

Molten salt synthesis of DyAlO₃ powders

Joo-Sin Lee*

Department of Advanced Materials Engineering, Kyung Sung University, Busan 608-736, Korea

In this work, the molten salt synthesis technique was applied to the synthesis of DyAlO₃ powder using NaCl or KCl salt as the flux. DyAlO₃ powder was synthesized by reacting equimolar amounts of Dy₂O₃ and Al₂O₃ powders in NaCl or KCl salt. The synthesis temperature for DyAlO₃ using NaCl or KCl salt was 1300 °C which is about 400 °C lower than that in the conventional mixed-oxide method. The synthesized powders have been characterized using powder X-ray diffraction (XRD) analysis and field emission scanning electron microscopy (FE-SEM). The synthesized DyAlO₃ powders retained the morphology of the original Al₂O₃ particles, indicating that a template formation mechanism plays an important role in the molten salt synthesis of DyAlO₃.

Key words: Molten salt synthesis, Powder, DyAlO₃.

Introduction

Lanthanide aluminate-based ceramics are promising materials for optical, magnetic, electronic and structural applications [1]. The perovskite aluminates have found wide applications as laser host materials, phosphors, ceramic microwave resonators, scintillators, solid electrolytes, chemical sensors, magnetic refrigeration materials, substrates for high-temperature superconductor deposition, catalyst supports and thermal barrier coatings [2, 3]. DyAlO₃ has potential applications as magnetic refrigerants for low-temperature region [4, 5], microwave components [6] and substrates for high-temperature superconductor deposition [7].

DyAlO₃ is normally synthesized by the solid-state reaction of dysprosia and alumina powders. This process involves extensive mechanical mixing and lengthy heat treatments at very high temperatures (~1700 °C) [8,9]. Recently, wet-chemical techniques, such as modified sol-gel [9] and polymer complex method [10] have been applied to prepare DyAlO₃ powders. Petrov et al. [9] prepared nanocrystalline DyAlO₃ powders at 950 °C by the modified sol-gel method, with particle sizes ranging from 30 to 60 nm. The fully crystalline single-phase DyAlO₃ was obtained at 1150 °C for 2 h via the polymer complex method by Takata et al. [10]. These wet-chemical techniques have led to fine DyAlO₃ powders with good chemical homogeneity and narrow particle size distributions at relatively low temperatures. However, these wet-chemical methods often suffer from drawbacks, such as the need to use expensive and environmentally unfriendly organic/inorganic precursors and solvents.

Molten salt synthesis is a well-established low-temperature synthesis technique that has recently attracted an increasing amount of interest. It is one of the simplest, most versatile and most cost-effective techniques for preparing single-crystalline particles with the desired composition in a low-melting-point flux. It has been used to synthesize ceramic powders such as Pb(Mg_{1/3}Nb_{2/3})O₃ [11], MgAl₂O₄ [12], LaAlO₃ [13], ZnAl₂O₄ [14] and CoFe₂O₄ [15]. To the best of our knowledge, the synthesis of DyAlO₃ powders by molten salt synthesis has not been reported.

In this work, the molten salt synthesis technique is applied to the synthesis of DyAlO₃ powder using NaCl or KCl salt as the flux. In addition, DyAlO₃ powder is also synthesized by the conventional mixed-oxide method for comparison. The synthesized powders have been characterized using powder X-ray diffraction (XRD) analysis and field emission scanning electron microscopy (FE-SEM), and the synthesis mechanism is discussed.

Experimental Procedure

High-purity commercial Dy₂O₃ (Sigma-Aldrich Co., 99.9%), Al₂O₃ (Alfa Aesar, 99.9%), NaCl (Sigma-Aldrich Co., 99.0%) and KCl (Sigma-Aldrich Co., 99.0%) were used as starting materials. Equimolar amounts of Dy₂O₃ and Al₂O₃ powders were mixed with NaCl or KCl salt using an agate mortar. The weight ratio of salt to oxides was 4 : 1. The mixtures were heated in a high-purity alumina crucible over the temperature range 700 °C - 1300 °C for 3 h. The heating rate was fixed to 10 °C/min.

