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Synthesis of $Co_xMn_{1-x}O_4$ ($0.9 \leq x \leq 2.7$) nanopowders with controlled phase and composition via a gel-combustion method

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ABSTRACT

$Co_xMn_{3-x}O_4$ (CMO) nanopowders with a wide compositional range ($0.9 \leq x \leq 2.7$) are synthesized using a gel combustion method. The effect of Co content and calcination temperature on the crystal structure of the CMO nanopowders is studied using X-ray diffraction. A highly crystalline cubic spinel structure can be obtained at a relatively low temperature (~700 °C) for CMO with a Co content of 1.8. Further increases in Co content to 2.7 leads to a higher formation temperature (~800 °C) required in order to form a crystalline cubic structure. X-ray photoelectron spectroscopy revealed that the Co and Mn cations have mixed valence states. Energy dispersive X-ray elemental mapping indicates that Co and Mn cations are homogeneously distributed in the CMO nanopowders. Thermogravimetric analysis, Fourier transform infrared, scanning electron microscopy, and X-ray fluorescence are utilized to investigate the formation of the CMO nanopowders, as well as the compositional and structural properties.

1. Introduction

Spinel oxides with the generic formula AB_2O_4, that consist of transition metals with A, B=Ni, Co, Mn, etc., are crucial in a variety of applications such as electronics and energy storage devices due to their excellent electronic properties [1–4]. Negative temperature coefficient (NTC) thermistors are a specialized device whereby resistivity decreases as temperature increases. $Co_xMn_{3-x}O_4$ (CMO, $0 < x < 3$) spinel oxides have been intensively investigated in order to achieve a high factor of the thermal sensitivity for NTC applications requiring precise resistance or temperature control. Thermal sensitivity of the CMO can be controlled by changing chemical composition. For example, when Co content increases above 1.0, Co ions begin to occupy octahedral B sites which is known to further enhance thermal sensitivity by rearranging the cationic distribution in the spinel structure [5].

Most recent studies on the control of chemical composition in CMO have been based on samples processed using solid state reaction methods [6]. However, CMO spinel oxides prepared by the solid state method usually result in irregular morphology and large particle sizes. In addition, the powder often consists of mixtures of cubic and tetragonal spinel possibly leading to mechanical failure in the sintered ceramics due to different thermal coefficients of two phases [7,8]. Thus, continuous efforts have been made to develop alternative synthesis techniques which result in single phase CMO spinel oxide powder with small and homogeneous particle size.

It is known that the Co/Mn ratio significantly affects the crystallographic phase formation. A low Co content ($0 < x < 1.8$) tends to facilitate the formation of tetragonal phase, while a high Co content ($1.8 < x < 3.0$) results in the formation of cubic spinel [7]. However, at least a partial phase transformation from cubic to tetragonal is difficult to avoid in Co-rich CMO oxides prepared by conventional sintering [7,8]. Therefore, it remains challenging to control phase formation during the synthesis of CMO spinel oxides over a wide composition range.

Gel combustion synthesis is a simple and cost-effective method which is a candidate for the preparation of oxide nanopowders with a wide composition range. In this technique, nitrate

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Table 1
Elemental contributions and ratios in different compositions of $Co_xMn_{3-x}O_4$ samples using XRF.

X*	0.9	1.2	1.5	1.8	2.1	2.4	2.7
Co (wt%)	19.5	26.9	34.2	42.4	49.5	58.1	63.9
Mn (wt%)	45.3	39.7	34.1	28.4	20.9	13.3	7.13
Co:Mn	0.90:2.09	1.21:1.78	1.50:1.49	1.79:1.20	2.10:0.89	2.44:0.55	2.69:0.30

* Molar amount of Co ions in starting precursor which is calculated by target composition.

