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Synthesis of $SrAl_{12}O_{19}$ via citric acid precursor

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Abstract

The citric acid precursor method was used to synthesize $SrAl_{12}O_{19}$. The effects of the pH of the starting solutions on the formation of $SrAl_{12}O_{19}$ were investigated. Single-phase $SrAl_{12}O_{19}$ was derived from precursor with unadjusted pH at 1200 °C for 2 h. Increasing the pH of the starting solutions to 7, the formation temperature of single-phase $SrAl_{12}O_{19}$ increased to 1300 °C. Differential thermal analysis and thermogravimetric (DTA/TG), X-ray diffractometry (XRD) and field emission scanning electron microscopy (FESEM) were used to characterize the precursors and the derived oxide powders.

Keywords: $SrAl_{12}O_{19}$; Citric acid; Chemical synthesis

1. Introduction

Strontium hexaluminates ($SrAl_{12}O_{19}$) are members of the "magnetoplumbite" group of structures, comprising a diverse set of oxide materials. It has some interest as reinforcement for ceramic composites [1] and catalytic substrates [2]. After doping with rare-earth metal ions such as Eu^{2+}, it can be used as long duration photoluminescence or thermoluminescence pigments [3–5]. Conventionally, they were produced by a conventional solid-state reaction of mechanically mixed powders. The inevitable inhomogeneity that is inherent to this technique inhibits the required compositional and microstructural homogeneity of sintered products.

Various wet chemical methods have been developed for the synthesis of pure, single-phase mixed-oxide powders. One of the successful techniques for single-phase mixed oxide powders is the Pechini process [6], which is a solution polymerization process. The process involves the ability of certain weak α-hydroxycarboxylic acids (citric acid is preferred) to form polybasic acid chelates with various cations. These chelates can undergo polyesterification when heated in a polyhydroxyl alcohol to form a polymeric resin. The cations are, ideally, uniformly dispersed on an atomic scale throughout the polymeric resin. Further heating of the resin in air results in removal of all organics and the formation of a char having a controlled cation stoichiometry, with little segregation of the cations. The char is then heated to higher temperatures and oxidized to form the mixed-metal oxides. This method has been used to produce niobates, titanates, zirconates, chromates, ferrites, manganites, aluminates, cobaltites, and silicates [7–14]. Cinibulk [15,16] synthesized $CaAl_{12}O_{19}$ via the same method, but no researcher reported the synthesis of $SrAl_{12}O_{19}$ via this method.

Up to date, very little literatures reported the synthesis of $SrAl_{12}O_{19}$ by wet chemical route. Douy and Capron [17] prepared $SrAl_{12}O_{19}$ powders by spray-drying aqueous solutions of strontium and aluminium nitrates followed by heating the powders to decompose the nitrates. Chen et al. [18] synthesized Eu^{2+} and Dy^{3+} co-doped $SrAl_{12}O_{19}$ by a sol–gel process. In this paper, we reported the synthesis of $SrAl_{12}O_{19}$ via citric acid precursors and the effect of the pH of the starting solutions on the formation of $SrAl_{12}O_{19}$ was investigated. Single phase $SrAl_{12}O_{19}$ was synthesized at 1200–1300 °C.

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2. Experimental procedure

2.1. Preparation of specimens

$SrAl_{12}O_{19}$ were synthesized through the citrate route. Citric acid (CA), ethylene glycol (EG), aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) and strontium carbonate ($SrCO_3$) were employed as the starting ingredients. First, citric acid was dissolved in ethylene glycol (EG), followed by the addition of aluminium nitrate nonahydrate. After achieving complete dissolution, the temperature of the solution was increased to 80 °C and a stoichiometric amount of $SrCO_3$ powders was added to the solution. With the evolution of CO_2 gases, the solution became transparent and the pH of the solution is about 1.5. In order to check the effect of the pH of the starting solutions on the crystallization behavior of $SrAl_{12}O_{19}$, the solution was divided into two parts, ammonium hydroxide (NH_3 25% by weight in water) was added to one part to adjust the solution pH to about 7. During the process, the molar ratio of citric acid to total metal cations concentration CA/M was 1, the molar ratio of EG to CA was 4. With continuous heating at 80 °C under constant stirring to evaporate superfluous water, the volume of the solution decreased and the solution viscosity increased continuously due to the gradual polymerization. The viscous mass was further heated for 2–4 h at 140 °C. This heating process accelerated esterifications between CA and EG and eliminated the remaining water, producing a clear, transparent, solid, amorphous resin. Throughout the process, no sign of precipitation was observed. Then the resins were placed into an oven (preheated to 250 °C) immediately to char the resin for 2 h. The resin was lightly ground to powder, to which we refer powder precursor. This solid resin precursor was then calcined at 700–1300 °C for 2 h to obtain the $SrAl_{12}O_{19}$ powders.

