Journal of Ceramic Processing Research. Vol. 18, No. 5, pp. 385~388 (2017)

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

Preparation of $EuAlO_3$ powders by molten salt method

Joo-Sin Lee*
Department of Advanced Materials Engineering, Kyungsung University, Busan 608-736, Korea

In this work, the molten salt synthesis technique was applied to the synthesis of $EuAlO_3$ powder using NaCl or KCl salt as the flux. $EuAlO_3$ powder was synthesized by reacting equimolar amounts of Eu_2O_3 and Al_2O_3 powders in NaCl or KCl salt. The synthesis temperature for $EuAlO_3$ using NaCl or KCl salt was 1200 °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 $EuAlO_3$ 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 $EuAlO_3$.

Key words: molten salt synthesis, powder, $EuAlO_3$.

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 refrigeration materials, substrates for high-temperature superconductor deposition, catalyst supports and thermal barrier coatings [2,3]. $EuAlO_3$ has potential applications as phosphors [4-6] and substrates for high-temperature superconductor deposition [7].

$EuAlO_3$ is normally synthesized by the solid-state reaction of europia and alumina powders. This process involves extensive mechanical mixing and lengthy heat treatments at relatively high temperatures (> 1600 °C) [8].

To overcome these drawbacks, several low-temperature wet-chemical synthesis techniques, such as modified sol-gel [8], polymer complex method [9] and combustion synthesis [4-6] have been applied to prepare $EuAlO_3$ powders. Petrov et al. [8] prepared nanocrystalline $EuAlO_3$ powders at 950 °C by the modified sol-gel method, with an average particle size of 50 nm. The fully crystalline single-phase $EuAlO_3$ was obtained at 1150 °C for 2 hrs via the polymer complex method by Takata et al. [9]. Hirata et al. [4] obtained nanocrystalline $EuAlO_3$ powders using low-temperature combustion synthesis.

These wet-chemical techniques have led to fine $EuAlO_3$ 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 of perovskite-type rare-earth aluminates such as $LaAlO_3$ [10], $GdAlO_3$ [11] and $YAlO_3$ [12, 13]. To the best of our knowledge, the synthesis of $EuAlO_3$ powders by molten salt synthesis has not been reported.

In this work, the molten salt synthesis technique is applied to the synthesis of $EuAlO_3$ powder using NaCl or KCl salt as the flux. In addition, $EuAlO_3$ powder is also synthesized by the conventional mixed-oxide method for comparison. The synthesized powders have been characterized using powder XRD analysis and FE-SEM, and the synthesis mechanism is discussed.

Experimental Procedure

High-purity commercial Eu_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 Eu_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 °C-1200 °C for 3 hrs. The heating rate was fixed to 10 °C/min. The

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

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, europium 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 Kα radiation. The microstructural morphologies of the raw Eu_2O_3 and Al_2O_3 and the synthesized $EuAlO_3$ 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 Eu_2O_3 and Al_2O_3 powders in NaCl salt at different temperatures. Only two phases, the Eu_2O_3(cubic) phase and the Al_2O_3 phase, are observed at 700 ºC. $EuAlO_3$ peaks begin to appear at 900 ºC. When the temperature is increased from 900 ºC to 1100 ºC, the $EuAlO_3$ peaks increase in height, whereas the heights of the Eu_2O_3 and Al_2O_3 peaks decrease. At 1100 ºC, $EuAlO_3$ is the main phase with small amounts of Eu_2O_3 and Al_2O_3. Upon a further increase in the temperature to 1200 ºC, the Eu_2O_3 and Al_2O_3 phases disappear, and single-phase $EuAlO_3$ can be observed.

The $Eu_4Al_2O_9$ phase appears at 800 ºC and disappears at 1200 ºC. The intermediate $Eu_4Al_2O_9$ phase is stable oxide phase in the Al_2O_3-Eu_2O_3 system [14, 15]. As the temperature increases, $Eu_4Al_2O_9$ is transformed into $EuAlO_3$ according to the reaction: $Eu_4Al_2O_9 + Al_2O_3 \rightarrow 4EuAlO_3$.

