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# Molten salt synthesis of $LaAlO_3$ powder at low temperatures

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## Abstract

Rhombohedral $LaAlO_3$ powder was synthesised by reacting equimolar $La_2O_3$ and $Al_2O_3$ in a molten KF–KCl eutectic salt for 3 h between 630 and 800 °C. The lowest synthesis temperature (630 °C) is about 1000 °C lower than that of conventional mixed oxide synthesis, and close to or lower than those used by most wet chemical methods. The $LaAlO_3$ particle size increased from <3 to 3–7 μm with increasing temperature from 630 to 700 °C, but changed little on further increasing temperature to 800 °C. On the other hand, it decreased with increasing salt/oxide weight ratio from 1:1 to 6:1. The "dissolution–precipitation" mechanism played a dominant role in the molten salt synthesis of $LaAlO_3$.

*Keywords:* Powders-chemical preparation; Grain size; Lanthanum aluminate; Perovskites; Functional applications

## 1. Introduction

Single crystal lanthanum aluminate ($LaAlO_3$) is widely used as substrates and electrically insulating buffers for depositing high-temperature superconducting films due to its high quality factor and excellent lattice and thermal expansion matching ability.[1,2] Its use as a gate dielectric material has also been explored.[3,4] In addition, $LaAlO_3$ powder has been studied as a catalyst for oxidative coupling of methane and hydrogenation and hydrogenolysis of hydrocarbons due to its high catalytic activity.[5]

$LaAlO_3$ is generally synthesised via a solid–solid reaction route (conventional mixed oxide synthesis (CMOS)) at >1550 °C.[2] Besides the high synthesis temperature, extensive crushing, grinding and milling are often required to generate sufficient reactivity and chemical homogeneity in the raw materials and product powders. To overcome these drawbacks, several low temperature wet chemical synthesis techniques have been developed. One of these is co-precipitation of lanthanum- and aluminium-bearing precursors followed by calcining the precipitates. Depending on the test conditions, synthesis temperatures for completely converting the co-precipitates to $LaAlO_3$ varied over a large range (from 700 to 1350 °C).[6–9] A similar low temperature synthesis route is sol–gel processing.[10–12] Sahu *et al.*[12] prepared nanosized $LaAlO_3$ at as low as 600 °C via a sol–gel process using aluminium and lanthanum chlorides as precursors. *In situ* polymerisation is another low temperature technique for synthesis of reactive $LaAlO_3$ powder, which could decrease the synthesis temperature to 700–900 °C.[13,14] In addition to these wet chemical techniques, several other low temperature routes for synthesis of $LaAlO_3$ have been investigated, including self-igniting combustion,[15] PVA (polyvinyl alcohol) evaporation route[16] and mechanochemical alloying (MA).[17]

Although the techniques described above could substantially decrease the synthesis temperature of $LaAlO_3$, they suffer from various drawbacks. For example, wet chemical synthesis techniques often use expensive and environmentally unfriendly organic/inorganic precursors and solvents, so are applicable only to niche cases and for small scale products. The MA technique, besides requiring extensive high energy ball milling and post-milling heat-treatment, suffers from a very limited production capacity (only a few grams).

In this work, the molten salt synthesis (MSS) technique has been used to synthesise $LaAlO_3$ powder at low temperatures and using cheap oxide raw materials. The synthesised $LaAlO_3$ powders have been characterised using powder X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM/EDS), and the synthesis mechanism discussed based on the results.