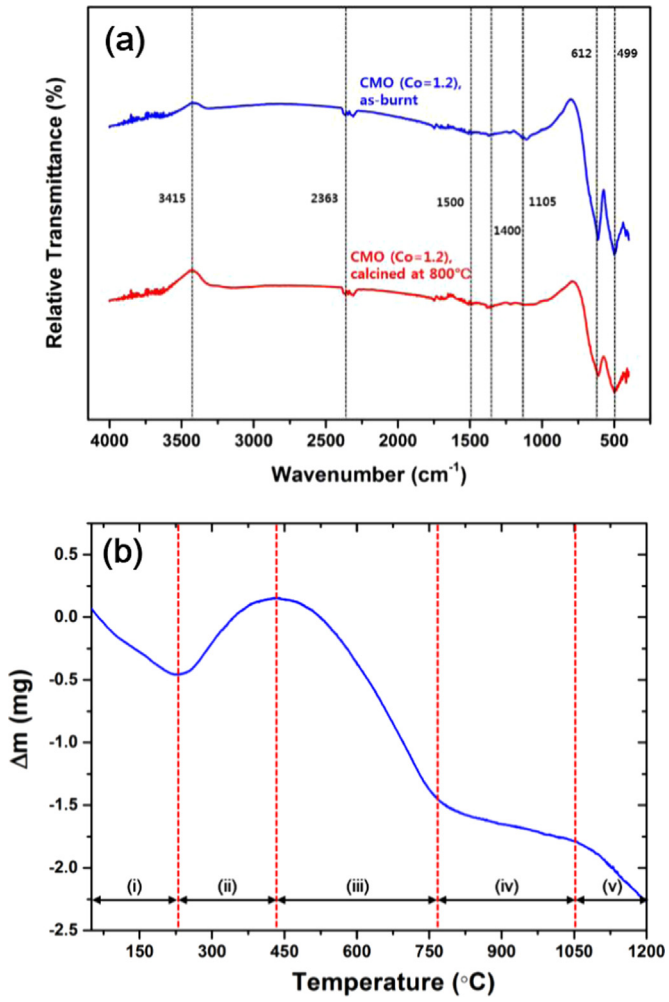

Fig. 1. (a) FT-IR spectra of CMO (Co=1.2) nanopowder measured for the range of wavenumber between 500 and 4000 cm^{-1}. (b) TGA spectrum of CMO (Co=1.2) nanopowder measured for the temperature range from room to 1200 °C under air.

compounds with redox agents may be used as the raw materials. A mixed solution of the raw materials is heated under a controlled pH in order to transform the sol to a viscous gel. Further higher temperature treatment leads to an exothermic combustion. Simultaneously, both reduction and oxidation agents such as organic materials and nitrates transform the gel to a very fine powder. The as-burnt powder is subsequently calcined at an elevated temperature to remove residual organics and complete the formation of the desired phase via crystallization. Importantly, the calcination temperature for the combustion method can be much lower than that of conventional solid state methods, since the powder is crystallized to a certain level during combustion at low temperature. This combustion method is a suitable technique to obtain fine nanopowders with low-temperature stable crystal phase (e.g., a cubic phase for CMO spinel) over a wide composition range.

In this work, we prepared CMO nanopowders with different crystal structures over a wide composition range ($0.9 \leq x \leq 2.7$) via a gel combustion method. Crystallographic evolution and microstructure of the CMO nanopowders during synthesis and post heat treatment were evaluated. Oxidation states and distribution of elements in the CMO nanopowders were investigated.

2. Experimental procedure

CMO powder was synthesized via a combustion method using manganese (II) nitrate ($Mn(NO_3)_2$; 50% aqueous solution), cobalt (II) nitrate hexahydrate ($Co(NO_3)_{26}H_2O$), and citric acid ($C_6H_8O_7$) as starting materials. Stoichiometric amounts of $Mn(NO_3)_2$, $Co(NO_3)_{26}H_2O$, and citric acid were dissolved in distilled water. The molar ratio of nitrate to citric acid was maintained at 1:1. Ammonia solution was added to the solution to vary the pH from 1 to 6. The solution was heated at 80 °C to transform the solution into a sol which was subsequently heated at 130 °C under constant stirring for the formation of a brownish gel. The temperature of the sol and gel were measured using an infrared thermometer (AR 500, Smart sensor®, China). A fine powder was obtained from the gel by heating at 300 °C until all the gel was burnt out. The prepared powder was calcined at selected temperatures from 400 °C to 800 °C with a heating rate of 5 °C /min for 2 h under air.

Quantitative analysis for the elements of the as-burnt powders after the combustion process was performed using X-ray Fluorescence (XRF, EDX-720, Shimadzu, Japan). Crystallographic information of the as-burnt and calcined CMO powder at different temperatures were investigated using X-ray diffraction (XRD) with Cu Kα radiation (λ=1.5404 Å) using a Panalytical X'pert–pro MPD (Netherlands). The valence states of the elements in both the as-burnt and calcined CMO powders were analyzed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220i, Thermo Scientific, USA). XPS low and high resolution scans were performed with the pass energies of 100 eV and 20 eV, respectively. Microstructures of the powders were investigated by scanning electron microscopy (SEM, Nova NanoSEM, FEI, USA) equipped with energy-dispersive X-ray (EDX) spectroscopy. EDX mapping was performed on the calcined powders to investigate elemental distribution. Thermogravimetric analysis (TGA, Setsys evolution TGA-DTA, Setaram, France) was undertaken in the temperature range from ambient to 1200 °C under air in order to characterize calcination behavior of the as-burnt powder. Fourier transform infrared (FT-IR, FTS-6000, Bio-rad, USA) spectra of the as-burnt and calcined CMO powders were collected in the range from 400 to 4000 cm^{-1}.

3. Results and discussion

Chemical compositions of as-burnt and calcined CMO nanopowders were analyzed using the XRF technique and the results are summarized in Table 1. It is shown that the molar ratio of Co and Mn in the precursors is similar to that of the as-burnt nanopowders, indicating that the chemical compositions of CMO ($0.9 \leq x \leq 2.7$) compositions were successfully controlled during nanopowder synthesis via the gel combustion technique.