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Rapid annealing: A novel processing technique for $Cr{:}ZnAl_2O_4$ nanoparticles

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ABSTRACT

Nanocrystalline $Cr{:}ZnAl_2O_4$ was synthesized for the first time by rapid thermal annealing the corresponding hydroxide precipitate in just 10 min. The XRD patterns showed that synthesis between 500 °C and 700 °C had smaller crystallites (~2.4 − 4 nm), while at 800 °C and 900 °C, had ~10 nm crystallites. HRTEM images of the 900 °C sample showed the well-developed lattice fringes confirming the high crystallinity. The particles were polyhedral having an average size of ~16 nm. The diffuse reflectance spectra showed characteristic $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions, while the photoluminescence emission spectrum comprised of the zero phonon line (R-line) along with other multi-phonon side bands that are characteristic of the spin − parity forbidden transitions of the Cr^{3+} ion. The emission spectra and photoluminescence lifetimes are comparable with reports on sensing and imaging applications. Our work demonstrates the suitability of this technique to quickly synthesise phosphors for a variety of applications.

1. Introduction

In view of their superior thermal and chemical stability, enhanced optical and electrical properties, mechanical strength, etc., nanocrystalline metal oxides have been widely explored in catalysis, displays, sensing, lasing, etc. [1–6]. Nanocrystalline $ZnAl_2O_4$, with a wide bandgap of 3.8 eV is known for its range of potential applications in photocatalysis, as phosphor hosts, for fabricating UV-optoelectronic devices, optomechanical stress sensors, and electroluminescent displays [7,8]. Several solid state and wet chemical recipes exist for the synthesis of the crystalline $ZnAl_2O_4$ spinel [9–11]. However, obtaining high-quality and phase-pure spinels requires that most synthesis methods be followed by a high-temperature annealing process where temperatures can go up to 1200 °C.

Annealing, at relatively slow heating rates, is a widely employed post-processing technique for glass and ceramics, including spinels [11–15]. Annealing is usually achieved through heating elements made of silicon carbide, molydisilicide, or chromium-iron-aluminium alloys, which bring about structural changes in the material through convective heating. It is already well established that annealing influences the material properties for the application of interest, be it as a catalyst, phosphor, or a magnetic device.

Rapid annealing (RA) can instantly raise the temperatures to several hundred degrees within minutes; a similar process, rapid thermal annealing (RTA) with heating rates ranging from 5 °C/sec to 25 °C/sec [16–19], is used extensively in the processing of integrated circuits [16,19,20]. RTA has been used for the fabrication of silicide layers [21], dopant activation of thin films, and to "heal" damage due to ion implantation [20]. RTA is particularly useful in thin film fabrication because it minimises interaction between the film and substrate. While RTA is an industrially well-established thin film processing technique, here we report on employing rapid annealing (RA), with the ramp up rates of ~150–200 °C/min, in the synthesis of ceramic powders. Even though the ramp up rates are lower than in RTA, the use of RA in the synthesis of ceramic powders such as Cr^{3+} doped $ZnAl_2O_4$ (Cr:ZAO), has not been explored previously. In fact, there are only a few reports on the RA of metal oxide powders [22].

Since RA can significantly reduce the synthesis/processing time of oxides, it may potentially be of technological importance. In view of the lack of literature on the use of RA for the synthesis of spinel/

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$ZnAl_2O_4$ nanoparticles, it is important to investigate the effects of RA on the structural and optical properties of such materials. Here, we explore the use of RA for the synthesis of Cr:ZAO, starting from the co-precipitate of the respective hydroxides. Cr:ZAO is a well-known red/NIR emitting phosphor [13] and we have investigated its emission properties in detail for different RA parameters. We show that 10 min of RA is sufficient for the synthesis of Cr:ZAO nanoparticles, making RA potentially useful for the rapid synthesis of nanoparticles of other metal oxides.

2. Experimental

2.1. Synthesis of Cr:ZAO

The aim was to prepare $ZnAl_{1.95}Cr_{0.05}O_4$ nanoparticles starting from zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) (Merck), aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) (Merck), and chromium chloride hexahydrate ($CrCl_3.6H_2O$) (Merck). Aqueous solutions of the corresponding salts taken in 1:1.95:0.05 mol ratio (Zn: Al: Cr) were mixed and precipitated using a 2 M solution of NaOH at a pH of 9.5, under constant stirring for 30 min. The precipitate was vacuum-filtered, washed and dried in an oven at 60 °C for 2 h, before subjecting it to RA at temperatures between 500 and 900 °C for 10 min, employing a ramp rate of ~200 °C/min. The corresponding heating profile (time vs. temperature) of the furnace for different temperature set-points are shown ESI, Fig. S1. The details of RA system are reported elsewhere [22]. The precipitate was evenly spread over a quartz boat that ensured uniform heating. The samples synthesized at temperatures from 500 °C–900 °C were labelled A – E, respectively.

