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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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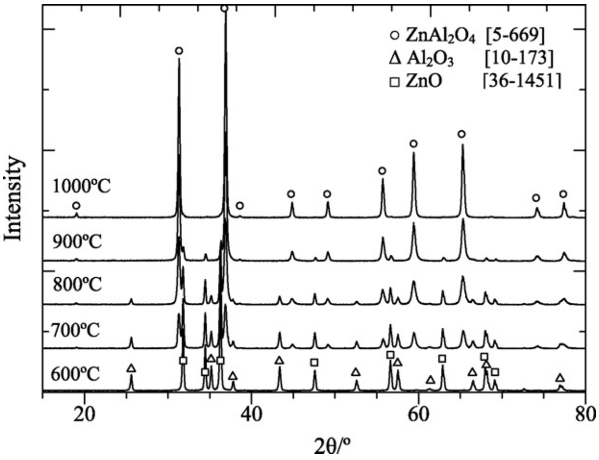

Fig. 1. XRD of powders prepared by heating equimolar ZnO and fine Al_2O_3 powders in LiCl salt at various temperatures for 3 h.

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 (λ = 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

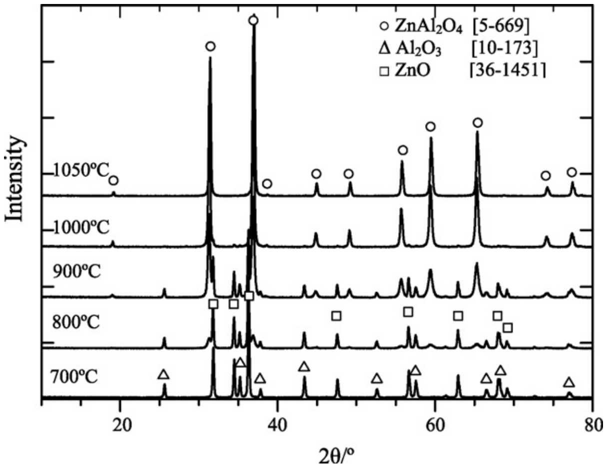

Fig. 2. XRD of powders prepared by heating equimolar ZnO and fine Al_2O_3 powders in NaCl salt at various temperatures for 3 h.

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

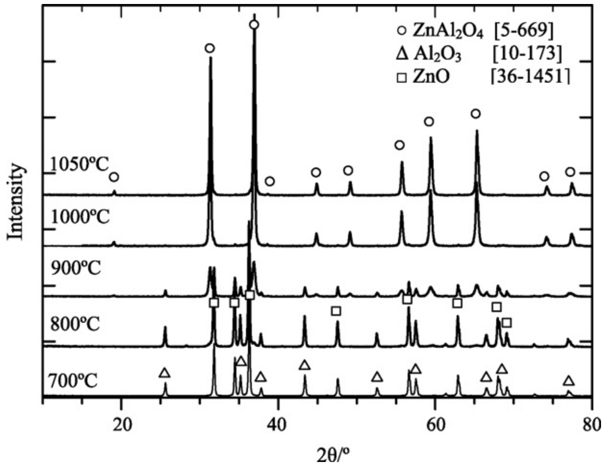

Fig. 3. XRD of powders prepared by heating equimolar ZnO and fine Al_2O_3 powders in KCl salt at various temperatures for 3 h.