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## 2. Experimental procedure

$La_2O_3$ powder (Sigma–Aldrich, ~1 μm, ≥99.9% pure), low-soda calcined Bayer-derived (i.e. precipitated) $Al_2O_3$ powder (Almatis, D50 = 0.80 μm, 99.8% pure with 0.08% $Na_2O$), ACS reagent KCl (Aldrich, ≥99.0% pure) and reagent grade KF (Aldrich, 98% pure) were used as starting materials. The $La_2O_3$ powder used is produced via solvent extraction after the trivalent rare-earth elements are separated from the insoluble rare-earth fraction in the cracking stage of bastnasite ((Ce, La)$CO_3$F) mineral. Equimolar $La_2O_3$ and $Al_2O_3$ powders were mixed in an agate mortar with various amounts of KF–KCl eutectic salt. The molar ratio of KF to KCl in the eutectic salt was 46.7/53.3, whereas the weight ratio of KF + KCl to $La_2O_3 + Al_2O_3$ (referred to as the salt/oxide ratio) varied from 1:1 to 6:1. The samples were heated to 630, 700 and 800 °C, respectively and held at temperature for 3 h. The heating and cooling rates were 3 and 5 °C/min, respectively. After cooling to room temperature, the reacted mass was washed with hot distilled water for 2 h followed by filtration to remove the salts, and this process was repeated for five times. The resultant powder was oven-dried at 105 °C for 4 h before further characterisation.

Phases in the resultant powders were identified by XRD analysis (Siemens D500 reflection diffractometer). Patterns were recorded at 30 mA and 40 kV using Ni-filtered Cu Kα radiation (λ = 1.54178 Å). The scan rate (2θ) was 1°/min at the step size of 0.02°. The impurity levels of K, F and Cl originating from the salts used were checked by XRF (X-ray fluorescence) spectrometry with diluted sample beads. The diluted sample beads were prepared by the following procedures: dry powder (0.7500 g) was transferred to a platinum crucible. $Li_2B_4O_7$ (7.5 g) were added as flux and 0.05 g of LiBr as releasing agent. These compounds were thoroughly mixed with the sample in the crucible.

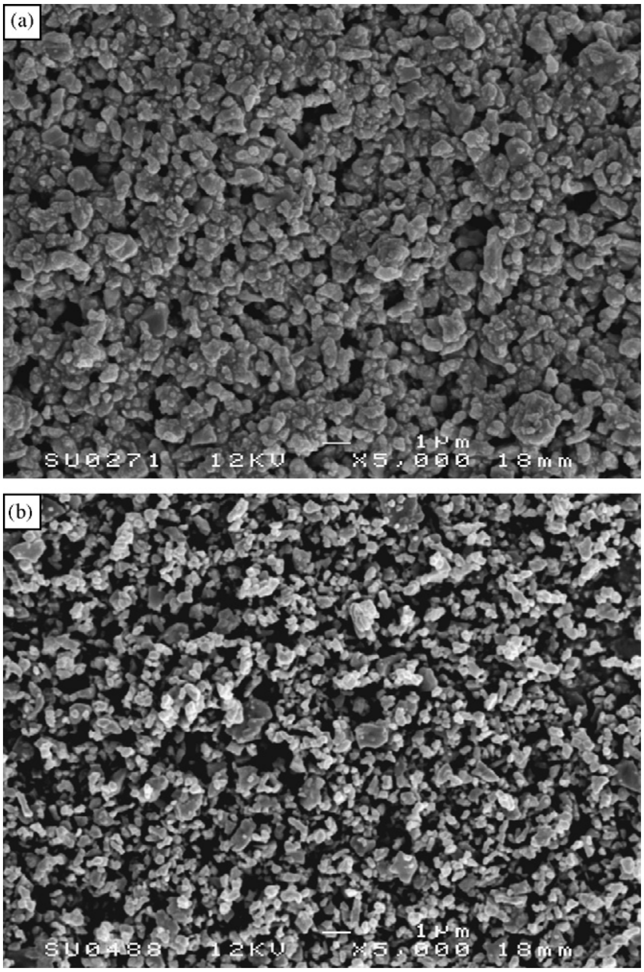

Fig. 1. SEI micrographs of as-received raw (a) $La_2O_3$ and (b) $Al_2O_3$ powders.

