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Molten salt synthesis of zinc aluminate powder

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Abstract

$ZnAl_2O_4$ powder was synthesised by reacting equimolar ZnO and Al_2O_3 powders in alkaline chlorides (LiCl, NaCl or KCl). Formation of $ZnAl_2O_4$ started at about 700 °C in LiCl and 800 °C in NaCl and KCl. With increasing temperature, the amounts of $ZnAl_2O_4$ in the resultant powders increased with a concomitant decrease of ZnO and Al_2O_3. $ZnAl_2O_4$ powder was obtained by water-washing the samples heated for 3 h at 1000 °C (LiCl) or 1050 °C (NaCl and KCl). $ZnAl_2O_4$ formed in situ on Al_2O_3 grains from the surface inwards. The synthesised $ZnAl_2O_4$ grains retained the size and morphology of the original Al_2O_3 powders, indicating that a template formation mechanism dominated formation of $ZnAl_2O_4$ by molten salt synthesis.

Keywords: Powders-chemical preparation; Zinc aluminate; Functional application; ZnO; Al_2O_3

1. Introduction

Zinc aluminate ($ZnAl_2O_4$) is extensively employed in functional ceramic materials due to its superior catalytic, thermal and optical properties. $ZnAl_2O_4$ is used as a catalyst in many catalytic reactions, such as cracking, dehydration, hydrogenation and dehydrogenation reactions.[1] It can also be used as a catalyst support since it has good thermal stability, low acidity and hydrophobic behaviour. Furthermore, $ZnAl_2O_4$ has potential for use in ultraviolet (UV) photoelectronic devices because the optical band gap of polycrystalline $ZnAl_2O_4$ (3.8 eV) indicates that it is transparent to light with wavelengths > 320 nm.[2,3] Finally, it can be used as a second phase in glaze layers of white ceramic tiles to improve wear resistance and mechanical properties and to preserve whiteness.[4]

Various methods have been developed to prepare $ZnAl_2O_4$. $ZnAl_2O_4$ powder can be produced by conventional mixed oxide synthesis (CMOS)[5,6] followed by repeatedly crushing and grinding. On the other hand, wet chemical approaches can prepare fine (nano and submicrometre) $ZnAl_2O_4$ powders with good chemical homogeneity and narrow particle size distribution at relatively low temperatures, although these wet chemical methods often suffer from drawbacks such as the need to use expensive and environmentally unfriendly organic/inorganic precursors and solvents. Reported wet chemical approaches include co-precipitation,[7] sol–gel,[2,7–9] hydrothermal[10–12] and pyrolysis[13] methods.

Molten salt synthesis (MSS) is a well established low temperature synthesis technique that has recently attracted increasing interest. It has been used to synthesise low melting electroceramic powders[14] and high temperature complex oxide powders (e.g., $MgAl_2O_4$).[15] The purpose of this work is to use MSS for the preparation of $ZnAl_2O_4$ powder by heating equimolar ZnO and Al_2O_3 powders in alkaline chlorides (LiCl, NaCl or KCl). Effects of processing factors (e.g., heating temperature, salt type and particle size of Al_2O_3 powder) on the formation of $ZnAl_2O_4$ have been investigated, and the synthesis mechanism discussed.

2. Experimental procedure

ZnO manufactured by the French process (Aldrich, <1 μm, ≥99.9% pure), low-soda calcined Bayer-derived Al_2O_3 (Almatis, $Na_2O < 0.10\%$, D50 = 0.80 μm, hereafter referred to as fine Al_2O_3) and intermediate-soda calcined Al_2O_3 (Almatis, $Na_2O < 0.15\%$, D50 = 5.0 μm, hereafter referred to as coarse Al_2O_3) powders, Aldrich reagent LiCl (99.0% pure), ACS reagent NaCl (>99.0% pure) and ACS reagent KCl (≥99.0%

