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Short communication

Low-temperature molten salt synthesis of $YAlO_3$ powders assisted by an electrochemical process

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Abstract

$YAlO_3$ (YAP) powders were successfully synthesized by a unique molten salt method, where YAP precursor was prepared by an electrochemical method at room temperature, followed by calcining it at a temperature of not exceeding 400 °C for 8 h using $LiNO_3$ as the molten salt medium. XRD analysis and TEM observation show that well-crystallized YAP powders can be obtained at 400 °C for a holding time of 8 h with 1:16 ratio of YAP precursor to $LiNO_3$ by weight. Greatly reduced temperature of forming YAP should be attributed to the incorporation of $LiNO_3$ salt in preparing process.

Keywords: A. Powders: chemical preparation; D. Perovskites; $YAlO_3$

1. Introduction

Recently, considerable attention has been paid to $YAlO_3$ (YAP) with orthorhombic, hexagonal, and cubic-phase in Y_2O_3–Al_2O_3 system [1]. Orthorhombic-phase YAP has found wide applications in laser materials, phosphors, scintillators [2,3], thermoluminescent (TL) dosimetry of ionizing radiation [4], and pigments [5] because of its fast scintillation [6], high light yield, good mechanical and electroluminescence properties [7], while cubic-phase YAP with perovskite structure is generally used for preparing transparent ceramics due to their high mechanical strength, hardness, heat conductivity, and transparency in a wide spectral range [8,9].

A variety of approaches for preparing YAP powders have been developed, but obvious shortcomings still exist in these methods; e.g. the traditional solid-state reaction route requires a high reaction temperature above 1500 °C [1], characteristic of large energy consumption. A calcining temperature over 1000 °C is necessary even in the soft chemistry process [10] reported recently. Other preparing methods like amorphous oxide combustion [11], sol–gel process [12], molecular beam epitaxy [13], solvothermal reaction [14], and modified polymeric precursor method [15] were also reported. Nevertheless, their wide applications are yet restricted owing to either excessive using organic materials, or strong relying on special equipments, and involving complicated manipulations and too long synthetic cycle. Therefore, how to prepare YAP powders under milder condition by a simpler and more convenient method is still a big challenge to be faced.

Here, we propose a new preparing route, based on a combination of the molten salt process with the electrochemical, to synthesize cubic-phase YAP powders, i.e. YAP precursor was firstly prefabricated using an electrochemical method at room temperature, and then calcined in the molten salt medium. After washed with hot distilled water and dilute nitric acid, a pure cubic-phase of $YAlO_3$ powders can be obtained. Obviously, this method possesses unique merits such as relatively low synthetic temperatures (below 400 °C), no organic additives, and easy manipulation compared to other approaches.

2. Experimental

All the chemicals were of analytical grade, and used as received without further purification.

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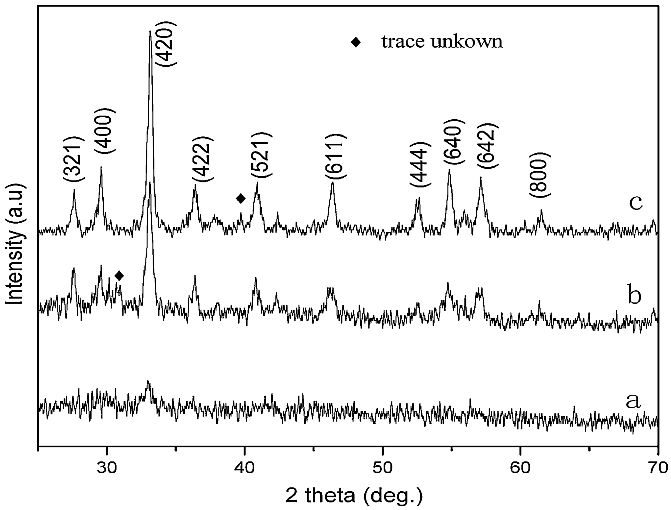

Fig. 1. XRD patterns of samples obtained at different calcining temperatures: (a) 280 °C, (b) 340 °C, and (c) 400 °C (1:8 weight ratio, holding time of 8 h).