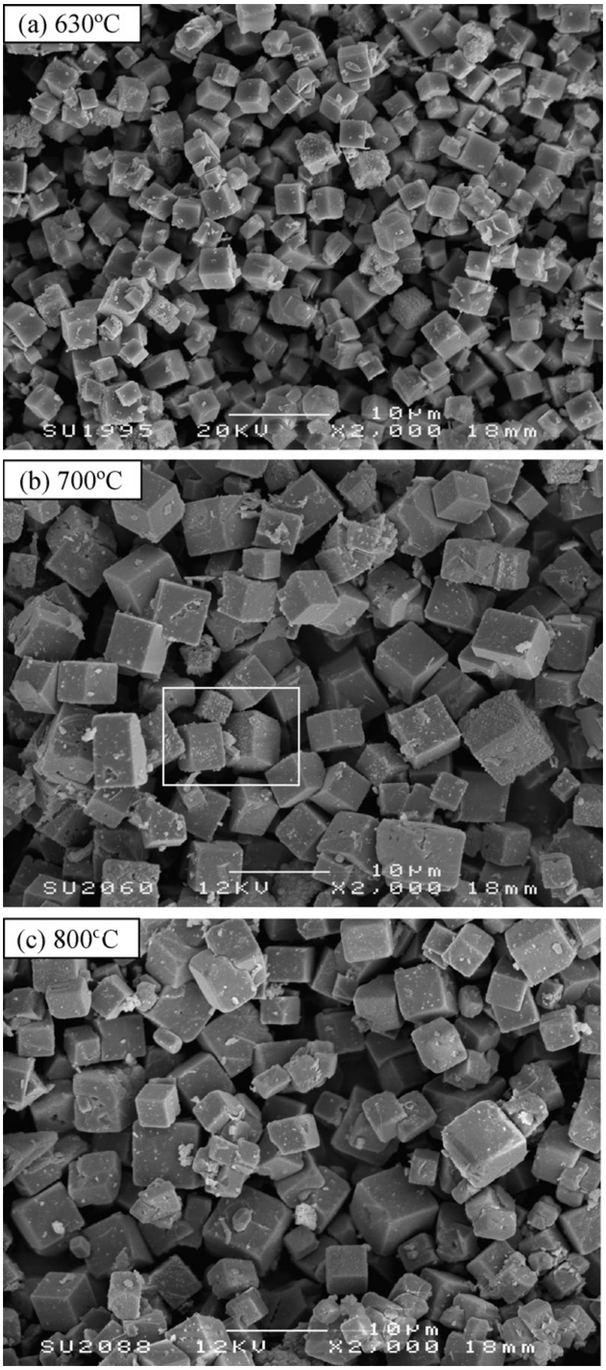

Fig. 2. SEI micrographs of $LaAlO_3$ particles synthesised for 3 h using salt/oxide weight ratio of 3:1 at (a) 630 °C, (b) 700 °C and (c) 800 °C, respectively. Cuboidal and smaller non-cuboidal crystals were observed. Higher magnification micrograph of the rectangular zone in (b) is shown in Fig. 3.