2.2. Characterisation

X-Ray diffraction (XRD) patterns of the powder samples were collected using a Rigaku Ultima-IV diffractometer (Cu-K_α radiation). Fourier transform infrared (FT-IR) spectra were recorded using Jasco FT/IR 6200 spectrometer. Bandgaps were deduced from diffuse reflectance spectra of the samples obtained from Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer with a 150 mm integrating sphere attachment. Diffuse reflectance measurements were made between 800 and 200 nm using $BaSO_4$ as the reflectance standard. Crystallinity and morphology of the powders were examined by high-resolution transmission electron microscopy (HR-TEM, JEOL 3010). Photoluminescence spectra were obtained at room temperature for the various samples (Jasco FP8300 fluorescence spectrometer equipped with a 450 W Xenon lamp and a high-speed chopper). The luminescence decay curves were processed by single-exponential fit to derive the lifetime in each sample.

3. Results and discussion

3.1. X-ray diffraction

The effect of RA on the formation of Cr:ZAO nanoparticles was investigated at different temperatures between 500 and 900 °C for 10 min, reached at a ramp rate of ~200 °C/min. The crystallinity and phase purity of the samples were determined by X-ray diffraction. The XRD patterns of the samples (Fig. 1a) show peaks corresponding only to the spinel phase. The broad peaks observed for sample A are due to the very small size of the crystallites (2 nm). As expected, crystallinity improves as the synthesis temperature is raised, causing the narrowing of the peaks. The change in crystallite size, bandgap, and lattice parameters are listed in Table 1.

The lattice parameter approaches the reported values as the temperature is raised (Table 1) [23,24]. The increase in the average crystallite size with temperature follows an exponential trend (Fig. 1b), suggesting that the significant crystal growth occurs between 700 °C and 900 °C. It is worth noting that mere 10 min of RA led to well crystallized Cr:ZAO nanoparticles starting from

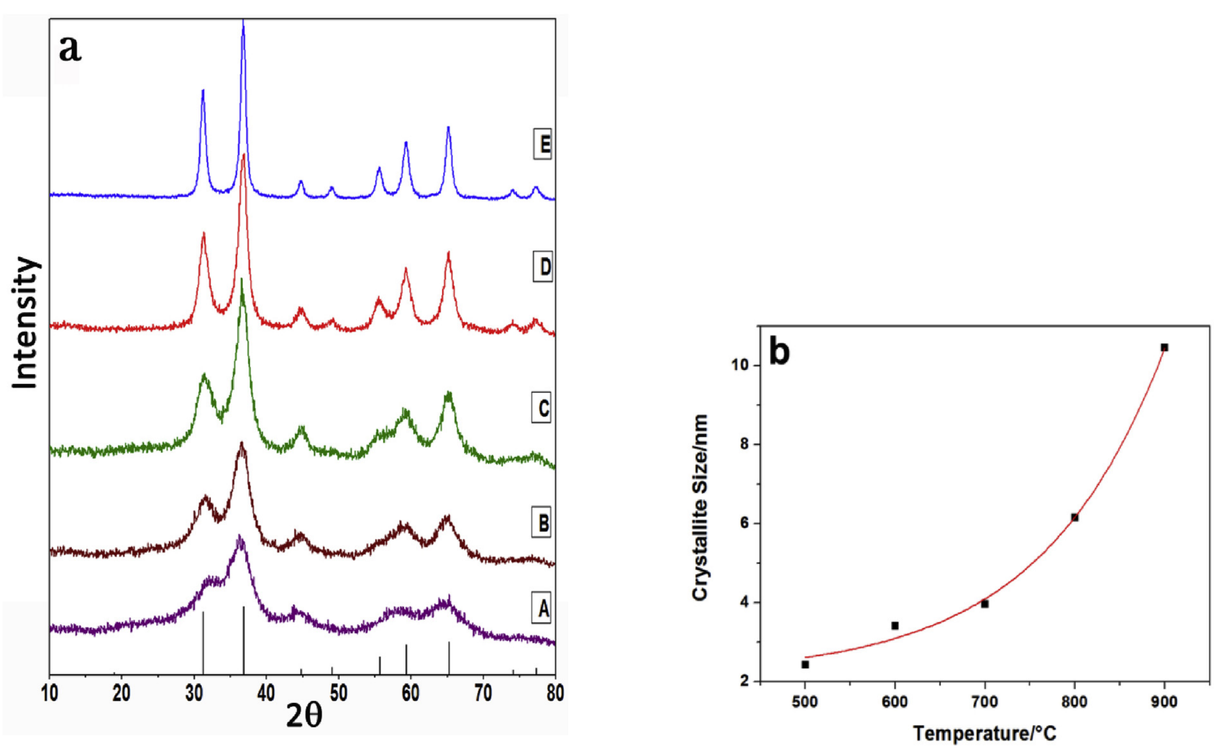

Fig. 1. (a) XRD patterns of Cr-doped $ZnAl_2O_4$ rapid-annealed at different temperatures and (b) plot showing the variation in crystallite size with temperature.