 1986;**69**:C-193–4.
16. White KW, Kelkar GP. Fracture mechanisms of a coarse-grained, transparent $MgAl_2O_4$ at elevated temperatures. *J Am Ceram Soc* 1992;**75**:3440–4.
17. Chen W, Wang P, Yan DS. Study on the formation behavior and crystallography of N-containing melilite solid solutions $Dy_2Si_{3-x}Al_xO_{3+x}N_{4-x}$ (R = Nd, Sm, Dy, Y, Yb). *Eur J Solid State Inorg Chem* 1997;**34**:871–80.
18. Dorner P, Gauckler LJ, Krieg H, Lucas HL, Petzow G, Weiss J. On the calculation and representation of multicomponent systems. *Mater Today* 1979;**3**:241–57.