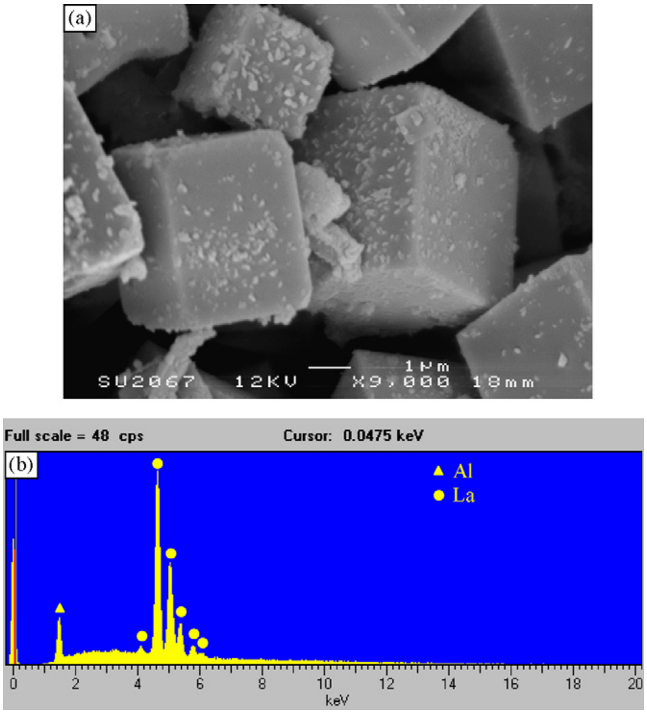

Fig. 3. Higher magnification SEI of area in box in Fig. 2b (a) revealing that some submicron-sized $LaAlO_3$ particles were present on the surfaces of cuboidal $LaAlO_3$ crystals. EDS spectrum (b) of cuboidal crystals, submicron particles on the surface of cuboidal grains and small non-cuboidal grains.

Beads were formed by holding the sample over a flame for 14 min. Once the sample was melted, the content of the crucible was cast in a platinum mould and allowed to cool. XRF analysis was carried out with a Bruker AXS SRS 3400 spectrometer (Bruker AXS, Karlsruhe, Germany). Microstructural morphologies of the as-received $La_2O_3$ and $Al_2O_3$ and the synthesised $LaAlO_3$ powders were observed using secondary electron imaging (SEI) mode in a SEM (JEOL6400, Japan). Energy dispersive spectroscopy (EDS) analysis of the elements in the resultant powders was carried out using the attached turreted Pentafet detector and ISIS 300 processing unit.

## 3. Results

### 3.1. *As-received raw materials*

The as-received $La_2O_3$ powder consisted mainly of small (around 1 µm) spheroidal particles, most of which are agglomerated (Fig. 1(a)). Compared to the as-received $La_2O_3$, better dispersion was seen in the as-received $Al_2O_3$ powder (Fig. 1(b)). The majority of the $Al_2O_3$ particles were <1 µm, but about 10% were up to 2 µm in size.

### 3.2. *Effect of heating temperature on synthesis*

XRD (not shown) of powders from samples (with salt/oxide ratio of 3:1) heated for 3 h at 630, 700 and 800 °C, respectively revealed that only $LaAlO_3$ with a rhombohedral perovskite crystal structure (ICDD card number 31-2) and no other phases were identified in any samples. Fig. 2 shows SEM of the synthesised $LaAlO_3$ powders. At 630 °C, the powder consisted mainly of <3 µm cuboidal particles, although a few non-cuboidal particles were also observed. On increasing temperature to 700 °C, the cuboidal particles became larger (3–7 µm). On further increasing temperature to 800 °C, the particle size changed very little, but the edges of the cuboidal crystals appeared less sharp. Higher magnification SEM of a sample produced at 700 °C further reveals many sub-micron particles on some of the large cuboidal particles (Fig. 3a). EDS (Fig. 3(b)) revealed that these small particles have an identical (La and Al) composition to that of cuboidal and non-cuboidal grains. This along with XRD confirmed that they all were $LaAlO_3$.

### 3.3. *Effect of salt/oxide ratio on synthesis*

XRD of the powders with different salt/oxide ratios heated for 3 h at 700 °C, similar to the case of varying temperature (see Section 3.2), showed only $LaAlO_3$ in all samples. Nevertheless, SEM (Fig. 4 and Fig. 2(b)) reveals that the salt/oxide ratio affected the size of the cuboidal crystals. With increasing salt/oxide ratio from 1:1 to 3:1, the grain size decreased

