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Low-temperature solid state synthesis of Eu-doped Ca_2SnO_4 ceramics under CO-CO₂ atmosphere

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ABSTRACT

High temperature solid state is reported the most common synthesis technique for Ca_2SnO_4 ceramics, nevertheless it requires high thermal treatment temperature and long synthesis time. Our previous studies indicated that Ca_2SnO_4 was much easier to form if SnO_2 and CaCO_3 were roasted under CO-CO₂ atmosphere at relatively low temperatures. In this study, the reaction mechanism between SnO_2 and CaCO_3 under 15 vol% CO/(CO+CO₂) atmosphere and air atmosphere were firstly investigated by using XRD, SEM, XPS, etc. In addition, the Eu-doped Ca_2SnO_4 was synthesized by low-temperature solid state reaction under CO-CO₂ atmosphere. The results indicated that the crystal structure and photoluminescence properties of the products were similar to those of samples synthesized under air atmosphere, whereas the synthetic temperature was reduced by more than 300 °C.

1. Introduction

Alkaline earth stannates have advantages of stable crystalline structure and semiconducting properties, which are widely used as ceramic dielectrics, gas-sensing materials, electrode bodies, photocatalysts, ferromagnets, battery anode, photoluminescence materials, etc. [1–7]. As is reported, only two phases of CaSnO_3 and Ca_2SnO_4 exist in the CaO-SnO₂ binary system [8–10].

Perovskite-type structure of CaSnO_3 is constructed of octahedral SnO_6 which is connected to each other by sharing vertexes. Besides, in the structure of Ca_2SnO_4 , SnO_6 octahedra is linked by the edges, and the Ca^{2+} is surrounded by seven oxygen ions. Hence, it is easy for metal ions (Ti^{4+} , Mg^{2+} , etc) and rare earth ions (RE, Eu^{2+} , Dy^{3+} , Eu^{2+} , Nd^{3+} , Tb^{3+} , Sm^{3+} , Tm^{3+} , etc) to implant into the host lattice of the low dimensional SnO_6 octahedra [11–20]. RE-doped Ca_2SnO_4 ceramics have excellent photoluminescence property and long-lasting phosphor property, which are commonly used to prepare field emission displays, plasma display panels, thin film electro-luminescent devices and solar cells.

High-temperature solid state method was the most common synthesis technique for RE-doped $\text{Ca}_2\text{SnO}_4/\text{CaSnO}_3$ ceramics. Generally, RE oxides, SnO_2 and CaCO_3 powders were firstly mixed and then roasted at 1250–1400 °C for 3–12 h [11–15]. In order to reduce the temperature and shorten the synthesis time, the additives of CaF_2 , SiO_2 , H_3BO_3 and TiO_2 were often used as flux agents, which inevitably brought impurities to the final products [13–15]. In addition,

some researchers tried to use sol-gel process, chemical precipitation method and combustion-assisted synthesis method. Through these methods, RE-doped $\text{Ca}_2\text{SnO}_4/\text{CaSnO}_3$ with more homogeneous granularity was synthesized at relatively low temperatures [15–20]. However, these methods have very low productivity so that most of them are only conducted in a laboratory bench scale.

Our previous studies indicated that $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$, Na_2SnO_3 and SnSiO_3 were much easily formed under CO-CO₂ atmospheres at temperatures lower than 1000 °C [21–30]. Our exploratory experiments also showed that $\text{Ca}_2\text{SnO}_4/\text{CaSnO}_3$ was much easily formed under CO-CO₂ atmosphere. However, the reaction mechanism between CaO and SnO_2 was undiscovered, and it was unknown whether RE-doped Ca_2SnO_4 ceramics could be synthesized at relatively low temperature under CO-CO₂ atmosphere.

In this investigation, the major objectives were: 1) to compare the formation mechanisms of Ca_2SnO_4 under 15 vol% CO/(CO+CO₂) and air atmosphere, 2) to reveal the effect of CO-CO₂ atmosphere on the formation of Ca_2SnO_4 during the roasting process by using XRD, SEM-EDS, XPS, etc, 3) to provide a novel solid state process for synthesizing RE-doped Ca_2SnO_4 at low temperatures.

