

SYNTHESIS AND ANALYSIS OF $\text{La}_{0.9}\text{MnO}_3$ BY COMBUSTION METHOD 121

B. I. ITA and C. A. EDEM

(Received 20 March, 2002; Revision accepted 3 November, 2003)

ABSTRACT

The $\text{La}_{0.9}\text{MnO}_3$ has been synthesized from lanthanum acetylacetonate, manganese acetylacetonate and urea by combustion method at 800°C . The analysis of the synthesized $\text{La}_{0.9}\text{MnO}_3$ show it to be a semi-conducting nanopolycrystalline material having orthorhombic geometry with unit-cell parameters: $a = 5.50335\text{\AA}$; $b = 5.7250\text{\AA}$; $c = 7.70028\text{\AA}$ and with Mn^{4+} content of 12%. The mean-size of the particles of $\text{La}_{0.9}\text{MnO}_3$ was obtained from TEM analysis at 80nm.

KEYWORD: $\text{La}_{0.9}\text{MnO}_3$, acetylacetonate, nanopolycrystalline, combustion method, semi-conductor.

INTRODUCTION

The synthesis, analysis and properties of nanopolycrystalline materials have become very active area of research in the last few years. In particular, nanopolycrystalline inorganic oxides offer many exciting properties. Conventional oxides such as $\text{La}_{0.9}\text{MnO}_3$ have been reported to be very important colossal magnetoresistance material (Maignan et al, 1997). Also $\text{La}_{0.9}\text{MnO}_3$ is used as a model for the study of the relationship between transport properties and magnetism in oxide materials.

For the synthesis of $\text{La}_{0.9}\text{MnO}_3$, methods including solid-state reaction (ceramic method) (Mahindiran et al, 1996, Troyanchuk et al, 1997) and sol-gel (Ita, 1998) have been reported in the literature. The conventional solid-state reaction method requires several heating and grinding steps to ensure homogeneous mixing of the various oxides (Ravindranathan et al, 1993). Also appropriate conditions for the completion of the reaction is normally decided only by carrying out x-ray diffraction and other analysis periodically. Due to this inherent difficulty with the solid-state reaction method, one frequently ends up, with mixtures of reactants and product (Rao and Raveau, 1995). Separation of the desired oxides from such mixtures is always very difficult. It is sometimes also difficult to obtain a compositional homogeneous product by the solid-state reaction method even when the reaction proceeds almost to completion. The sol-gel technique is an improvement on the solid-state reaction method but has some problems including the much effort required to obtain homogeneous sol solution. It is therefore not uncommon to find several modifications of the solid-state reaction and sol-gel methods to circumvent some of the

limitations. By using combustion method and other techniques such as freeze-drying and spray drying, it is possible to obtain a more intimate mixing of the reactants. In view of the fact that a particular material may have different electrical, magnetic and structural properties depending upon its particle size (Ita, 2000), which also depends upon the method of preparation, starting materials and temperature, this paper reports on the instant synthesis of $\text{La}_{0.9}\text{MnO}_3$ using the combustion method involving the use of lanthanum acetylacetonate, manganese acetylacetonate as precursors and urea as fuel. In this way, the firing temperature and the time required to obtain the product are reduced. The main advantage of this method is in achieving the synthesis at low temperature, so that the products formed are made up of fine-particulate of nanometric dimension.

EXPERIMENTAL

Exactly 3.9332g of lanthanum acetylacetonate (0.009 mol) was mixed with 2.53g of manganese acetylacetonate (0.01 mol) and 1.1411g of urea (0.019 mol) in an agate mortar and ground for 10 min. The mixture (in a pyrex dish) was then introduced into a muffle furnace maintained at 800°C . Combustion took place leading to the production of fine-particles of $\text{La}_{0.9}\text{MnO}_3$ in less than 5min. The muffle furnace was cooled to room temperature ($27\pm 1^\circ\text{C}$) and the dish containing the $\text{La}_{0.9}\text{MnO}_3$ was removed for the analysis of the powder, which was done by x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis of x-ray (EDAX), transmission electron microscopy (TEM), electron diffraction (ED) and resistivity measurements. A Seifert 3000TT x-ray powder diffractometer with $\text{Cu-K}\alpha$ radiation was