Fig. 2 shows the XRD patterns of the powders obtained by heating equimolar amounts of Eu_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 $EuAlO_3$ begin to occur at 900 ºC and is completed at 1200 ºC. The $Eu_4Al_2O_9$ phase appears at 800 ºC and disappears at 1200 ºC.

For comparison, europium aluminate was also prepared by the conventional mixed-oxide method. Equimolar amounts of Eu_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 $EuAlO_3$ has not been detected even at 1600 ºC. The $EuAlO_3$ phase begin to be detected at 1000 ºC, which is 100 ºC higher than when using NaCl salt or KCl salt. At 1200 ºC, $EuAlO_3$ is the main phase with small amounts of Eu_2O_3(monoclinic) and Al_2O_3.

Cubic Eu_2O_3 has been detected up to 1000 ºC. The Eu_2O_3 transforms from the cubic to the monoclinic form at 1100 ºC [16]. Monoclinic Eu_2O_3 exists up to 1600 ºC.

The synthesis temperature for $EuAlO_3$, using NaCl or

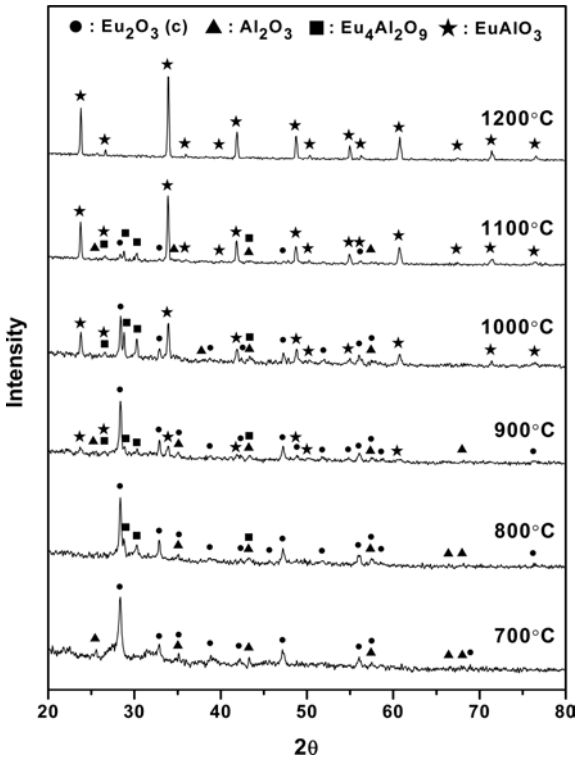

Fig. 1. XRD patterns of the powders heated in NaCl at different temperatures.

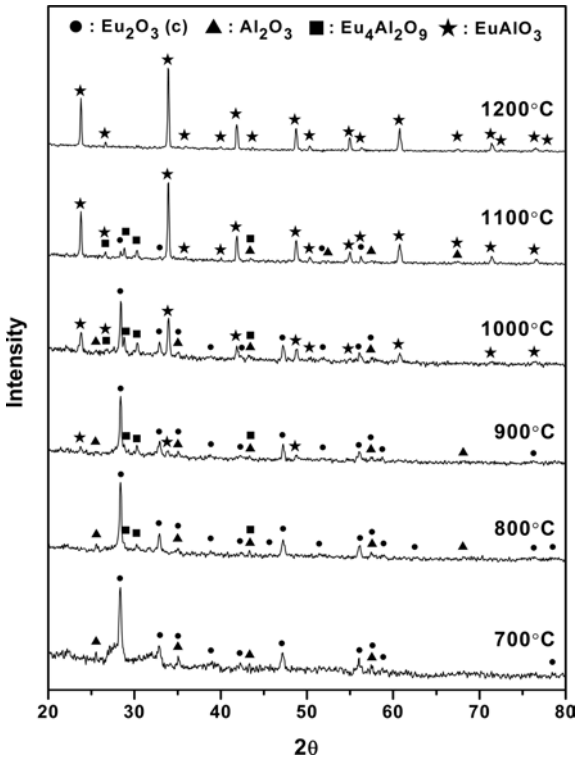

Fig. 2. XRD patterns of the powders heated in KCl at different temperatures.

