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Ce/Mn dual-doped $LaAlO_3$ ceramics with enhanced far-infrared emission capability synthesized *via* a facile microwave sintering method

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A B S T R A C T

In this work, Ce/Mn dual-doped $LaAlO_3$ ceramics have been synthesized *via* a facile microwave sintering method. From the detailed investigations of Fourier transform infrared spectroscopy, it has been found that Ce/Mn co-doping can dramatically improve the far-infrared emission capability of $LaAlO_3$ ceramics in the range of 8–14 μm. After co-doping of Ce and Mn, Ce^{4+} ions in polyhedron site (A-site) induce the transformation of Mn^{4+} to Mn^{2+} in octahedron site (B-site), which causes the severe lattice distortion of the unit cell and strengthens the vibration intensities of asymmetrical Mn-O-Mn and Mn-O-Al bonds for the promotion of the far-infrared emissivity. Such dual-doped and perovskite-type $LaAlO_3$ ceramics with excellent far-infrared emission shows great potential as a new generation of far-infrared radiation materials for energy conservation applications.

1. Introduction

With the growing global energy shortage and consumption issues in industrial production, far-infrared radiation materials have been attracted considerable attention in current scientific and industrial researches for energy-saving application, such as electric furnace, roller kiln, and other high-temperature processing equipment [1–4]. Especially, high-performance far-infrared radiation materials can significantly emit the invisible electromagnetic wave beyond the visible light scope, which retains thermal energy to reduce energy dissipation and substantially promotes thermal efficiency in the industry [5,6]. The far-infrared light with unique thermal and resonance effects has been regarded as a new, clean and reproducible energy [7]. Therefore, it is an excellent potential to develop novel high-performance far-infrared radiation materials for the green and sustainable future.

The emissivity is a vital parameter to evaluate the materials' far-infrared emission properties [8,9]. While the perovskite-type (ABO_3) materials are popular electromagnetic materials due to their prominent magnetic performances [10,11], their high far-infrared emissivity has not been received sufficient attention over decades [12]. Shen et al. found that the Cu doping in octahedron site (B-site) significantly enhanced the far-infrared emission capability of $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ in the range of 8–14 μm from 0.693 to 0.894 [13]. Ye and his co-workers fabricated Ca/Cr co-doped $LaAlO_3$ microspheres through flame-spraying technique and explored the mechanism of their excellent far-infrared radiation property. They found that the far-infrared emissivity of $La_{0.8}Ca_{0.2}Cr_{0.5}Al_{0.5}O_3$ perovskite improved to over 0.9 in the spectral region of 3–5 μm [2]. Han et al. prepared Ca-doped $LaCrO_3$ ceramics by traditional solid-state sintering exhibited a substantial increase in far-infrared emissivity from 0.62 to 0.95 in the range of 3–5 μm [14]. Recently, $La_{0.7}Sr_{0.3}MnO_3$ powders were synthesized through the traditional solid-state reaction in various temperatures, and effects of sintering temperatures on the infrared emissivity were studied. It is found

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that the emissivity of $La_{0.7}Sr_{0.3}MnO_3$ powders reduced first and then increased with the sintering temperature from 1273 K to 1523 K [15]. These previous efforts have demonstrated that perovskite-type materials can be classified as a promising far-infrared radiation system with improved far-infrared emissivity [16].

Recently, $LaAlO_3$-based perovskites have captured broad interest because of their eco-friendly behavior [17,18]. Besides, compared with $LaCrO_3$ and its derivatives, $LaAlO_3$ has higher stability and better compatibility and refractoriness (melting point of about 2180 °C). In this study, we first employed MnO_2 and CeO_2 as dopants to fabricate Ce/Mn dual-doped $LaAlO_3$ ceramics *via* microwave sintering and investigate their far-infrared emission property. The two raw materials (MnO_2 and CeO_2) display good chemical stability and durability, excellent abrasion and corrosion resistance, as well as high melting-point. Their typical preparation methodology is shown in the schematic diagram of Fig. 1. Compared with traditional sintering approach, microwave sintering effectively promotes the rapid lattice diffusion and the formation of crystalloid, which increases thermal efficiency and enhances the stability of the crystalline structure [19,20]. Besides, the Ce/Mn co-doping causes the ionic rearrangement and significant lattice distortion, which enhances the effect of asymmetrical vibration and dramatically improves the far-infrared emissivity. Our study provides a new strategy to develop a high-performance $LaAlO_3$-based far-infrared radiation ceramics using a facile microwave sintering technology.