The reacted mass was washed in hot distilled water, followed by filtration to remove the salts. The washing process was repeated five times. After washing, the

*Corresponding author:
Tel : +82-51-663-4763
Fax: +82-51-622-8452
E-mail: leejs@ks.ac.kr

powders were dried at 120 °C for 4 h.

For comparison, dysprosium aluminate was also prepared by the conventional mixed-oxide method using the same heating schedules.

The XRD technique was employed to identify the phases. XRD was performed on the reacted powders by using a Rigaku D/MAX IIIA diffractometer with Ni-filtered Cu K α radiation. The microstructural morphologies of the raw Dy₂O₃ and Al₂O₃ and the synthesized DyAlO₃ powders were observed using FE-SEM (Model JSM-6700F, JEOL).

Results and Discussion

Fig. 1 shows the XRD patterns of the powders obtained by heating equimolar amounts of Dy₂O₃ and Al₂O₃ powders in NaCl salt at different temperatures. Only two phases, the Dy₂O₃ phase and the Al₂O₃ phase, are observed at 700 °C. DyAlO₃ peaks begin to appear at 800 °C. When the temperature is increased from 800 °C to 1200 °C, the DyAlO₃ peaks increase in height, whereas the heights of the Dy₂O₃ and Al₂O₃ peaks decrease. At 1100 °C, DyAlO₃ is the main phase with a small amount of Dy₂O₃ and no Al₂O₃. Upon a further increase in the temperature to 1300 °C, the Dy₂O₃ phase disappears, and single-phase DyAlO₃ can be observed.

The Dy₄Al₂O₉ phase appears at 800 °C and disappears at 1100 °C. The intermediate Dy₄Al₂O₉ phase is stable oxide phase in the Al₂O₃-Dy₂O₃ system [8, 16]. As the temperature increases, Dy₄Al₂O₉ is transformed into DyAlO₃ according to the reaction: Dy₄Al₂O₉ + Al₂O₃

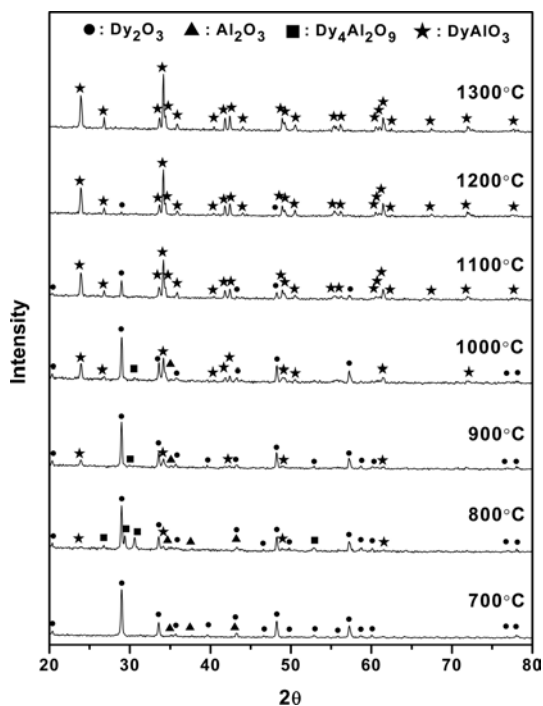


Fig. 1. XRD patterns of the powders heated in NaCl at different temperatures.

