Journal of Ceramic Processing Research. Vol. 15, No. 1, pp. 17~20 (2014)

J O U R N A L O F
Ceramic Processing Research

Molten salt synthesis of $NdAlO_3$ powders

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$NdAlO_3$ powder was synthesized by reacting equimolar amounts of Nd_2O_3 and Al_2O_3 powders in NaCl or KCl salt. The synthesis temperature for $NdAlO_3$, using NaCl or KCl salt was 1100 ºC which is 500 ºC lower than that in the conventional mixed-oxide method. The synthesized $NdAlO_3$ 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 of $NdAlO_3$.

Key words: molten salt synthesis, powder, $NdAlO_3$.

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 re-frigeration materials, substrates for high-temperature superconductor deposition, catalyst supports and thermal barrier coatings [2, 3]. $NdAlO_3$ has potential applications as microwave components [4], substrates for high-temperature superconducting microwave devices [4, 5], luminescent devices [6] and diffusion barriers in solid-oxide fuel cell structures [7].

$NdAlO_3$ is normally synthesized by the solid-state reaction of neodymia and alumina powders. This process involves extensive mechanical mixing and lengthy heat treatments at relatively high temperatures (~ 1600 ºC) [8].

Recently, wet-chemical techniques, such as sol-gel [6], coprecipitation [9], combustion synthesis [10] and polymer complex method [11] have been applied to prepare $NdAlO_3$ powders.

These wet-chemical techniques have led to fine $NdAlO_3$ 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 $Pb(Mg_{1/3}Nb_{2/3})O_3$ [12], $MgAl_2O_4$ [13], $LaAlO_3$ [14], $ZnAl_2O_4$ [15] and $CoFe_2O_4$ [16]. To the best of our knowledge, the synthesis of $NdAlO_3$ powders by molten salt synthesis has not been reported.

In this work, the molten salt synthesis technique is applied to the synthesis of $NdAlO_3$ powder using NaCl or KCl salt as the flux. In addition, $NdAlO_3$ 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 Nd_2O_3 (Sigma-Aldrich Co., 99.9%), Al_2O_3 (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 Nd_2O_3 and Al_2O_3 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 ºC-1200 ºC for 3 hrs. The heating rate was fixed to 10 ºC/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 powders were dried at 120 ºC for 4 hrs. For comparison, neodymium 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-

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filtered Cu Kα radiation. The microstructural morphologies of the raw Nd_2O_3 and Al_2O_3 and the synthesized $NdAlO_3$ powders were observed using FE-SEM (JSM-6700F, JEOL, Japan).

Results and Discussion

Fig. 1 shows the XRD patterns of the powders obtained by heating equimolar amounts of Nd_2O_3 and Al_2O_3 powders in NaCl salt at different temperatures. Only two phases, the $Nd(OH)_3$ phase and the Al_2O_3 phase, are observed at 700 °C. $NdAlO_3$ peaks begin to appear at 800 °C. When the temperature is increased from 800 °C to 1000 °C, the $NdAlO_3$ peaks increase in height, whereas the heights of the $Nd(OH)_3$ and Al_2O_3 peaks decrease. At 1000 °C, $NdAlO_3$ is the main phase with a small amount of $Nd(OH)_3$ and Al_2O_3. Upon a further increase in the temperature to 1100 °C, the $Nd(OH)_3$ and Al_2O_3 phases disappear, and single-phase $NdAlO_3$ can be observed. It should be noted that the $Nd(OH)_3$ phase instead of the Nd_2O_3 phase is observed. This is caused by the fact that in washing process of the reacted mass, unreacted Nd_2O_3 is transformed into $Nd(OH)_3$ according to the reaction: $Nd_2O_3 + 3H_2O \rightarrow 2Nd(OH)_3$.

To confirm the transformation into $Nd(OH)_3$, XRD was performed on the as-received Nd_2O_3 powders and the Nd_2O_3 powders washed with water. Fig. 2 shows the XRD patterns of (a) the commercial Nd_2O_3 powders and (b) the Nd_2O_3 powders washed with water. The patterns of the hexagonal Nd_2O_3 phase are shown in the as-received Nd_2O_3 powders, but the

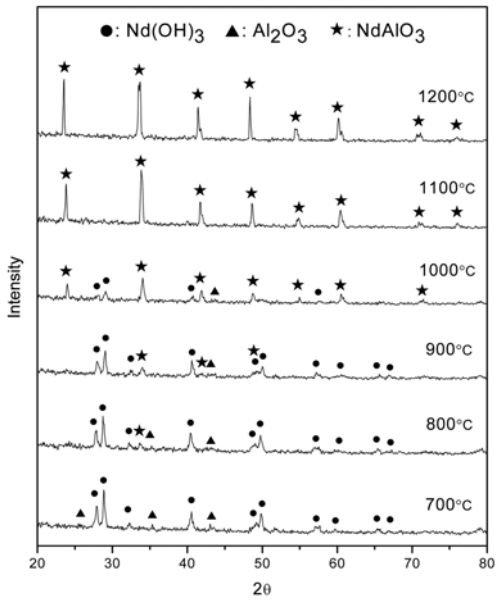

Fig. 1. XRD patterns of the powders heated in NaCl at different temperatures.

