Ain Shams University
Faculty of Science
Chemistry Department

Investigation and Sintering of Nano-manganite Ceramics Powders Prepared Via Different Methods

Thesis Submitted

By

Rehab El-Sayed Abd-Alaziz Negida

(M. Sc. in Chemistry)

For Fulfillment of the Degree of Ph. D. in Chemistry

Chemistry Department
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Rehab El-Sayed Ngida

CONTENTS

List of Abbreviations

- **ABO_3** Perovskite compounds
- **LMO** Lanthanum manganites
- **LCMO** Lanthanum calcium manganites
- **LSMO** Lanthanum strontium manganites
- **SEM** Scanning Electron Microscopy
- **TEM** Transmission electron microscope
- **BDS** Broadband dielectric spectrometer
- **XRD** X-ray Diffraction Analysis
- **XRF** X-ray fluorescernce
- **AP** Apparent porosity
- **BD** Bulk density
- **SOFC** Solid oxide fuel cell

Keywords:

Perovskite structure, Manganite compounds, SOFC, Nanoparticles, Hydrothermal Synthesis, Mechanical activation method.

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Abstract

During the last decade ABO_3 manganites with perovskite structure exhibit a widely studying due to its physical, magnetic and electric properties that improve their various applications like sensors, catalysts electrode materials for solid-oxide fuel cell. This work concerns on studying: 1) the effect of various cation substitution such as Ca and Sr cations on phase and microstructural of $LaMnO_3$ phase and 2) the role of these cation on changing electrical, physical and magnetic properties of such material. Two different ways of preparation have been applied i.e. a hydrothermal method and mechanical activation method in this work. In hydrothermal synthesis, the crystalline powder can be prepared in one step from solutions of metal salts at a temperature of 230 °C in 48 h. On other hand, the mechanical activation method are carried out by preparation the metal oxides depending on using manganese oxide that were extracted from low-grade ores by using glucose as a reducing agent in dilute nitric acid. Then the prepration of perovskite manganite samples by milling and mixing the reactant metal oxides with the extracted MnO_2 has been carried out and then added to other various oxides to prepare manganite compounds. In all the samples the Perovskite manganites have been prepared in a general formula $La_xCa_{1-x}MnO_3$ and $La_xSr_{1-x}MnO_3$ (x = 0.1, 0.3, 0.5 and 1.00) and then sintered at different temperatures ranging from 1100^{o}C to 1450^{o}C. The powder characteristics of metal-doped lanthanum manganites are characterized utilizing x-ray diffraction to elucidate the phase transformation, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were used to elucidate

the size and morphology of the particles and crystalline structure of these powders. For hydrothermal procedures the results revealed that the maximum sintering temperature for LCMO is 1400^{o}c while for LSMO is 1450^{o}c. XRD patterns show that the pervoskite phase is detected at 2θ at 33-34. By addition of Ca^{2+} and Sr^{2+} the peaks are shifted to lower 2θ. SEM micrographs of all grains are rod like shape. The magnetic properties of hydrothermally prepared samples are detected, where the magnetization of perovskite samples is improved by the addition of Ca^{2+} and Sr^{2} and the highest results are observed for $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.5}Sr_{0.5}MnO_3$. For mechanical activation method, MnO_2 is obtained by leaching method at 95^{o}C and characterized by XRD. Studying the bulk density and apparent porosity show that the sintering temperature of LCMO samples is 1300 ^{o}C while for LMO and LSMO is 1350^{o}C. TEM images of an individual $La_{0.1}Ca_{0.9}MnO_3$ nanoparticles and $La_{0.1}Sr_{0.9}MnO_3$ nanoparticles exhibits single-crystalline particles. XRD results for sintered samples prepared by mechanosynthesis show that perovskite phases are prepared after 8 h of milling with sharp peaks at 2θ ranged between 32-34 that shifted to lower 2θ values by the substitution of La^{3+} with Ca^{2+} and Sr^{2+}. Scanning electron microscopy (SEM) morphology for the sintered samples appears in spherical shapes. The grain sizes are different for LCMO and LSMO samples according to x values. For magnetic properties, LSMO samples have higher magnetization than LMO and LCMO samples. $La_{0.5}Sr_{0.5}MnO_3$ exhibits higher magnetization than the others. The electrical resistivity for both producers shows that LCMO samples are higher than LSMO samples due to their different atomic size, while $LaMnO_3$ exhibits the highest resistivity.