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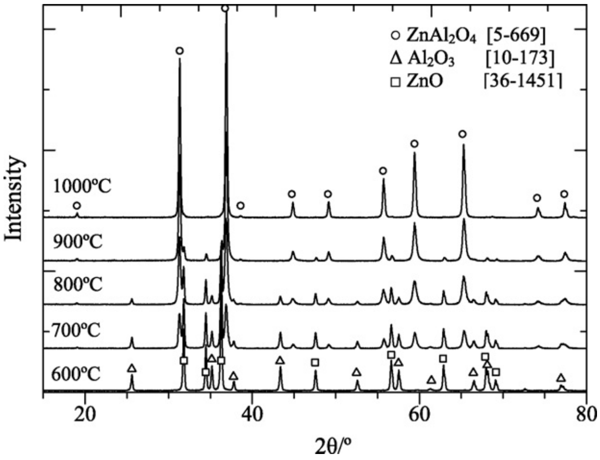

Fig. 1. XRD of powders prepared by heating equimolar ZnO and fine Al_2O_3 powders in LiCl salt at various temperatures for 3 h.

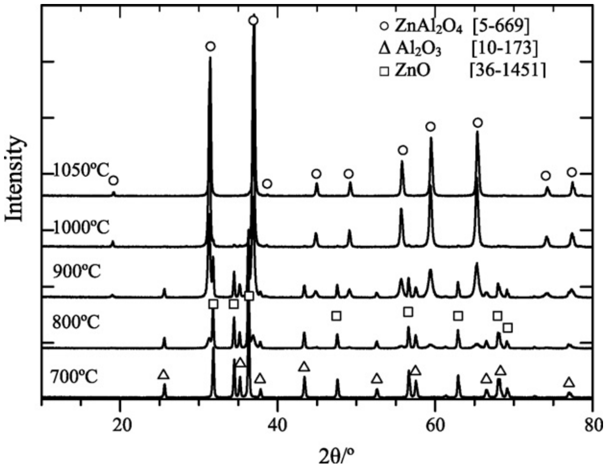

Fig. 2. XRD of powders prepared by heating equimolar ZnO and fine Al_2O_3 powders in NaCl salt at various temperatures for 3 h.

pure) were used as starting materials. Equimolar ZnO and (fine or coarse) Al_2O_3 powders were mixed with alkaline chloride (LiCl, NaCl or KCl) salts using an agate mortar. The weight ratio of salt to oxides was 4:1. The mixtures were heated in a high purity alumina crucible for 3 h at a temperature between 600 and 1100 °C. The heating and cooling rates were 3 and 5 °C/min, respectively. After cooling to room temperature, the reacted mass was washed for 2 h in hot distilled water followed by filtration to remove the salts. This washing process was repeated five times. The resultant powder was oven-dried at 105 °C for 4 h prior to characterisation.

Phases in the resultant powders were identified by powder X-ray diffraction (XRD) analysis (Siemens D500 reflection diffractometer). Patterns were recorded at 30 mA and 40 kV using Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å). The scan rate (2θ) was 1°/min at a step size of 0.02°. ICDD cards used to identify phases present were 36–1451 (ZnO), 10–173 (Al_2O_3) and 5–669 ($ZnAl_2O_4$). Microstructural morphologies of the raw ZnO and Al_2O_3 and the synthesized $ZnAl_2O_4$ powders were observed using a field-emission gun scanning electron microscope (JEOL 6500 FEGSEM, Japan). Element (Zn and Al) distributions in the powders, obtained by heating equimolar ZnO and coarse Al_2O_3 powders in molten KCl salt at 1100 °C for 3 h, were mapped using a turreted Pentafet detector and ISIS 300 processing unit attached to a scanning electron microscope (JEOL 6400 SEM, Japan).

Chemical analyses of the synthesised powders were performed using X-ray fluorescence (XRF) (Bruker AXS, Karlsruhe, Germany, SRS 3400, wavelength dispersive) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Perkin-Elmer 3300 RL, Boston, MA) to check the impurity levels of Li, Na, K and Cl originating from the salts used.