2.2. Analysis of specimens

Simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) analysis (NETZSCH STA 449C) at a heating rate of 15 °C/min in static air were employed to analyze the decomposition and the oxidation process of the precursor. X-ray diffraction (XRD) analysis using monochromatic Cu Kα radiation (X'Pert PRO of PANalytical B.V.) was used to identify the phases of the samples. Field emission scanning electron microscopy (FESEM; Sirion 200, FEI Inc.) was used to observe the particle size and the morphology of the $SrAl_{12}O_{19}$ powders.

3. Results and discussions

Fig. 1 shows the results of differential thermal analysis (DTA) and thermogravimetric (TG) analysis for $SrAl_{12}O_{19}$ precursor with unadjusted pH. The endothermic peak in the DTA curve around 78 °C, corresponding to the first weight loss shown by TG curve, is due to the dehydration of the

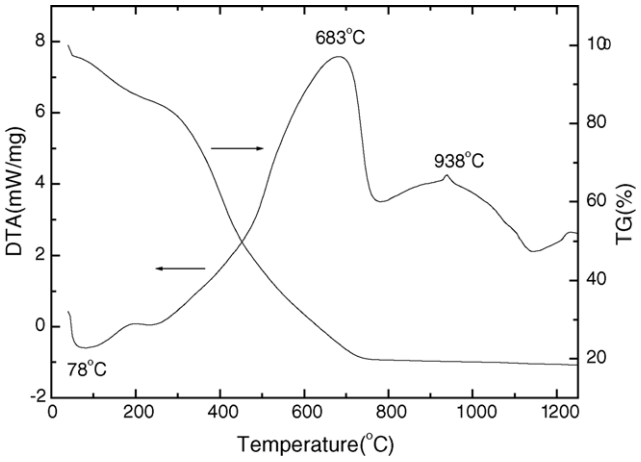

Fig. 1. DTA and TG curves of $SrAl_{12}O_{19}$ precursors with unadjusted pH.

precursor. The strong exothermic peak around 683 °C in the DTA curve, accompanied by the second sharp weight loss in the TG curve, is due to the carbonization or bond breaking of organic moieties in precursors together with the evolution of great amounts of gases such as CO_2. The small exothermic peak around 938 °C is associated with the crystallization of γ-Al_2O_3 solid solution. It is consistent with the result of Douy and Capron [17]. They reported that γ-Al_2O_3 solid solution crystallized from an amorphous precursor after an exothermal peak at 936 °C. Fig. 2 shows the results of DTA and TG analysis for $SrAl_{12}O_{19}$ precursor with unadjusted pH calcined at 700 °C for 2 h. Compared with Fig. 1, the exothermal peak around 938 °C can be also found although the strongest exothermal peak becomes weaker and moves to 571 °C. The result proves further that the exothermic peak around 938 °C is associated with the crystallization of γ-Al_2O_3 solid solution.

Fig. 3 shows the XRD patterns of the $SrAl_{12}O_{19}$ precursor with unadjusted pH calcined in static air at 700–1300 °C for 2 h. The powder heated at 700 °C for 2 h is X-ray amorphous. After heating the precursor at 900 °C for 2 h,

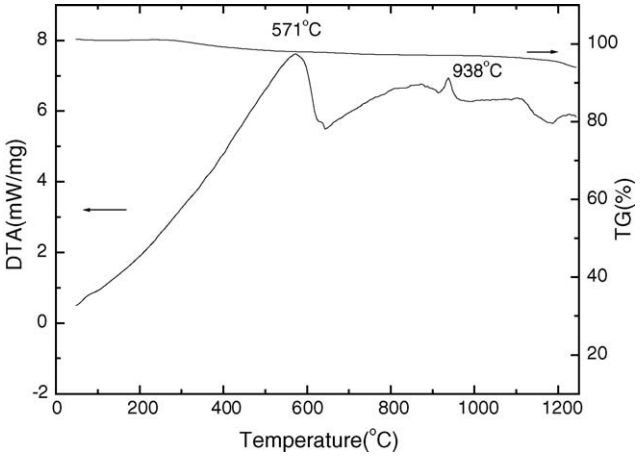

Fig. 2. DTA and TG curves of $SrAl_{12}O_{19}$ precursors with unadjusted pH calcined at 700 °C for 2 h.