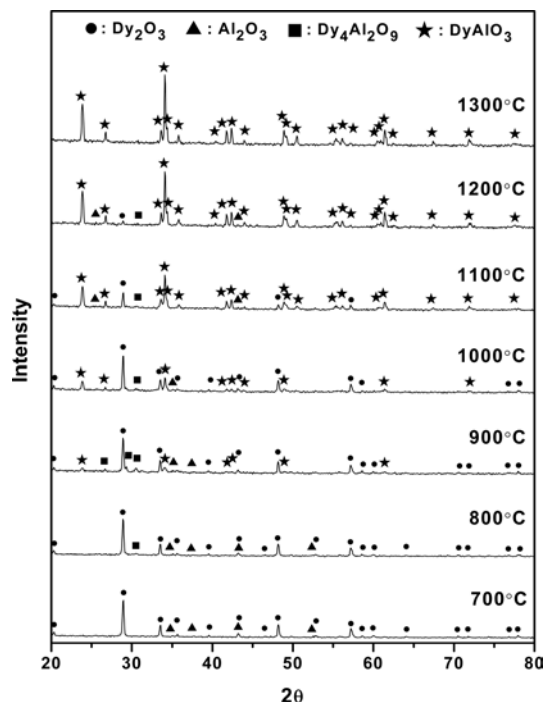


Fig. 2. XRD patterns of the powders heated in KCl at different temperatures.

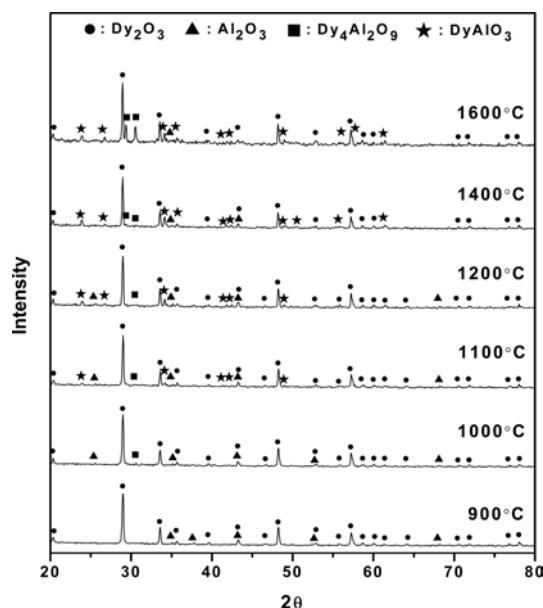
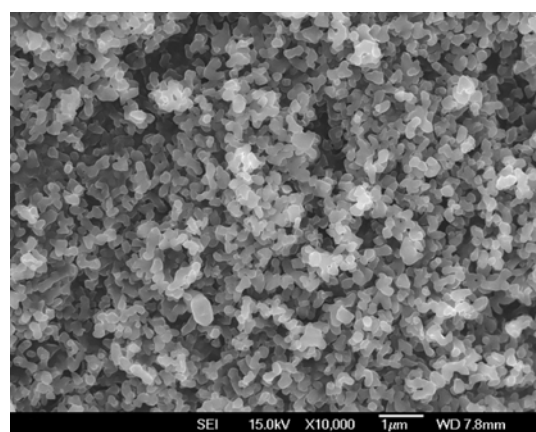


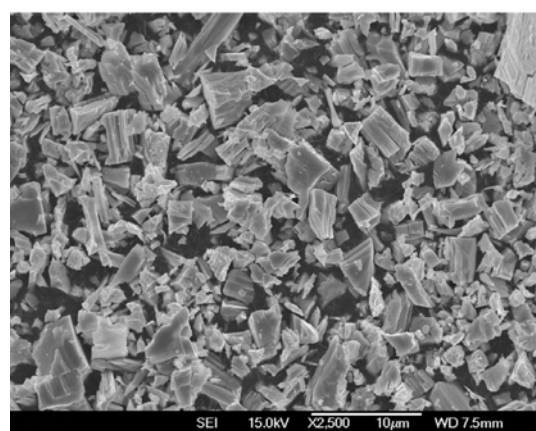
Fig. 3. XRD patterns of the powders prepared by the conventional mixed-oxide method.

→ 4DyAlO₃.