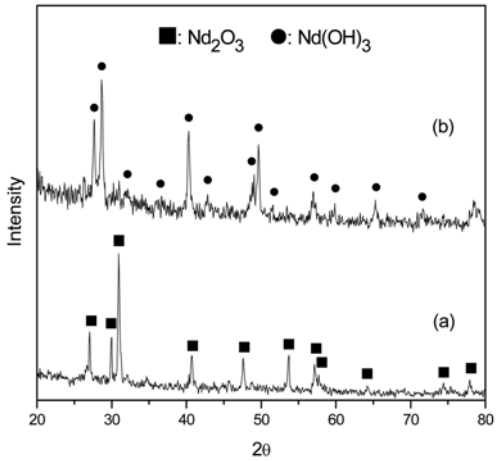

Fig. 2. XRD patterns of the Nd_2O_3 powders; (a) as-received and (b) washed with water.

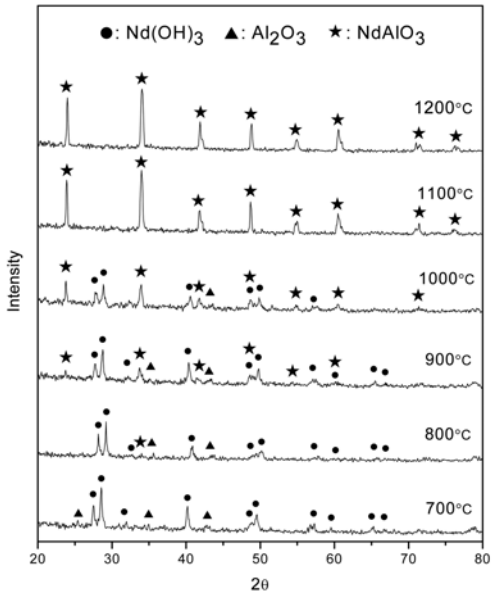

Fig. 3. XRD patterns of the powders heated in KCl at different temperatures.

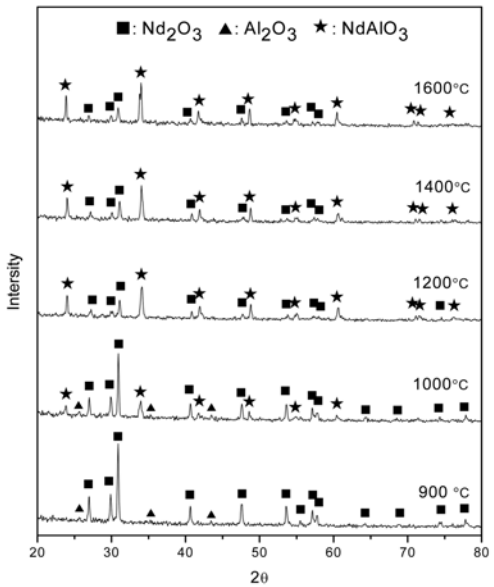

Fig. 4. XRD patterns of the powders prepared by the conventional mixed-oxide method.

patterns of the $Nd(OH)_3$ phase are shown in the Nd_2O_3 powders washed with water. Fig. 3 shows the XRD patterns of the powders obtained by heating equimolar amounts of Nd_2O_3 and Al_2O_3 powders in KCl salt at different temperatures. The XRD patterns of the powders prepared using KCl salt are similar to those found for the NaCl salt. The formation of $NdAlO_3$ begins to occur at 800 °C and is completed at 1100 °C.

For comparison, neodymium aluminate was also prepared by the conventional mixed-oxide method. Equimolar amounts of Nd_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. 4. Single-phase $NdAlO_3$ has not been detected even at 1600 °C. The $NdAlO_3$ phase begin to be detected at 1000 °C, which is 200 °C higher than when using NaCl or KCl salt. At 1100 °C, $NdAlO_3$ is the main phase with a small amount of Nd_2O_3 and no Al_2O_3.

The synthesis temperature for $NdAlO_3$, using NaCl or KCl salt was 1100 °C which is much lower than that in the conventional mixed-oxide method. The synthesis temperature for $NdAlO_3$ could be decreased by about 500 °C, when using NaCl or KCl salt. This suggests that the presence of NaCl or KCl salt greatly promotes the formation of $NdAlO_3$, since a liquid medium can speed up the diffusion rates of the components and lower the formation free energy of the products.