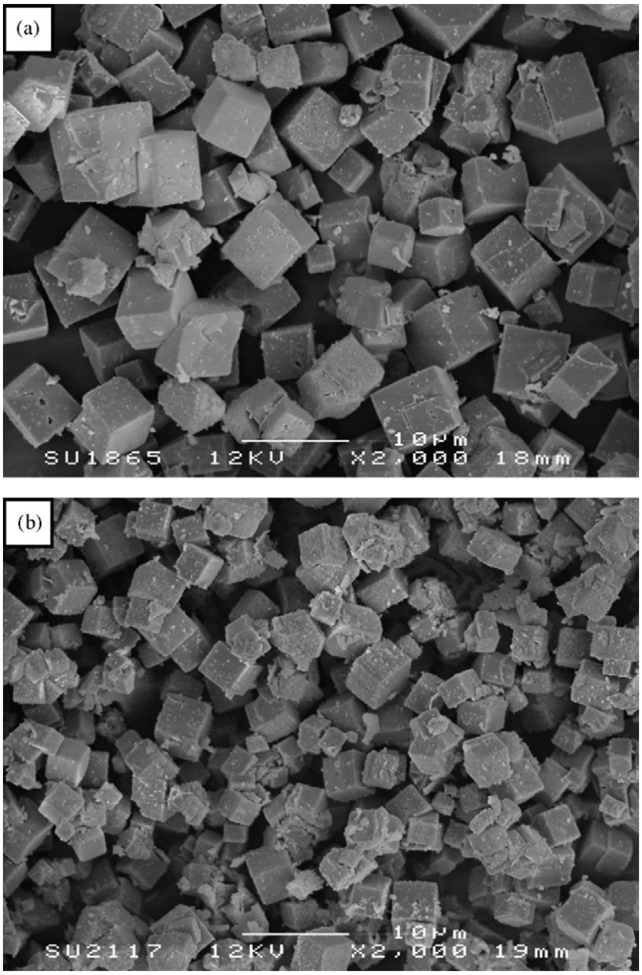

Fig. 4. SEI micrographs of $LaAlO_3$ powders synthesised at 700 °C for 3 h using different salt/oxide ratios: (a) 1:1 and (b) 6:1.

slightly, however, on further increasing the ratio from 3:1 to 6:1, it decreased more significantly from 3 to 7 to <4 µm.

### 3.4. Impurity levels in synthesised powders

The impurity levels of K, F and Cl in the raw $La_2O_3$ and $Al_2O_3$ powders are considered to be trace (not tested by the supplier) since both are high purity forms (>99.9% $La_2O_3$ and 99.8% $Al_2O_3$ with 0.08% $Na_2O$, respectively). XRF analysis results revealed that only 0.016% K, 0.008% F and 0.01% Cl remained in the $LaAlO_3$ powders synthesised in the KF–KCl eutectic salt followed by repeatedly water-washing. Because the main objective of this paper is to illustrate the feasibility of MSS for synthesis of high-melting complex oxide ($LaAlO_3$) at low temperatures, no further study has yet been carried out to purify the synthesised $LaAlO_3$ powders and to examine the effects of such levels of salt contamination on the properties of ceramics made from the synthesised $LaAlO_3$ powders.

## 4. Discussion

### 4.1. Synthesis mechanism

Since the melting temperature of the KF–KCl eutectic salt is ∼610 °C,[18] they are liquid at the test temperatures (630–800 °C). As both $La_2O_3$ and $Al_2O_3$ are highly soluble in molten potassium fluoride/chloride salts,[19–21] they dissolve into the molten eutectic salt according to reactions (1) and (2) (species in brackets refer to those dissolved in the molten salt).