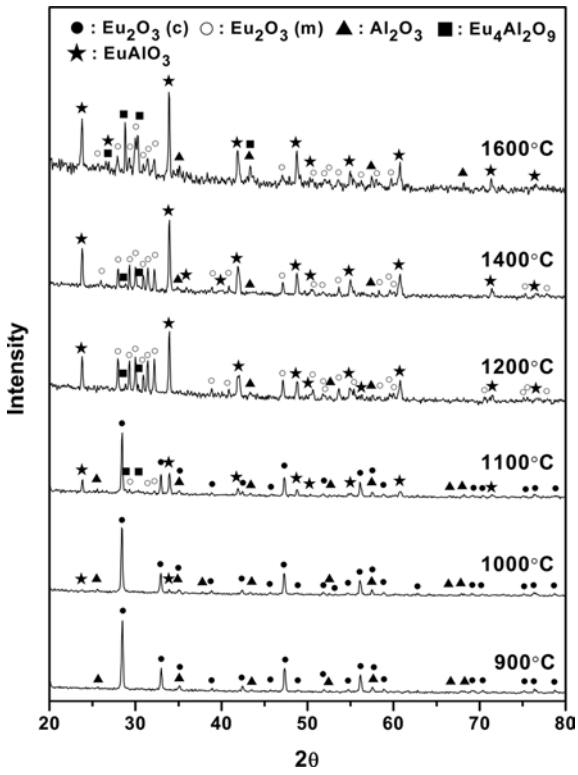

Fig. 3. XRD patterns of the powders prepared by the conventional mixed-oxide method.

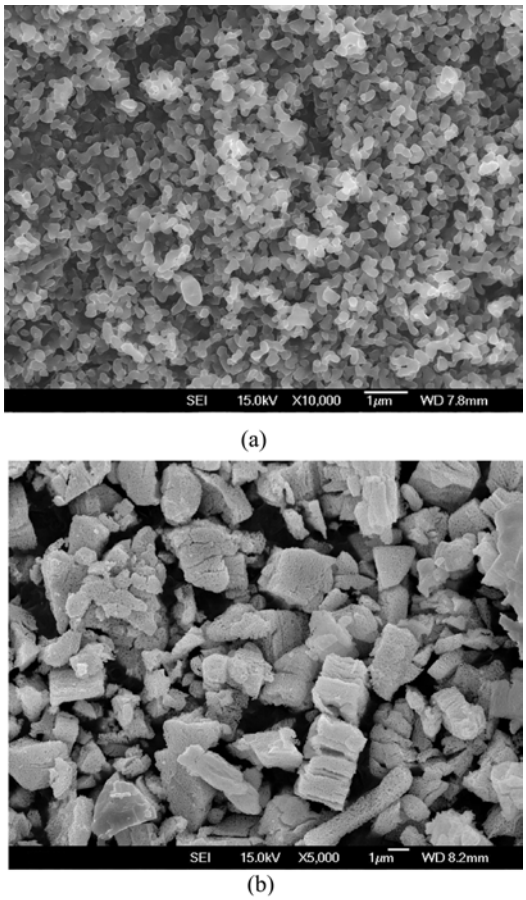

Fig. 4. FE-SEM micrographs of the as-received (a) Al_2O_3 (x10,000) and (b) Eu_2O_3 (x5,000) powders.