Fig. 2 shows the XRD patterns of the powders obtained by heating equimolar amounts of Dy₂O₃ and Al₂O₃ powders in KCl salt at different temperatures. Only two phases, the Dy₂O₃ phase and the Al₂O₃ phase, are observed at 700 °C. DyAlO₃ peaks began to appear at 900 °C which is by 100 °C higher than in case of using NaCl salt. At 1100 °C, DyAlO₃ is the main phase with small amounts of Dy₂O₃ and Al₂O₃. Upon a



(a)



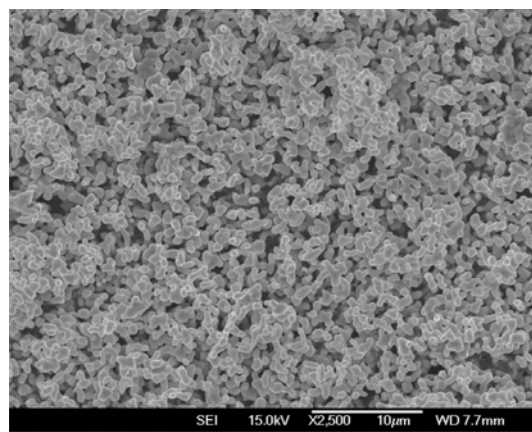
(b)

Fig. 4. FE-SEM micrographs of the as-received (a) Al_2O_3 ($\times 10,000$) and (b) Dy_2O_3 ($\times 2,500$) powders.

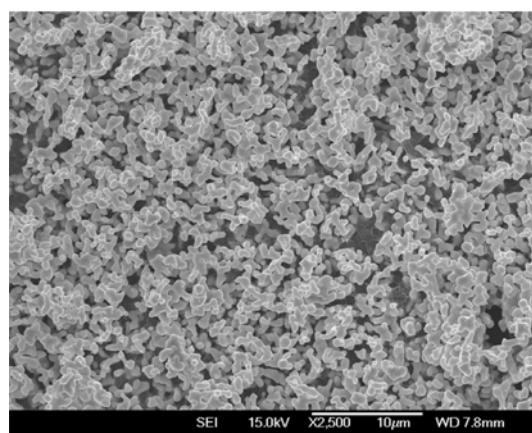
further increase in the temperature up to 1200 °C, the DyAlO_3 peaks increase in height, whereas the heights of the Dy_2O_3 and Al_2O_3 peaks decrease. Single-phase DyAlO_3 is also observed at 1300 °C. The $\text{Dy}_4\text{Al}_2\text{O}_9$ phase appears at 800 °C and disappears at 1300 °C. The XRD patterns of the powders prepared using KCl salt are similar to those found for the NaCl salt. The formation of DyAlO_3 begin to occur at 900 °C and is completed at 1300 °C.

For comparison, dysprosium aluminate was also prepared by the conventional mixed-oxide method. Equimolar amounts of Dy_2O_3 and Al_2O_3 powders were mixed without salt. The XRD patterns of the powders prepared by the conventional mixed-oxide method are shown in Fig. 3. Single-phase DyAlO_3 has not been detected even at 1600 °C. The DyAlO_3 phase begin to be detected at 1100 °C, which is 300 °C higher than when using NaCl salt.

The synthesis temperature for DyAlO_3 , using NaCl or KCl salt was 1300 °C which is much lower than that in the conventional mixed-oxide method. The synthesis temperature for DyAlO_3 could be decreased by about 400 °C, when using NaCl or KCl salt. This suggests



(a)



(b)

Fig. 5. FE-SEM micrographs of the DyAlO_3 powders ($\times 2,500$) synthesized by heating equimolar amounts of Dy_2O_3 and Al_2O_3 powders in (a) NaCl or (b) KCl salts at 1300 °C.

that the presence of NaCl or KCl salt greatly promotes the formation of DyAlO_3 , since a liquid medium can speed up the diffusion rates of the components and lower the formation free energy of the products.