3. Results

Figs. 1–3 show XRD of powders obtained after water-washing the reacted masses of equimolar ZnO and fine Al_2O_3 powders in LiCl, NaCl and KCl salts, respectively. After heating the fine Al_2O_3–ZnO–LiCl mixture for 3 h at 600 °C (Fig. 1), only ZnO and Al_2O_3 were identified in the resultant powder. $ZnAl_2O_4$ peaks began to appear at 700 °C increased in height with increasing temperature from 700 to 900 °C whereas those of ZnO and Al_2O_3 decreased. In the powder obtained at 900 °C, $ZnAl_2O_4$ was the main phase with a small amount of ZnO and no Al_2O_3 detected. On further increasing temperature to 1000 °C, ZnO disappeared, and single phase $ZnAl_2O_4$ was obtained. XRD data for ZnO, Al_2O_3 and $ZnAl_2O_4$ phases in the powders prepared using NaCl (Fig. 2) and KCl (Fig. 3) salts are similar to those using LiCl salt (Fig. 1). However, $ZnAl_2O_4$ peaks only began to appear at ∼800 °C which is 100 °C higher than when using LiCl salt and a small amount of ZnO was still seen in the powders heated for 3 h at 1000 °C. On heating 3 h at 1050 °C, single phase $ZnAl_2O_4$ powder was obtained in both cases.

Fig. 4 shows SEI micrographs of as-received ZnO and fine Al_2O_3 powders and $ZnAl_2O_4$ powders synthesised by heating equimolar ZnO and fine Al_2O_3 in KCl salt at 1050 °C for 3 h. The as-received ZnO powder is less than 0.3 μm in size and mainly

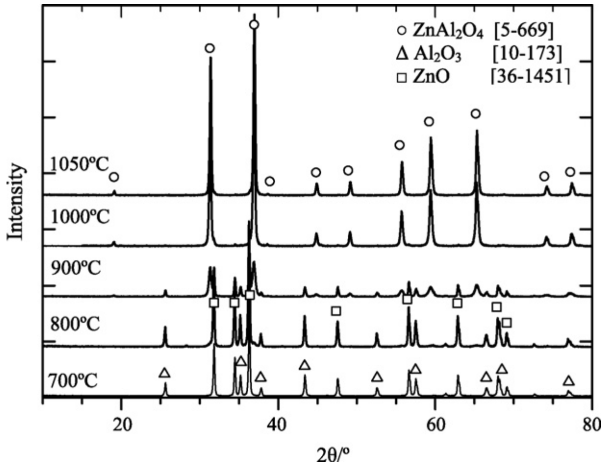

Fig. 3. XRD of powders prepared by heating equimolar ZnO and fine Al_2O_3 powders in KCl salt at various temperatures for 3 h.