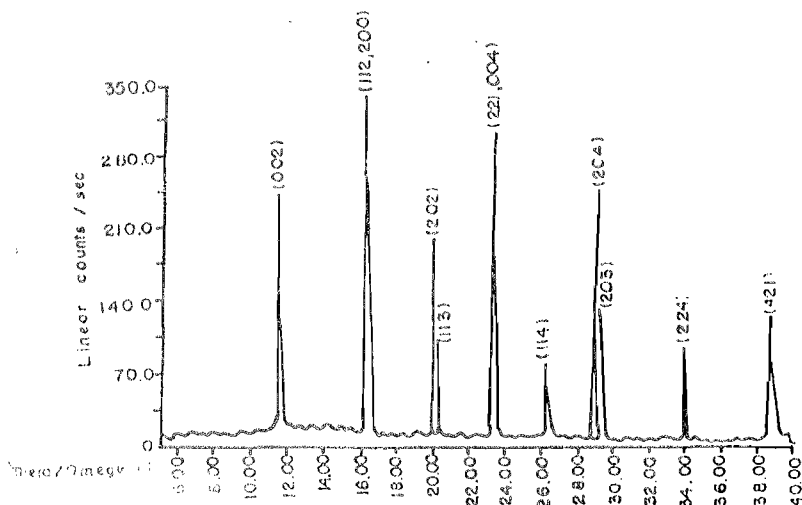


Fig.1 X-ray diffraction spectrum of the $\text{La}_{0.9}\text{MnO}_3$ nanopolycrystals obtained by combustion method.

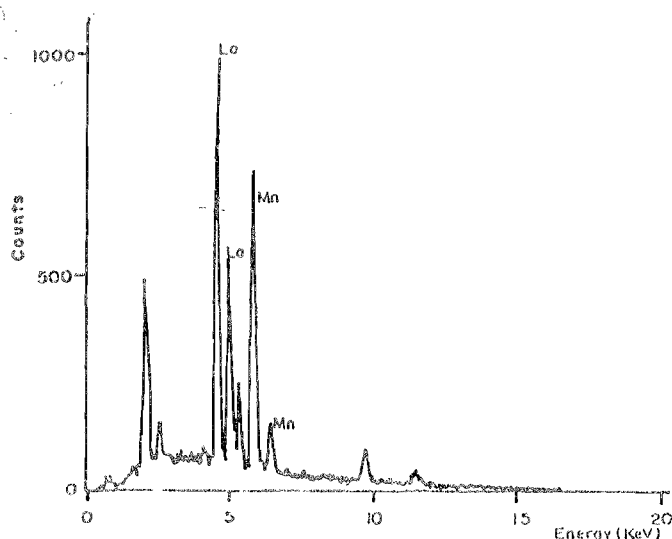


Fig.2 EDAX pattern of the $\text{La}_{0.9}\text{MnO}_3$ nanopolycrystals obtained by combustion method.

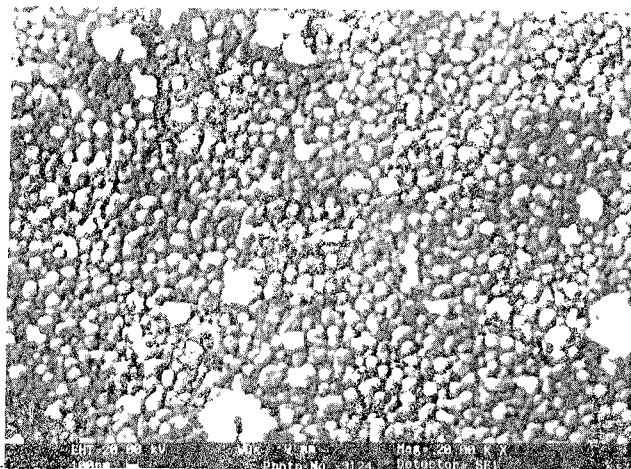


Fig.3 The SEM photograph of the $\text{La}_{0.9}\text{MnO}_3$ nanopolycrystals obtained by combustion method

employed for x-ray diffraction analysis. A Leica S4401 SEM was used for microstructural analysis and EDAX analysis was done by employing an Oxford instrument ISIS Si detector., TEM and ED images were recorded with a JEOL 3010 microscope. Resistivity measurement was done using the four-probe technique (JNC 401 IN model).