2. Experimental procedure

The purity of the raw materials of analytical pure reagents (CaCO_3 , SnO_2 , SnO , Sn and Eu_2O_3) used in this study was higher than 99.8 wt %, and all the reagents were pre-ground to 100 wt% passing through a

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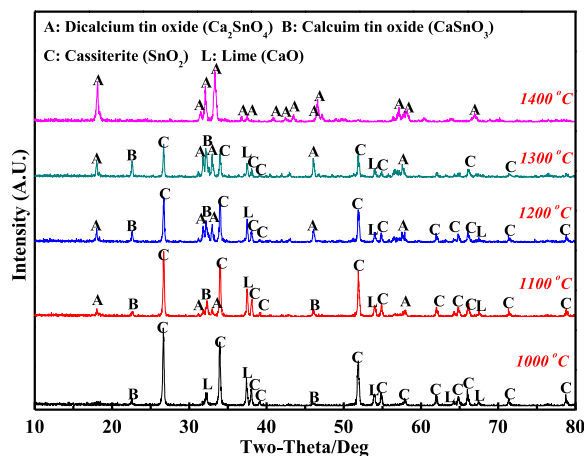


Fig. 1. XRD patterns of the products roasted at different temperature under air atmosphere (roasting time of 30 min).

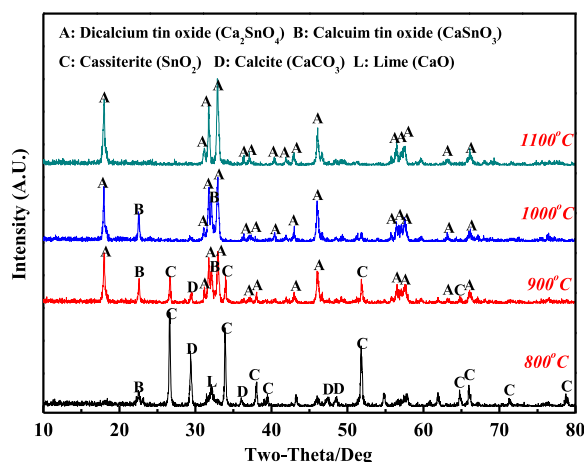


Fig. 2. XRD patterns of the products roasted at different temperature under 15 vol% CO atmosphere (roasting time of 30 min).

0.037 mm sieve. The materials were weighed precisely as certain mole ratio and mixed up gently with an agate mortar and pestle for 30 min. After that, the mixture was put into a corundum crucible. The crucible carrying with mixture was straightly placed in the high-temperature zone of the horizontal furnace [24–27]. The total flow rate of the inlet mixed gas was fixed at 4.0 L/min. The sample was then subjected to 15 vol% CO atmosphere or air atmosphere at a given temperature for a period. After that, the roasted products were rapidly taken out and quenched into liquid nitrogen. Finally, the products were finely ground and prepared for characterization.

The phase constituents of the roasted samples were identified by X-ray diffraction (XRD, D/max 2550PC, Japan Rigaku Co., Ltd) with the step of 0.02° at $10^\circ \text{ min}^{-1}$ ranging from 10° to 80° . XPS experiment was performed with a Thermo Fisher ESCALAB 250Xi using an Al K α X-ray source (1486.6 eV), and a nonlinear least-square curve-fitting program (Avantage software 5.52) was used to deconvolve the XPS data. The morphological change was detected using a scanning electron microscope (ESEM; FEI QUANTA 200; FEI, Eindhoven, The Netherlands) equipped with an EDAX energy dispersive x-ray spectroscopy (EDS) detector (EDAX Inc., Mahwah, NJ). Room temperature photoluminescence (RTPL) emission spectrum of the samples were detected on a Hitachi H-4500 fluorescence spectrometer using a Xe lamp as the light source.