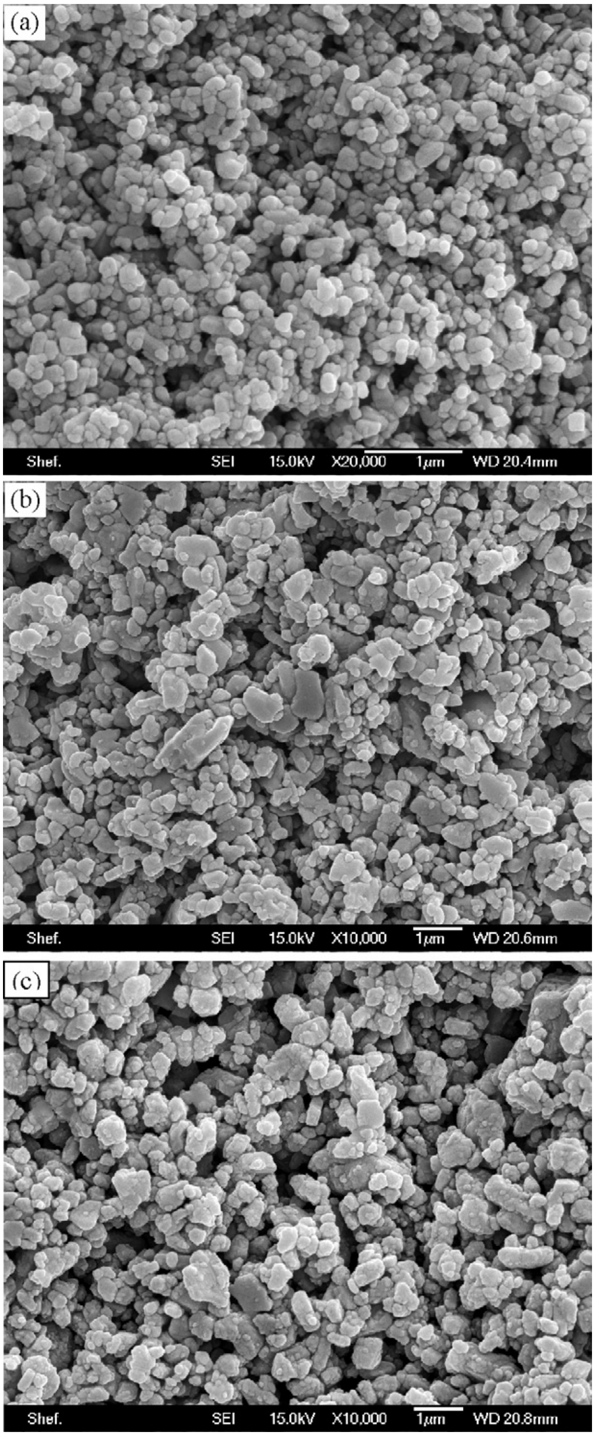

Fig. 4. SEI micrographs of as-received (a) ZnO, (b) fine Al_2O_3 and (c) synthesised $ZnAl_2O_4$ powders by heating equimolar ZnO and fine Al_2O_3 powders in KCl salt at 1050 °C for 3 h.

spheroidal in shape. The calcined and ground fine Al_2O_3 crystals are less than 1.6 μm in size with various shapes such as spheroidal, rectangular and platelet. $ZnAl_2O_4$ powders synthesised using fine Al_2O_3 powder in LiCl at 1000 °C and NaCl at 1050 °C are similar to those obtained in KCl at 1050 °C (Fig. 4(c)). The synthesised $ZnAl_2O_4$ powders have similar shape and size to the fine Al_2O_3 powders.

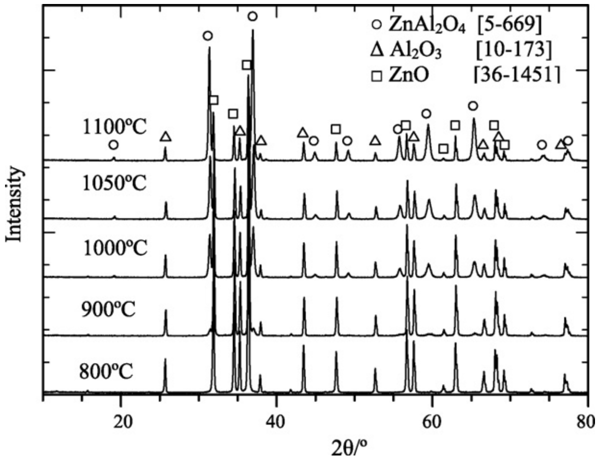

Fig. 5. XRD of powders prepared by heating equimolar ZnO and coarse Al_2O_3 powders in KCl salt at various temperatures for 3 h.

XRD of powders obtained by heating equimolar ZnO and coarse Al_2O_3 powders in KCl salt is shown in Fig. 5. No $ZnAl_2O_4$ was detected in the powder after heating 3 h at 800 °C. $ZnAl_2O_4$ was detected at 900 °C, a temperature 100 °C higher than when using fine Al_2O_3 powders. The $ZnAl_2O_4$ peak heights increased with increasing temperature, but ZnO and Al_2O_3 were still the main phases in the powders obtained at 1100 °C for 3 h.