Fig. 5 shows the FE-SEM micrographs of the commercial Al_2O_3 and Nd_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 Nd_2O_3 particles were several micrometers in size and had various shapes. Fig. 6 shows the FE-SEM micrographs of the $NdAlO_3$ powders synthesized by heating equimolar amounts of Nd_2O_3 and Al_2O_3 powders in NaCl or KCl salt at 1100 °C. The morphologies of $NdAlO_3$ powders prepared using NaCl salt are similar to those using KCl salt. The synthesized $NdAlO_3$ powders retained the shapes of the original Al_2O_3 particles, but their particle size increased up to approximately 1 μm. Fig. 7 shows the FE-SEM micrograph of the powders prepared by heating equimolar amounts of Nd_2O_3 and Al_2O_3 powders without salt at 1600 °C. The powders prepared

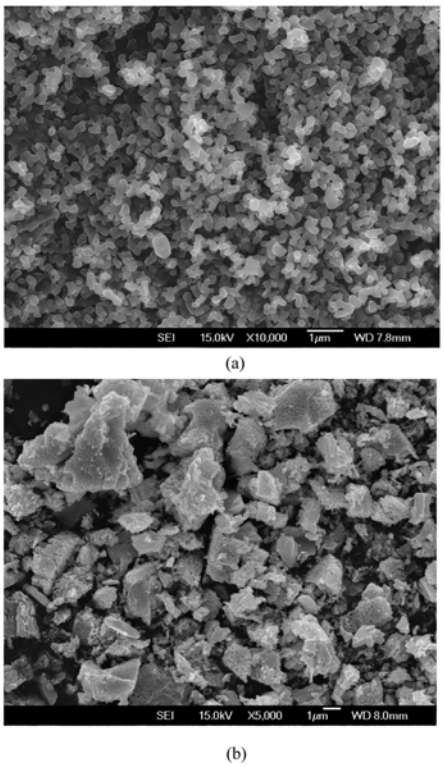

Fig. 5. FE-SEM micrographs of the as-received; (a) Al_2O_3 (x10,000) and (b) Nd_2O_3 (x5,000) powders.

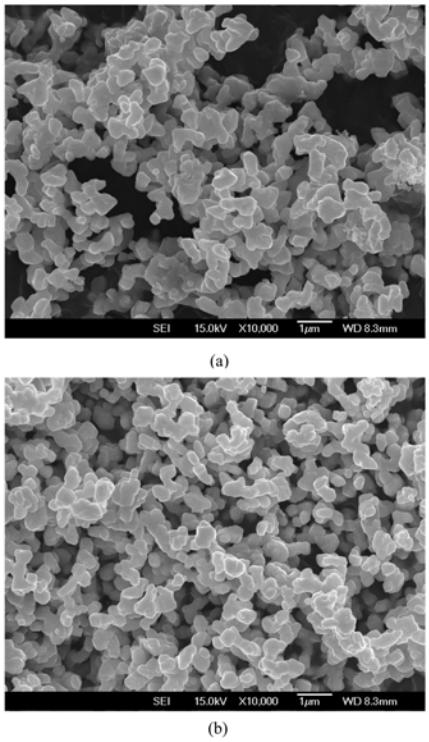

Fig. 6. FE-SEM micrographs of the $NdAlO_3$ powders (x10,000) synthesized by heating equimolar amounts of Nd_2O_3 and Al_2O_3 powders in (a) NaCl or (b) KCl salts at 1100 °C.

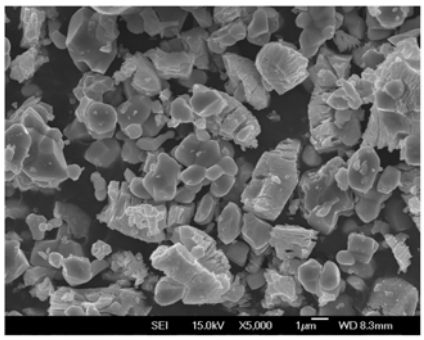

Fig. 7. FE-SEM micrograph of the powders (x5,000) prepared by heating equimolar amounts of Nd_2O_3 and Al_2O_3 powders without salt at 1600 °C.

without salt consisted of particles with the shapes of the synthesized $NdAlO_3$ particles and the original Nd_2O_3 particles. The reaction between Nd_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 1200 °C. No data on the solubility of Nd_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.% [15]. It is known that the solubility of Al_2O_3 is much lower [15]. It is expected that Nd_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 $NdAlO_3$ which retains the morphology of the starting Al_2O_3 grains. The template formation mechanism [13, 15] is consistent with the observation that the synthesized $NdAlO_3$ powders retained the shapes of the original Al_2O_3 particles.

The increase in the size of the synthesized $NdAlO_3$ 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 $NdAlO_3$ powders by the molten salt synthesis method using cheap oxide raw materials.

Conclusions

$NdAlO_3$ powder was synthesized by the molten salt synthesis method at a relatively low temperature of 1100 °C, utilizing NaCl or KCl as molten salts. It was found that the molten salt synthesis method could lower the formation temperature of $NdAlO_3$ by about 500 °C compared to the conventional mixed-oxide method.

The formation temperature and morphologies of $NdAlO_3$ prepared using NaCl salt were similar to those using KCl salt. Any effect of the salt type on the formation of $NdAlO_3$ was not seen within these results. The synthesized $NdAlO_3$ 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

This work was supported by Kyungsung University Research Grants in 2014.

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