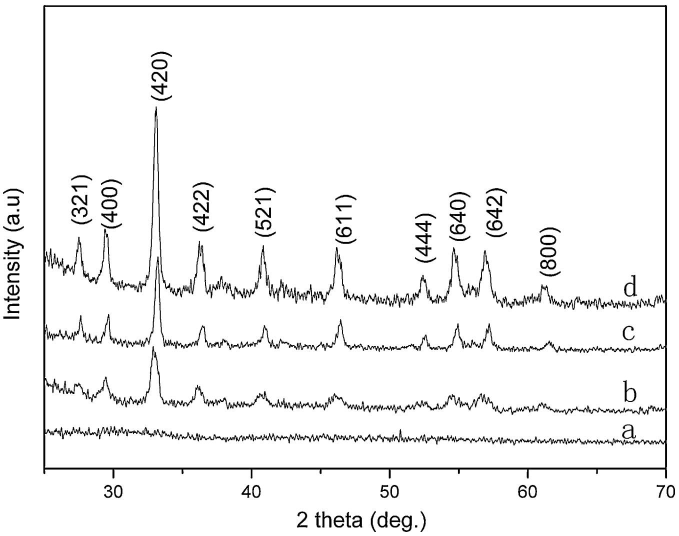

Fig. 3. XRD patterns of the samples prepared with different weight ratios of YAP precursor/$LiNO_3$ mixtures: (a) 1:0, (b) 1:4, (c) 1:8, and (d) 1:16 (calcining temperature: 400 °C, holding time: 8 h).

2.1. Synthesis of YAP precursors

0.005 mol $Y(NO_3)_3 \cdot 6H_2O$ was dissolved in 100 ml distilled water as an electrolyte, two rectangular aluminum plates with a dimension of 100 mm × 20 mm × 2 mm were used as an anode and cathode. The electrochemical process was carried out using a DC power supply in the applied voltage range of 40–50 V, wherein both Al electrodes were parallel put into a 150 ml glass beaker containing 100 ml electrolyte prepared before. 5 min later, a greenish black precipitate could be collected by centrifugation, followed by drying at 60 °C for 8 h. The obtained product is YAP precursor.

2.2. Synthesis of YAP powders

YAP precursor was well mixed with $LiNO_3$ in 1:8 weight ratio of the precursor/$LiNO_3$, and then put into an alumina crucible and calcined at a given temperature (280 °C, 340 °C and 400 °C) in a muffle oven for 8 h. Similar procedure was also repeated at 400 °C, only varying the weight ratio of YAP precursor to $LiNO_3$ (1:0, 1:4, and 1:16); and all the holding time at the calcining temperature was 8 h. Finally, the resulting products were washed with hot distilled water and dilute nitric acid for several times, and dried at 60 °C for 8 h.

2.3. Characterization

XRD analysis was carried out on a D8 ADVANCE X-ray diffractometer (Bruker, Germany), using Cu Kα radiation. The particle size and morphology of the as-prepared powders were observed by a JEM-1200EX transmission electron microscope (JEOL Ltd., Japan). Their chemical analysis was performed by a PROFILE inductively coupled plasma atomic emission spectrometer (Leeman Labs Inc., USA).

3. Results and discussion

Fig. 1 presents XRD patterns of the as-prepared samples by calcining YAP precursor/$LiNO_3$ mixture (1:8 weight ratio) at

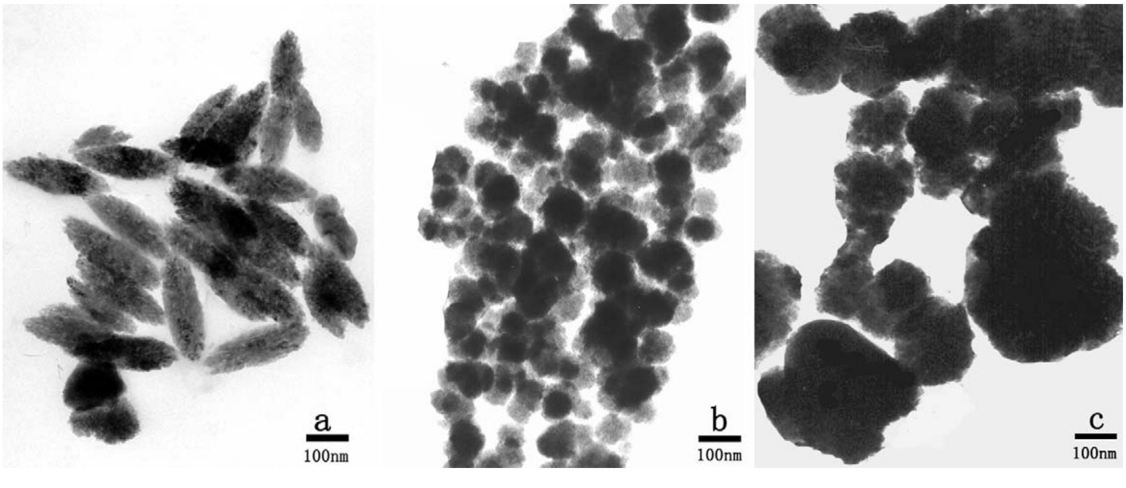

Fig. 2. TEM images of the as-prepared samples at different calcining temperatures: (a) 280 °C, (b) 340 °C, and (c) 400 °C.