Fig. 6 shows micrographs of as-received coarse Al_2O_3 and powders resulting from heating equimolar ZnO and coarse Al_2O_3 powders in KCl salt at 1100 °C for 3 h followed by water-washing. The calcined and ground coarse Al_2O_3 particles are less than 13 μm in size with various shapes such as spheroidal, rectangular and platelet. The resultant powders (Fig. 6(b)) retained the shapes and sizes of the original Al_2O_3 particles (Fig. 6(a)). Back-scattered image (BSI) of cross-sections of the resultant powders (Fig. 6(c)) shows that they have three types of contrast: light, grey and grey shells with dark cores. Particles with dark cores are generally larger than those without them. Zn and Al X-ray dot maps in the SEM (Fig. 6(d)) in combination with XRD (Fig. 5) revealed that the light particles are ZnO, the grey $ZnAl_2O_4$ and the dark core Al_2O_3. Some ZnO particles in the obtained powders were larger in size (∼3 μm) than the as-received ZnO powder (<1 μm).

The impurity levels in the resultant powders determined by XRF and ICP-AES are 0.05% Li and 0.08% Cl for fine Al_2O_3–ZnO–LiCl mixture after heating at 1000 °C for 3 h, 0.05% Na and 0.04% Cl for fine Al_2O_3–ZnO–NaCl mixture after heating at 1050 °C for 3 h, and 0.04% K and 0.07% Cl for fine Al_2O_3–ZnO–KCl mixture after heating at 1050 °C for 3 h, respectively. Because the main objective of this paper is to illustrate the MSS method for synthesis of high-melting complex oxide $ZnAl_2O_4$, no further study has yet been carried out to purify the synthesised $ZnAl_2O_4$ powders and to examine the effects of such levels of salt contamination on the properties of $ZnAl_2O_4$ ceramics synthesised from the powders.

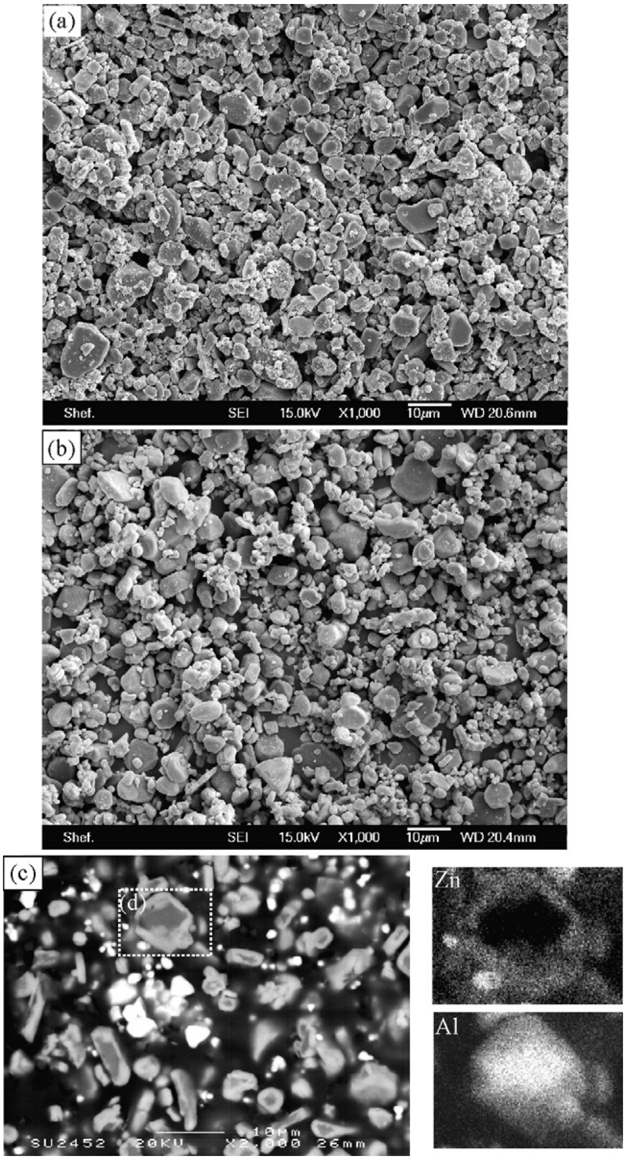

Fig. 6. SEI of (a) as-received coarse Al_2O_3, (b) powders after heating equimolar ZnO and coarse Al_2O_3 powders in KCl salt at 1100 °C for 3 h followed by distilled water washing, (c) BSI of the cross-section of the resultant powders and (d) X-ray dot maps of Zn and Al of zone.