Fig. 4 shows the FE-SEM micrographs of the commercial Al_2O_3 and Dy_2O_3 powders used as starting materials. The as-received Al_2O_3 powders consisted of particles with sizes of much less than 1 µm. The fine Al_2O_3 particles had a shape with curved surfaces. The as-received Dy_2O_3 particles were several micrometers in size and had various shapes.

Fig. 5 shows the FE-SEM micrographs of the DyAlO_3 powders synthesized by heating equimolar amounts of Dy_2O_3 and Al_2O_3 powders in NaCl or KCl salt at 1300 °C. The morphologies of DyAlO_3 powders prepared using NaCl salt are similar to those using KCl salt. The synthesized DyAlO_3 powders retained the shapes of the original Al_2O_3 particles, but their particle size increased up to several micrometers.

Fig. 6 shows the FE-SEM micrograph of the powders prepared by heating equimolar amounts of Dy_2O_3 and Al_2O_3 powders without salt at 1600 °C. The powders prepared without salt consisted of particles with the

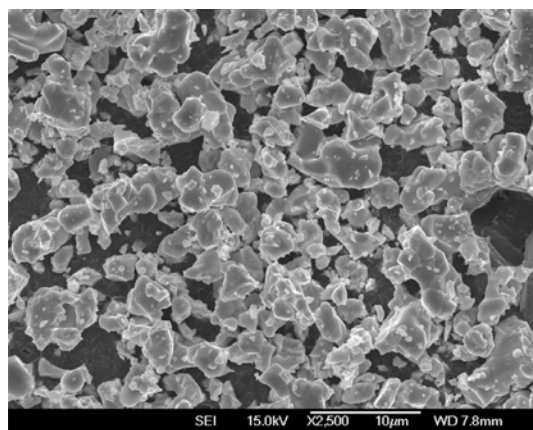


Fig. 6. FE-SEM micrograph of the powders ($\times 2,500$) prepared by heating equimolar amounts of Dy_2O_3 and Al_2O_3 powders without salt at 1600°C .

shapes of the synthesized DyAlO_3 particles and the original Dy_2O_3 particles. The reaction between Dy_2O_3 and Al_2O_3 particles is much slower than in the molten salt synthesis process, because of the limited contacts of the two solid phases.

The melting points of NaCl and KCl salts are 801°C and 771°C , respectively [17]. They are liquid at the experimental temperatures from 900°C to 1300°C . No data on the solubility of Dy_2O_3 in molten NaCl or KCl salt was found, but the solubility of Al_2O_3 in these salts is on the order of 10^{-5} wt\% [14]. It is known that the solubility of Al_2O_3 is much lower [14]. It is expected that Dy_2O_3 would dissolve more easily in the molten salts, diffuse to Al_2O_3 particle surface, and then react with the Al_2O_3 template to form in situ DyAlO_3 which retains the morphology of the starting Al_2O_3 grains. The template formation mechanism [12, 14] is consistent with the observation that the synthesized DyAlO_3 powders retained the shapes of the original Al_2O_3 particles. The increase in the size of the synthesized DyAlO_3 powders can be attributed to the Ostwald ripening [18] that the particles grow up by the expense of the smaller particles.

The present paper is the first successful report on the formation of single-phase DyAlO_3 powders by the molten salt synthesis method using cheap oxide raw materials.

Conclusions

DyAlO_3 powder was synthesized by the molten salt synthesis method at a relatively low temperature of 1300°C , utilizing NaCl or KCl as molten salts. It was

found that the molten salt synthesis method could lower the formation temperature of DyAlO_3 by about 400°C compared to the conventional mixed-oxide method.

The formation temperature and morphologies of DyAlO_3 prepared using NaCl salt were similar to those using KCl salt. Any effect of the salt type on the formation of DyAlO_3 was not seen within these results. The synthesized DyAlO_3 powders retained the morphology of the original Al_2O_3 particles, indicating that a template formation mechanism plays an important role in the molten salt synthesis process.

Acknowledgments

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