different temperatures. It is obvious that the calcining temperature is an important factor that affects the crystallization and development of YAP phase. At 280 °C, only can an amorphous phase be obtained (Fig. 1(a)). With the increase of calcining temperature, at 340 °C, cubic-phase YAP (JSPDS: 38-222) appears, but showing a poor crystallization (Fig. 1(b)). On further elevating the calcining temperature to 400 °C, a well-crystallized cubic-phase YAP can be formed, as shown in Fig. 1(c). That means, the formation temperature of cubic-phase YAP should be in a temperature range of 340–400 °C, which is much lower than the reported 1500 °C by the traditional solid-state reaction [1] and 1000 °C by the soft chemistry route [8].

Their TEM images are given in Fig. 2. All the samples were obtained with a 1:8 weight ratio of YAP precursor/$LiNO_3$ mixture, and the holding time at the calcining temperature was 8 h. At 280 °C, the amorphous phase mainly consists of spindle-like particles, showing a somewhat loose microstructure (Fig. 2(a)). When the temperature increases to 340 °C, the cubic-phase YAP crystallites (Fig. 2(b)) have an uniform and nearly spherical particle morphology with the average size of ca. 100 nm. At 400 °C, a remarkable growth of YAP crystallites can be seen (Fig. 2(c)). Their particle size increases to ca. 200 nm. The TEM observation further confirms that elevating the calcining temperature would favor the crystallization and development of YAP phase, well consistent with the former XRD analysis.

The effect of incorporated $LiNO_3$ amount on cubic-phase YAP formation was also initially studied. Fig. 3 shows XRD patterns of samples obtained at 400 °C by calcining YAP precursor/$LiNO_3$ mixtures with different weight ratios. Without using $LiNO_3$ (1:0), even at the same calcining temperature, no any crystalline phase can be detected by XRD (Fig. 3(a)). Once $LiNO_3$ is added in the process, cubic-phase YAP (JSPDS: 38-222) can be observed (Fig. 3(b)–(d)). Moreover, their XRD intensity gradually strengthens with the increase of the weight