4. Discussion

4.1. Synthesis mechanism and effect of Al_2O_3 particle size on synthesis

The salt melting points are 610 °C for LiCl, 801 °C for NaCl and 771 °C for KCl, respectively.[16] After holding 3 h at 700 °C for LiCl and 800 °C for KCl, all the salts melt. NaCl also should be liquid after holding 3 h at 800 °C due to the effect of the impurities in the salt. ZnO is slightly soluble in the chlorides used in this work with solubility on the order of 10^{-2} wt.%,[17–19] while the solubility of Al_2O_3, on the order of 10^{-5} wt.% in these salts,[17,20] is much lower than that of ZnO. As a result, during MSS, ZnO would dissolve more easily in the molten salts, diffuse to Al_2O_3 particle surfaces, and then react with the Al_2O_3 "template" to form in situ $ZnAl_2O_4$ which retains the morphology of the starting Al_2O_3 grains.

The "template formation" mechanism is consistent with the observation that the synthesised $ZnAl_2O_4$ powders retained the approximate shapes and sizes of the original Al_2O_3 powders (Figs. 4 and 6). BSI and X-ray dot maps of the resultant powders using coarse Al_2O_3 (Fig. 6) provided further evidence that $ZnAl_2O_4$ formed in situ on the Al_2O_3 template and grew from the surface inwards.

This MSS of $ZnAl_2O_4$ involves (1) diffusion of dissolved ZnO (in the form of Zn^{2+}) onto Al_2O_3 particle surfaces, (2) diffusion of ZnO (probably in the form of Zn^{2+}) to the unreacted Al_2O_3 core through the formed continuous $ZnAl_2O_4$ spinel layer and (3) reaction between diffused ZnO and unreacted Al_2O_3. The kinetics of the solid–solid reaction as well as the mechanism of $ZnAl_2O_4$ formation have been studied by various authors.[5,21–23] Branson[21] determined that in the solid–solid reaction between ZnO and Al_2O_3 the diffusion of Zn ions through the $ZnAl_2O_4$ layer is the rate-controlling step especially in the late stages of the reaction.

In the MSS process, diffusion of ZnO to the Al_2O_3 particle surfaces in the molten salt media should be much quicker than in the solid–solid reaction via the limited contacts of two solid phases. Therefore, in this case diffusion of ZnO from the Al_2O_3 particle surface to the unreacted Al_2O_3 core via the formed $ZnAl_2O_4$ layer can be assumed to be the rate-controlling step for the formation of $ZnAl_2O_4$.

Based on this assumption, the larger the alumina particle used, the farther the ZnO must diffuse from the original Al_2O_3 particle surface to the unreacted Al_2O_3 core via the formed $ZnAl_2O_4$ layer, so that longer times are needed for completion of $ZnAl_2O_4$ formation. This is supported by the fact that even after heating 3 h at 1100 °C in KCl molten salt the formation of $ZnAl_2O_4$ was not completed if using coarse Al_2O_3 powder compared to the completion temperature of 1050 °C for fine Al_2O_3 powder. The starting temperature for $ZnAl_2O_4$ formation in KCl molten salt also increased from ~800 to ~900 °C with increasing the original Al_2O_3 particle size (D50) from 0.80 to 5.0 μm presumably a result of the reduced surface area for reaction. These results are in good agreement with those of Hong et al.[5] on reaction sintering ZnO–Al_2O_3. These results imply that in order to accelerate the formation of $ZnAl_2O_4$ finer Al_2O_3 particles are preferred in the MSS process.

