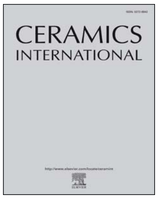
Ceramics International 44 (2018) 6337–6342

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Fully dense hot pressed calcium cobalt oxide ceramics

Nidhi Puri, Ram P. Tandon, Ajit K. Mahapatro*

Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

ARTICLE INFO

Keywords:
D. $Ca_3Co_4O_9$
A. ball milling
A. hot press

ABSTRACT

The processing parameters have been optimized to achieve highly pure and fully dense pellets of calcium cobalt oxide ($Ca_3Co_4O_9$) from solid-state ball milled calcium carbonate and cobalt oxide mixtures, calcined at optimized temperature and time, and consolidated by hot-pressing. The microscopic, spectroscopic, and thermal analysis suggest samples with longer ball-milling time require less calcination time for synthesizing highly pure crystalline phases of $Ca_3Co_4O_9$, and provide 99.2 ± 0.5% relative density.

1. Introduction

Synthesis of highly pure materials by optimizing the process parameters and formation of fully dense pellets, are the key issues in preparing efficient materials for development of high yield thermoelectric (TE) devices. Recently, the research works focus on development of new materials with enhanced TE properties, which requires preparing materials with high electrical conductivity and low thermal conductivity [1]. The misfit cobalt oxides [2,3], especially the calcium cobalt oxide ($Ca_3Co_4O_9$) show high TE performance, and considered as a potential TE material due to its unique layered structures [4] providing excellent thermal and chemical stabilities at elevated temperatures with additional advantages of ease in preparing desired sized ceramics of $Ca_3Co_4O_9$ at low cost. Various physical [5–8] and chemical [9–12] methods have been employed for synthesis of $Ca_3Co_4O_9$ powder. The conventional top-down physical method utilizes solid state ball milling (BM) technique with the idea of grinding the precursors for several hours, followed by calcination at high temperature for specific duration [6,7]. The chemically followed bottoms-up procedures [10–12] are relatively complex to handle due to requirement of precise control over several chronologically followed series of steps and difficulty in maintaining the stoichiometric ratio with the presence of inevitable residual contents, and lead to production of ceramic materials with low densities [10].

Powder processing of $Ca_3Co_4O_9$ through calcination of the mixed precursors and further consolidating into perfectly dense pellets, are the two essential steps followed sequentially to develop test materials for utilization in thermoelectric modules. Calcination of the mixture above the decomposition temperatures of precursors helps formation of new highly pure crystalline structures by rearranging the atoms from the perfectly mixed precursors. Earlier, relatively dense pellets of polycrystalline CCO material have been achieved by using the HP technique [13,14] that utilizes a static pressure at elevated temperatures, allows fast heating and cooling rates, assists sintering of materials in few minutes with formation of highly compact textured ceramics [13,14], and widely preferred over other available methods of conventional sintering (CS) [5,7,13] and spark plasma sintering (SPS) [7,12,13].

The present work optimizes the processing times for BM and calcination on the phase formation of polycrystalline $Ca_3Co_4O_9$ powder, by monitoring the evolution of morphological, crystallographic, and spectroscopic measurements. The optimized recipe followed by consolidating the highly pure powders using hot press technique produces densely packed ceramics of $Ca_3Co_4O_9$.

2. Materials and experimental methods

Misfit-layered $Ca_3Co_4O_9$ powder was synthesized by solid-state BM technique using calcium carbonate ($CaCO_3$) and cobalt oxide (Co_3O_4) precursors in stoichiometric ratio of 3:4:9 for Ca, Co, and O. The planetary BM was performed at a speed of 500 rpm using 5 mm diameter tungsten carbide balls with ball-*per*-powder weight ratio of 10:1 and considering acetone as the dispersion media. The BM process was continued for different time durations of 6 h, 24 h, 48 h, and 72 h, and dried on a heating plate, and identified as BM6, BM24, BM48, and BM72, respectively. The resulting as ball milled powders were calcined at 1123 K for 2 h (BM6C2, BM24C2, BM48C2, and BM72C2), 6 h (BM6C6, BM24C6, BM48C6, and BM72C6), 12 h (BM6C12, BM24C12, BM48C12, and BM72C6), and 24 h (BM6C24, BM24C24, BM48C24, and BM72C24). The as-calcined BM48C6 powders were consolidated into pellets by HP technique, performed in a vacuum chamber by placing the calcined powders in a graphite paper wrap within the graphite

---

* Corresponding author.
E-mail address: amahapatro@physics.du.ac.in (A.K. Mahapatro).

https://doi.org/10.1016/j.ceramint.2018.01.024
Received 14 September 2017; Received in revised form 26 December 2017; Accepted 4 January 2018

die of diameter 20 mm and heating to 1173 K under a hydraulic pressure of 200 MPa for 25 min, and cooling passively down to room temperature. The outer graphite wrap was chopped-off and the disk-shaped hot pressed pellet (HPP) of $Ca_3Co_4O_9$ in 20 mm diameter and 3 mm thickness was collected, and micromachined to prepare sample bars of $15 \times 8\ mm^2$ dimensions for further characterization.