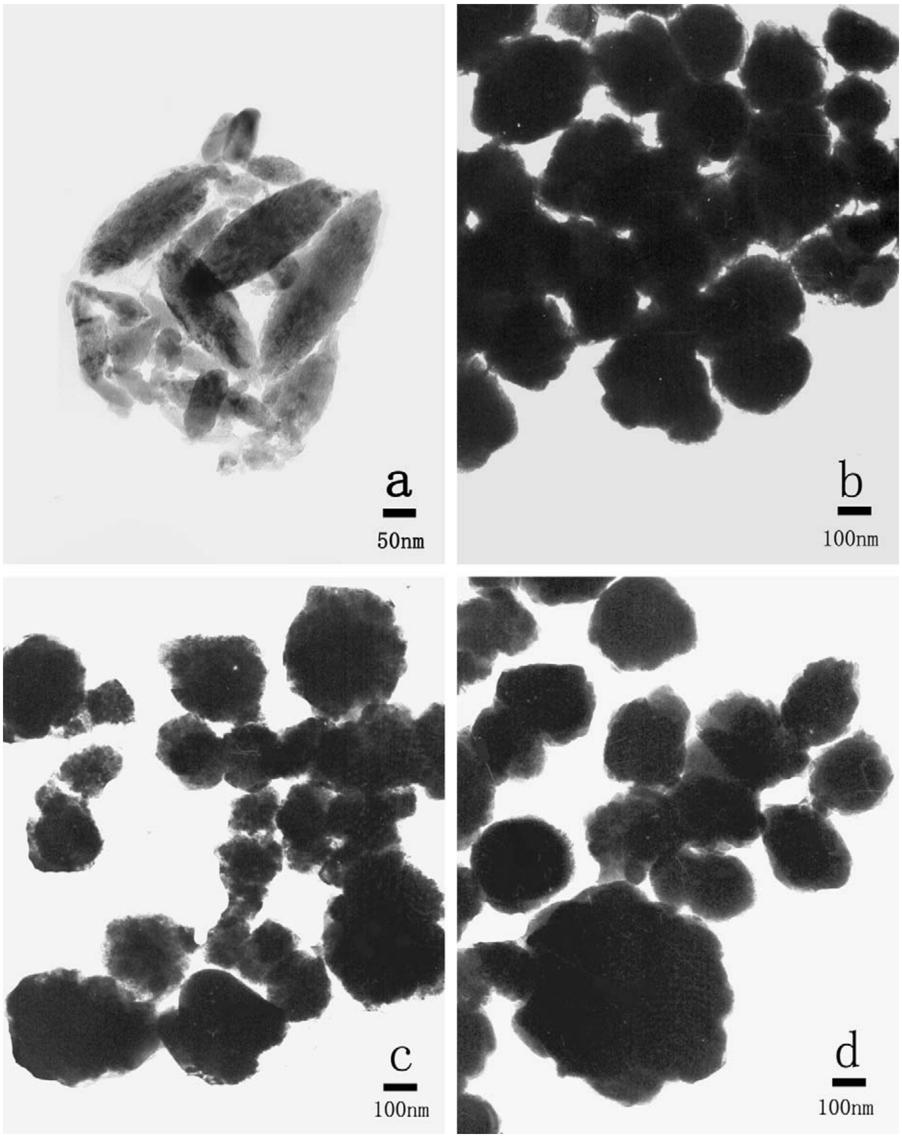

Fig. 4. TEM images of the samples prepared at 400 °C with different weight ratios of YAP precursor/$LiNO_3$ mixtures: (a) 1:0, (b) 1:4, (c) 1:8, and (d) 1:16 (holding time: 8 h).

ratio. It suggests that the presence of $LiNO_3$ would greatly promote the formation and crystallization of cubic YAP phase since liquid medium can speed up the diffusing rates of the components and lower the formation free energy of products [16,17].

Fig. 4 displays their TEM images. The amorphous phase, obtained without using $LiNO_3$, still has spindle-like particle morphology, similar to Fig. 2(a); i.e. the original morphology of the YAP precursor cannot be changed by direct calcination even at 400 °C. However, with the increase of $LiNO_3$ amount, at the same calcining temperature, homogeneous and round-shaped YAP crystallites can be easily prepared, and progressively grow up (Fig. 2(b)–(d)). TEM observation results, being in a good agreement with the XRD analysis of Fig. 3, not only reveal the importance of $LiNO_3$ incorporation in the preparing process, but also prove the promotion of $LiNO_3$ to the crystallization and development of cubic-phase YAP crystallites. In addition, as a good solvent for the precursor, $LiNO_3$ didnot react with YAP precursors. The chemical analysis showed that Li content in the as-prepared $YAlO_3$ powders (obtained by calcining at 400 °C for 8 h YAP precursor/$LiNO_3$ mixture with 1:16 weight ratio) was only 0.073 wt.%, which can be neglected.

The formation mechanism of YAP crystallites should belong to dissolution–recrystallization: while calcining (over the melting point of $LiNO_3$), YAP precursor particles would gradually dissolve from their surface toward core, accompanied by the increase of the precursors' concentration near their region so as to produce a concentration gradient in the liquid medium. Once their saturation is reached, YAP crystallites would nucleate and grow up, which would lead to the decrease of the concentration gradient. Meanwhile, low viscosity liquid would speed up the diffusing and transporting rates of components, thus resulting in constant dissolution of the precursor particles and growth of YAP crystallites. The whole process could be considered as one controlled by dynamics, it would be affected by such processing factors as calcining temperature and time, and weight ratio of YAP precursor to $LiNO_3$.

4. Conclusions

A unique synthetic route to cubic-phase YAP powders was put forward: YAP precursor was prepared at room temperature by an electrochemical method, followed by the calcination of the precursor using $LiNO_3$ as the molten medium. Well-crystallized cubic-phase YAP powders with homogeneous and round-shaped morphology can be easily prepared below 400 °C; but without using $LiNO_3$, only can an amorphous phase be obtained. Elevating calcining temperature and/or increasing $LiNO_3$ amount would be beneficial to the crystallization and development of cubic-phase YAP crystallites. The formation mechanism of YAP crystallites should belong to dissolution–recrystallization.

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