In samples obtained by heating at 900 °C in LiCl and 1000 °C in NaCl and KCl, small amounts of ZnO were detected but without Al_2O_3 in the XRD (Figs. 1–3). Small amounts of Al_2O_3 should exist but are likely to be in the centre of larger $ZnAl_2O_4$ particles but at levels below the detection limit of XRD. As shown in Fig. 6(c), some ZnO particles in the resultant powder were larger than the original ZnO particles, possibly due to coalescence of fine ZnO particles with the dissolving surface in the molten salts.

4.2. Effect of salt type

Figs. 1–3 show that the starting and completion temperatures of $ZnAl_2O_4$ formation varied with different salts. LiCl is more effective in forming $ZnAl_2O_4$ than NaCl and KCl attributable to the differences of LiCl, NaCl and KCl in melting point, viscosity and the solubility of the oxides in these molten salts.

Firstly, the melting point of the different salts affected the starting temperature of $ZnAl_2O_4$ formation. The lower the melting point, the earlier the salt melted and ZnO dissolved, and subsequently, the earlier the formation of $ZnAl_2O_4$ began. The starting temperature of $ZnAl_2O_4$ formation using LiCl was ~700 °C lower than those (~800 °C) by NaCl and KCl since the melting point of LiCl is 610 °C, lower than those of NaCl (801 °C) and KCl (771 °C).[16]

Secondly, the viscosities of different molten salts influence the formation of $ZnAl_2O_4$. The diffusion of cations in a solvent depends not only on the temperature and size of the cations but also on the solvent viscosity. The lower the viscosity of the solvent, the quicker the cations diffuse. In this work, the viscosity of molten LiCl is 0.86 mPa s at 800 °C[24] which is lower than those of NaCl (1.03 mPa s) and KCl (1.02 mPa s) at identical temperatures,[24,25] the diffusion of ZnO (in the form of Zn^{2+}) to Al_2O_3 particle surfaces was more rapid than in NaCl and KCl molten salts, resulting in the earlier completion of $ZnAl_2O_4$ synthesis in LiCl.

Finally, the solubility difference of ZnO and/or Al_2O_3 in different molten salts also effects $ZnAl_2O_4$ formation. No data on the solubility of ZnO in molten LiCl salt was found, but the solubility of ZnO in molten NaCl at 900 °C is 1.7×10^{-6} mol/g salt higher than in KCl (9.1×10^{-7} mol/g salt) at the same temperature.[18] This explains why the XRD peaks of $ZnAl_2O_4$ synthesised using NaCl at 800 and 900 °C are higher than those using KCl at the same temperatures. Increasing the solubility of both reactant species in the molten salt would promote the formation of $ZnAl_2O_4$. It should be pointed out that if the solubility of both reactant species is close, the formation mechanism would change from template formation to dissolution–precipitation which would significantly accelerate the rate of $ZnAl_2O_4$ formation.

Therefore, future work will concentrate on finding a salt/mixed salts with low melting point, low viscosity and relatively higher solubility of both oxides promoting the formation of $ZnAl_2O_4$ at lower temperature.

5. Summary

Zinc aluminate ($ZnAl_2O_4$) powder was synthesised by using zinc oxide (ZnO, <0.3 μm) and aluminium oxide (Al_2O_3, <1.6 μm) powders and alkaline chloride salt (LiCl, NaCl or KCl). The formation of $ZnAl_2O_4$ started at ~700 °C for LiCl and 800 °C for NaCl and KCl. With increasing temperature, the amounts of $ZnAl_2O_4$ increased with a concomitant decrease of ZnO and Al_2O_3. After water-washing the samples heated 3 h at 1000 °C (LiCl) and 1050 °C (NaCl and KCl), single phase $ZnAl_2O_4$ powders were obtained. $ZnAl_2O_4$ formed in situ on Al_2O_3 grains growing from the surface inwards. The synthesised $ZnAl_2O_4$ grains are close in size to the original Al_2O_3 powders, and retained the shapes of the original Al_2O_3 powders, indicating that a template formation mechanism dominated the formation of $ZnAl_2O_4$ by the MSS process. Future work will concentrate on finding a salt with low melting point, low viscosity and relatively higher solubility of both oxides promoting the formation of $ZnAl_2O_4$ at lower temperature.

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