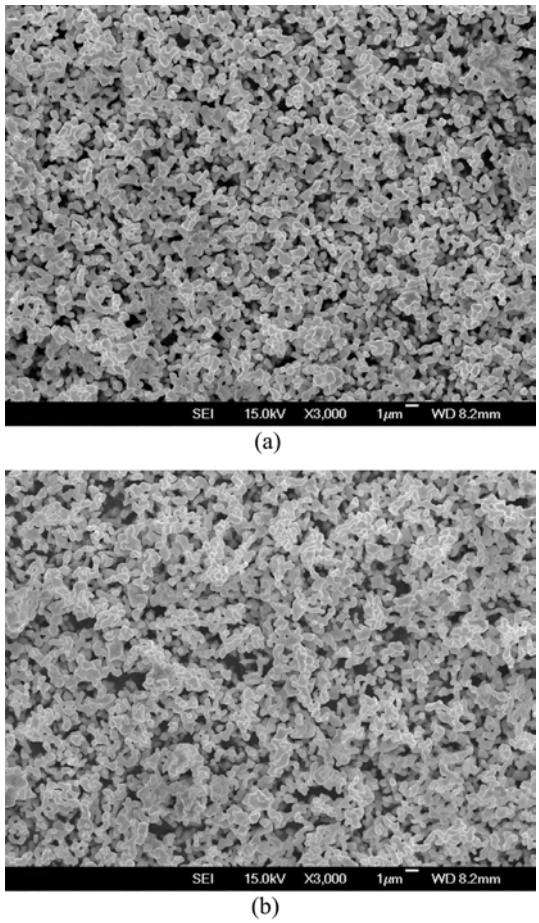

Fig. 5. FE-SEM micrographs of the $EuAlO_3$ powders (x3,000) synthesized by heating equimolar amounts of Eu_2O_3 and Al_2O_3 powders in (a) NaCl or (b) KCl salts at 1200 ºC.

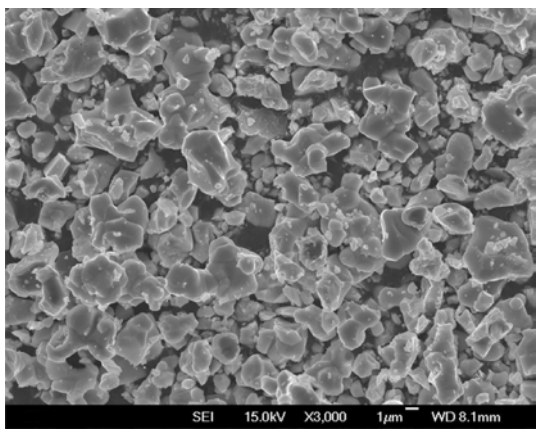

Fig. 6. FE-SEM micrograph of the powders (x3,000) prepared by heating equimolar amounts of Eu_2O_3 and Al_2O_3 powders without salt at 1600 ºC.

KCl salt was 1200 ºC which is much lower than that in the conventional mixed-oxide method. The synthesis temperature for $EuAlO_3$ could be decreased by about 400 ºC, when using NaCl or KCl salt. This suggests that the presence of NaCl or KCl salt greatly promotes the formation of $EuAlO_3$, 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 Eu_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 Eu_2O_3 particles were several micrometers in size and had various shapes.

Fig. 5 shows the FE-SEM micrographs of the $EuAlO_3$ powders synthesized by heating equimolar amounts of Eu_2O_3 and Al_2O_3 powders in NaCl or KCl salt at 1200 °C. The morphologies of $EuAlO_3$ powders prepared using NaCl salt are similar to those using KCl salt. The synthesized $EuAlO_3$ 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 Eu_2O_3 and Al_2O_3 powders without salt at 1600 °C. The powders prepared without salt consisted of particles with the shapes of the synthesized $EuAlO_3$ particles and the original Eu_2O_3 particles. The reaction between Eu_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 Eu_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% [18]. It is known that the solubility of Al_2O_3 is much lower [18].