3. Results and discussion

3.1. Phase transformation of $\text{CaCO}_3\text{-SnO}_2$ mixture during the roasting process

In order to compare the formation mechanism of Ca_2SnO_4 under 15 vol% CO atmosphere and air atmosphere, the mixed samples of CaCO_3 and SnO_2 as mole ratio of 2:1 were roasted and analyzed by XRD and SEM-EDS.

Fig. 1 shows the XRD patterns of the roasted products under air atmosphere, and the roasting temperature was in the range of 1000–1400 °C. The main phases of the roasted products at 1000 °C were SnO_2 and CaO , which was similar to the raw materials. The diffraction peaks of calcium stannate increased gradually with the increase of the temperature from 1100 °C to 1300 °C, meanwhile the diffraction peaks of CaO and SnO_2 were decreased and then vanished. Ca_2SnO_4 was the only phase when the temperature was 1400 °C. The results indicated that the solid phase reactions between CaO and SnO_2 were promoted by increasing the temperature as previous studies showed [11–15]. However, exorbitant roasting temperature could lead to the formation of the liquid-phase and large grain size of the roasted products.

The XRD patterns of the products roasted under 15 vol% CO atmosphere are shown in Fig. 2, and the roasting temperature varies from 800 °C to 1100 °C. The results illustrated that the formation of calcium stannate under the CO-CO_2 atmosphere was much easier than that under air atmosphere. The diffraction peaks of CaSnO_3 and Ca_2SnO_4 appeared at 900 °C, while the peaks of CaO and SnO_2 vanished as the roasting temperature was increased to 1000 °C. When the roasting temperature was raised to 1100 °C, Ca_2SnO_4 was the only phase in the roasted products.

SEM-EDS analysis was used to observe the morphologies of the roasted products, and the results of **Sample 1#** (mixture of CaCO_3 and SnO_2 roasted under air atmosphere at 1400 °C for 30 min) and **Sample 2#** (mixture of CaCO_3 and SnO_2 roasted under 15 vol% CO atmosphere at 1000 °C for 30 min) are shown in Fig. 3. As is shown in Fig. 3, the particle size of Ca_2SnO_4 in **Sample 1#** was 5–10 μm , which was caused by the excessively high temperature of 1400 °C and liquid-phase was easily formed. However, the grain sizes of the newly formed Ca_2SnO_4 particles in **Sample 2#** were 100–500 nm, and the crystal grains were spherical and cubic-like shapes.

Based on the XRD results in Figs. 1 and 2, it is inferred that the reactions between CaO and SnO_2 were obviously promoted and the Ca_2SnO_4 was much easier to form under 15 vol% CO-CO_2 atmosphere. The reaction was much fast and the suitable reaction temperature was decreased by more than 300 °C.

3.2. Occurrence state of tin in the roasted product

Figs. 1–3 have suggested that no SnO or metallic tin was found in the roasted products, XPS analysis was conducted to check the chemical state of tin in the roasted products. The results of **Sample 1#** and **Sample 2#** are shown in Fig. 4. As is observed in Fig. 4-b, the Sn 3d photoelectron peak of **Sample 2#** was well matched with the peaks of Sn^{4+} in previous literatures [4,31,32]. However, the XPS photoelectron peak of Sn 3d in Fig. 4-b can be resolved into Sn^{2+} and Sn^{4+} [4,31,32], and both of Sn 3d 5/2 and Sn 3d 3/2 clearly showed two groups of Sn chemical bonding energy of 486.6 eV and 495.0 eV for Sn^{4+} , and 494.3 eV and 485.9 eV for Sn^{2+} . The XRD results in Figs. 2 and 3 have proved that there was no phase constitution of SnO existing in the roasted samples, hence, the resolved peaks of Sn^{2+} just displayed the electron deficiency state of Sn on the surface of **Sample 2#**, which indicated that intermediate product of SnO might be crucial to the formation of calcium stannate.

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