$$La_2O_{3(s)} \rightarrow (La_2O_3) \tag{1}$$

$$Al_2O_{3(s)} \rightarrow (Al_2O_3) \tag{2}$$

The $La_2O_3$ and $Al_2O_3$ dissolved in the molten salt are mixed homogeneously at the atomic level, and diffusion is more rapid than in the solid state. Consequently, the dissolved $La_2O_3$ and $Al_2O_3$ react rapidly to form $LaAlO_3$ in the molten salt according to reaction (3). Once the molten salt is oversaturated with $LaAlO_3$, $LaAlO_3$ crystals start to precipitate from the salt according to reaction (4) and grow (Figs. 2 and 4). The precipitation of $LaAlO_3$ from the oversaturated salt leads to further dissolution and reaction of $La_2O_3$ and $Al_2O_3$ (reactions (1)–(3)) and then more precipitation of $LaAlO_3$ (reaction (4)). This cycle (reactions (1)–(4)) is repeated until all of the starting $La_2O_3$ and $Al_2O_3$ are used up in forming $LaAlO_3$.

$$(La_2O_3) + (Al_2O_3) \rightarrow 2(LaAlO_3) \tag{3}$$

$$(LaAlO_3) \rightarrow LaAlO_{3(s)} \tag{4}$$

The dissolution–precipitation mechanism described here is consistent with the different morphologies of the reactant and product phases. Although spheroidal $La_2O_3$ and $Al_2O_3$ starting powders were used (Fig. 1), the synthesised $LaAlO_3$ particles showed well-crystallised euhedral shapes (Figs. 2–4). These results further indicated that the “template formation mechanism” involved in many MSS processes (e.g. 22,23) is not significant in the present case.

As shown in Figs. 2–4, small (submicron) $LaAlO_3$ particles were seen on the surfaces of some of the cuboidal $LaAlO_3$ crystals. They most likely formed on cooling as some $LaAlO_3$ always remains in the liquid salt. On cooling, with decreasing solubility of $LaAlO_3$, the salt becomes oversaturated with $LaAlO_3$. As a result small $LaAlO_3$ particles subsequently precipitate from the salt onto the large euhedral crystals already formed.

### 4.2. Effects of heating temperature or salt/oxide ratios on synthesis

XRD shows that $LaAlO_3$ forms at all three test temperatures (between 630 and 800 °C), suggesting that temperature had little effect on the phase composition of the synthesised powder. Nevertheless, it did affect the morphologies/sizes of the $LaAlO_3$ particles synthesised. As shown in Fig. 2, with increasing temperature from 630 to 700 °C, the particle size increased from <∼3 to 3–7 µm attributable to accelerated crystal growth with temperature in the molten salt media. However, on further increasing temperature from 700 to 800 °C, the particle size changed very little, but the edges of the crystals became less sharp. This behaviour may arise from slight “re-dissolution” of $LaAlO_3$ at 800 °C. The solubility of $LaAlO_3$ in the salt at 800 °C is higher than that at 700 °C, so some high surface energy edges of the already-formed $LaAlO_3$ crystals might be re-dissolving into the salt because of their higher reactivity.

Besides heating temperature, the salt/oxide ratio affected the $LaAlO_3$ particle size. As shown in Fig. 4, $LaAlO_3$ particle size generally decreased with increasing salt/oxide ratio from 1:1 to 6:1. This might be attributable to the changes of the number of nuclei in the salt from which $LaAlO_3$ can precipitate and grow. With increasing relative content of the salt, the number of nuclei would increase, decreasing the final size.

## 5. Conclusions

$LaAlO_3$ powder was synthesised at 630–800 °C using $La_2O_3$ and $Al_2O_3$ as reactants and KF–KCl eutectic salts as reaction media. The lowest synthesis temperature (630 °C) is about 1000 °C lower than by CMOS, and close to or lower than those used by most wet chemical techniques. The rhombohedral $LaAlO_3$ crystal size increased from <∼3 to 3–7 µm with temperature from 630 to 700 °C, but changed very little with further increasing temperature to 800 °C. With increasing salt/oxide weight ratio from 1:1 to 6:1, the $LaAlO_3$ particle size generally decreased. The dissolution–precipitation mechanism played an important role in the MSS process, i.e., $La_2O_3$ and $Al_2O_3$ initially dissolved and reacted in the molten salt and later $LaAlO_3$ precipitated and grew from the salt oversaturated with it.

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