2. Materials and methods

2.1. Ceramics preparation

A series of doped perovskite-type $La_{1-x}Ce_xAl_{1-y}Mn_yO_3$ (x = 0.2, 0.4, y = 0.15, 0.3, 0.45) were synthesized through a facile microwave sintering method. Lanthanum oxide (La_2O_3, ≥99.95%, <5 μm), cerium oxide (CeO_2, ≥99.99%, <10 μm), aluminum oxide (Al_2O_3, ≥99.95%, 3−6 μm), and manganese dioxide (MnO_2, ≥85%, <10 μm) were used as raw materials. According to the stoichiometric ratio of $La_{1-x}Ce_xAl_{1-y}Mn_yO_3$, certain starting powders were first mixed in 3% ethanol solution using a ball grinder for 4 h. The ball milling parameters were shown below: vial material: polytetrafluoroethylene; ball material: zirconium dioxide (ZrO_2); ball-to-power weight ratio: 1.5. The mixture slurry was screened *via* 74 μm sieve, air-dried at 350 °C for 6 h to remove most of water and ethanol, and then pressed into cylinders at 50 MPa with cold uniaxial using polyvinyl alcohol (PVA) as molding adhesive. The cylinders with a dimension of 15 mm diameter and 4 mm thick were subsequently dried at 100 °C for 2 h and then finally sintered at 1400 °C for 4 h in a microwave-sintering furnace (SX2-36-13, HUAYAN EAF Plant, China).

2.2. Characterization

The crystal structure of products was examined by the X-ray diffraction analysis (XRD, PANalytical B.V., Netherlands) with a Cu target as the radiation source (λ = 1.54059 Å) at 20 kV with the

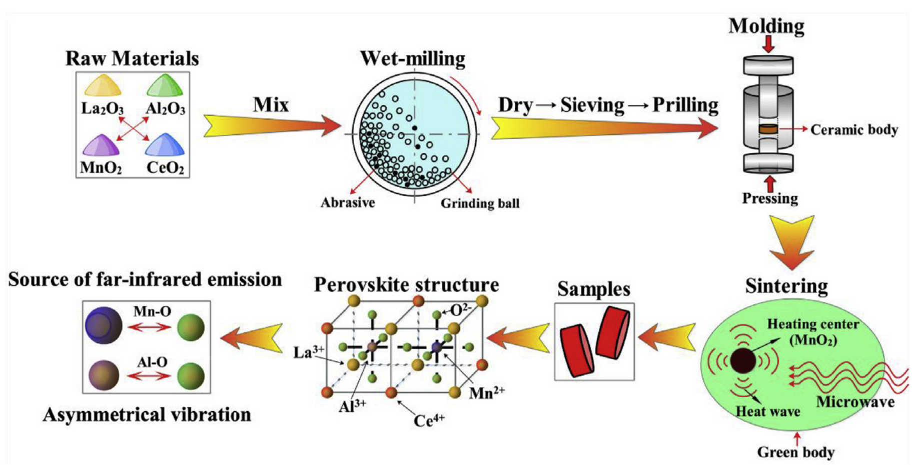

Fig. 1. Schematic diagram of preparation of Ce/Mn dual-doped $LaAlO_3$ perovskite-type ceramics.

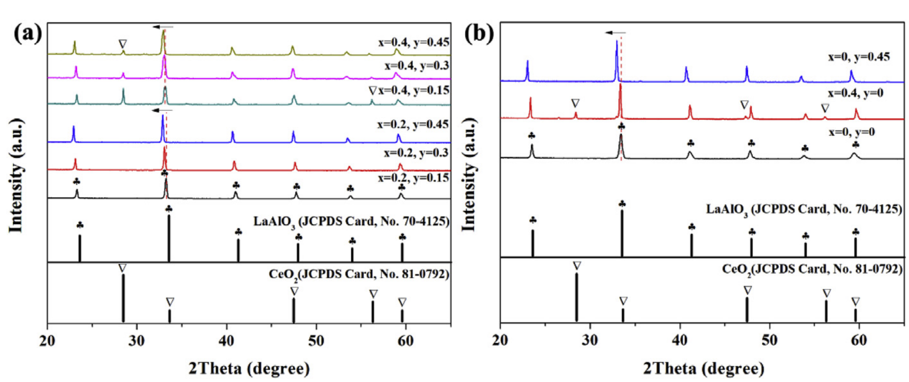

Fig. 2. XRD patterns of the $La_{1-x}Ce_xMn_yAl_{1-y}O_3$: (a) x = 0.4, 0.2 with y = 0.45, 0.3, 0.15 samples; (b) $LaMn_{0.45}Al_{0.55}O_3$, $La_{0.6}Ce_{0.4}AlO_3$, $LaAlO_3$.