It is expected that Eu_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 $EuAlO_3$ which retains the morphology of the starting Al_2O_3 grains.

The template formation mechanism [18, 19] is consistent with the observation that the synthesized $EuAlO_3$ powders retained the shapes of the original Al_2O_3 particles.

The increase in the size of the synthesized $EuAlO_3$ powders can be attributed to the Ostwald ripening [20] 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 $EuAlO_3$ powders by the molten salt synthesis method using cheap oxide raw materials.

Conclusions

$EuAlO_3$ powder was synthesized by the molten salt synthesis method at a relatively low temperature of 1200 °C, utilizing NaCl or KCl as molten salts. It was found that the molten salt synthesis method could lower the formation temperature of $EuAlO_3$ by about 400 °C compared to the conventional mixed-oxide method.

The formation temperature and morphologies of $EuAlO_3$ prepared using NaCl salt were similar to those using KCl salt. Any effect of the salt type on the formation of $EuAlO_3$ was not seen within these results.

The synthesized $EuAlO_3$ 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 2017.

References

1. S. Cizauskaite, V. Reichlova, G. Nenartaviciene, A. Beganskiene, J. Pinkas and A. Kareiva, Mater. Chem. Phys. 102 (2007) 105-110.
2. P. Voňka and J. Leitner, J Solid State Chem. 182 (2009) 744-748.
3. A. Sinha, B.P. Sharma, H. Näfe and P. Gopalan, J. Alloys Compd. 502 (2010) 396-400.
4. G.A. Hirata, F.E. Ramos and J. McKittrick, Opt. Mater. 27 (2005) 1301-1304.
5. C.E. Rodríguez-García, N. Perea-López and G.A. Hirata, Adv. Mater. Sci. Eng. 11 (2011) 790517.
6. C.R. García, L.A. Diaz-Torres, J. Oliva and G.A. Hirata, Opt. Mater. 37 (2014) 520-524.
7. I. Yamaguchi, T. Manabe, M. Sohma, T. Tsuchiya, Y. Yamaguchi, S. Suzuki, T. Kumagai and S. Mizuta, Physica C 382 (2002) 269-275.
8. D. Petrov, B. Angelov and V. Lovchinov, J. Alloys Compd. 509 (2011) 5038-5041.
9. H. Takata, M. Iiduka, Y. Notsu and M. Harada, J. Alloys Compd. 408-412 (2006) 1190-1192.
10. Z. Li, S. Zhang and W.E. Lee, J. Eur. Ceram. Soc. 27 (2007) 3201-3205.
11. J.S. Lee, J. Ceram. Process. Res. 13 (2012) 627-630.
12. Z. Liu, J. Ma, Y. Sun, Z. Song, J. Fang, Y. Liu, C. Gao and J. Zhao, Ceram. Int. 36 (2010) 2003-2006.
13. J.S. Lee, Mater. Sci.-Poland 31 (2013) 240-245.
14. M. Mizuno, T. Yamada and T. Noguchi, Yogyo-Kyokai-Shi 85 (1977) 543-548.
15. P. Wu and A.D. Pelton, J. Alloys Compd. 179 (1992) 259-287.
16. B. Antic, M. Mitric and D. Rodic, J. Phys:Condens. Matter 9 (1997) 365-374.
17. R.S. Roth, M.A. Clevinger and D. Mckenna, Phase Diagrams for Ceramists, Am. Ceram. Soc., 1984.
18. Z. Li, S. Zhang and W.E. Lee, J. Eur. Ceram. Soc. 27 (2007) 3407-3412.
19. S. Zhang, D.D. Jayaseelan, G. Bhattacharya and W.E. Lee, J. Am. Ceram. Soc. 89 (2006) 1724-1726.
20. W. Ostwald, Z. Phys. Chem. 34 (1901) 495-512.