The morphology was imaged through field emission scanning electron microscopy (FESEM, MIRA3, TESCAN, USA) and transmission electron microscopy (TEM, FEI, Tecnai G2 T-30 U-TWIN, USA). The materials properties for all the $Ca_3Co_4O_9$ samples prepared with different process parameters of BM and calcination were characterized by studying the crystallographic structure through X-ray diffraction (XRD, Rigaku, Ultima IV X-ray diffractometer, Japan) using Cu-Kα radiation with excitation wavelength of 1.541 Å in the angular range of $2\theta = 15^\circ$ to 70° at scanning rate of 2°/min, and selected area electron diffraction (SAED) patterns through TEM. The elemental analysis was studied using energy-dispersive X-rays (EDX) attachment to the FESEM. Thermal stability was tested with thermogravimetric and differential thermal analysis (TG-DTA, TA Instruments, SDT Q600, USA), scanned from room temperature to 1273 K at heating rate of 5°/min and performed in nitrogen atmosphere. Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, USA) was recorded in spectral range from

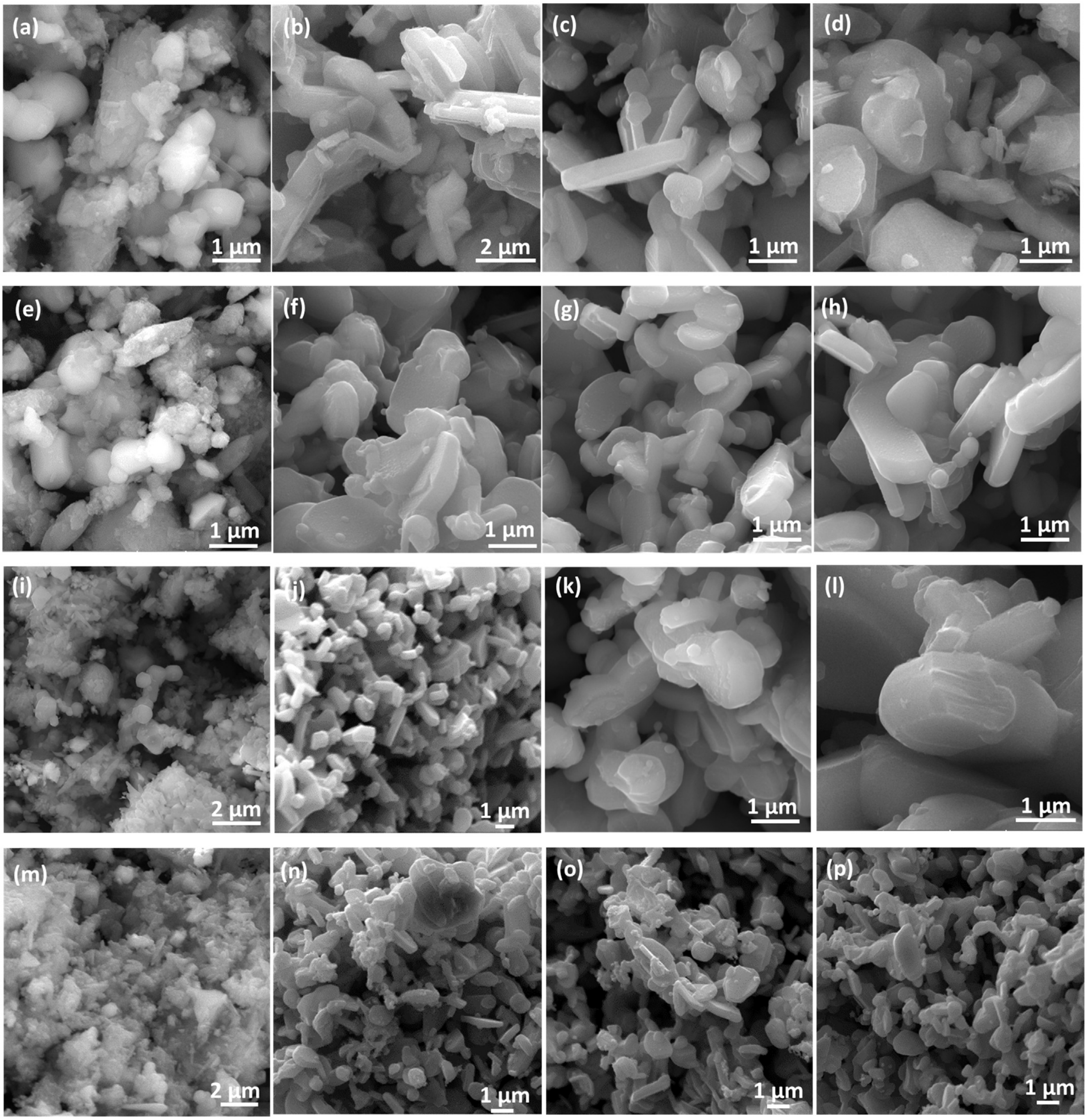


Fig. 1. FESEM images of the (a) BM6, (b) BM6C6, (c) BM6C12, (d) BM6C24, (e) BM24, (f) BM24C6, (g) BM24C12, (h) BM24C24, (i) BM48, (j) BM48C6, (k) BM48C12, (l) BM48C24, and (m) BM72, (n) BM72C6, (o) BM72C12, and (p) BM72C24 powders of $Ca_3Co_4O_9$.