RESULTS AND DISCUSSION

Fig. 1 illustrates the XRD spectrum of the synthesized $\text{La}_{0.9}\text{MnO}_3$. The Fig. 1 shows the formation of pure-phase of $\text{La}_{0.9}\text{MnO}_3$ when compared with JCPDS card number 33-713 and the pattern obtained by Arulraj et al (1996). An attempt to investigate the structure of the synthesized $\text{La}_{0.9}\text{MnO}_3$ using the popular prozski computer program for lattice parameters refinement reveals that the synthesized $\text{La}_{0.9}\text{MnO}_3$ crystallizes in orthorhombic geometry having unit-cell parameters; $a = 5.50335\text{\AA}$; $b = 5.72507\text{\AA}$; $c = 7.70028\text{\AA}$. This result is also consistent with the Mn^{4+} content, an essential aspect of characterization of the manganates. The Mn^{4+} content obtained as 12% as determined by the redox titration using potassium permanganate and ferrous sulphate solutions also confirms the orthorhombic nature of the oxides (Ita, 2000). Elemental analysis using EDAX reveals La: Mn ratio to be 0.9:1 in the sample (Fig. 2) indicating the presence of La and Mn in the sample. Further more, Figs. 1 and 2 ascertain the phasic-purity of the synthesized $\text{La}_{0.9}\text{MnO}_3$. The SEM shows that the particles of the synthesized $\text{La}_{0.9}\text{MnO}_3$ are nearly spherical and form structure of tinier particles which are of nanometric dimension and less than 100nm. Further microscopic analysis of the $\text{La}_{0.9}\text{MnO}_3$ reveals that the mean-particle size from TEM

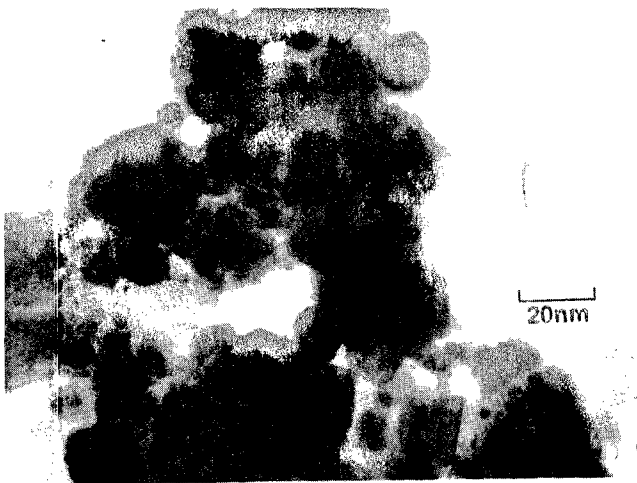
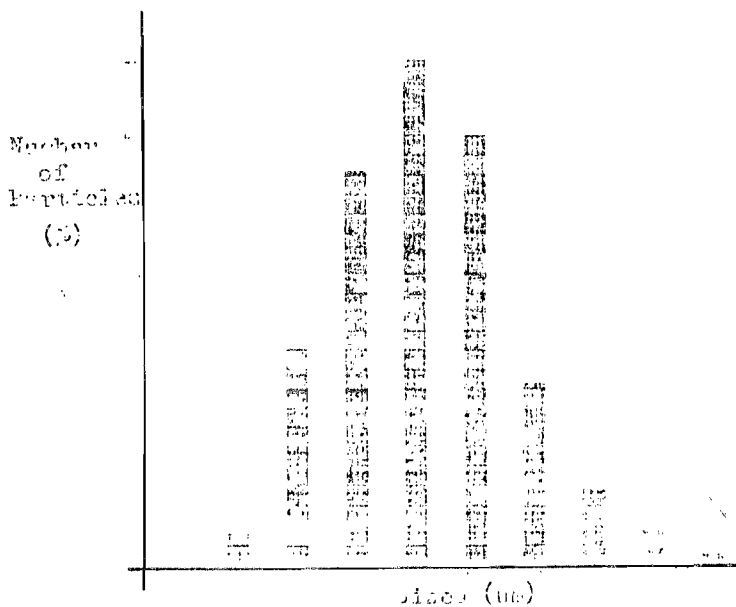


Fig.4 The TEM photograph of the $\text{La}_{0.9}\text{MnO}_3$ nanopolycrystals obtained by combustion method.



(Fig. 4) is about 80nm which further confirms the nanometric dimension of the particles. The nanopolycrystalline nature of $\text{La}_{0.9}\text{MnO}_3$ is actually revealed from the particle-size histogram (Fig. 5) where most of the particles fall within the 80nm range whereas others fall within 40, 60, 100 and 120nm range with very few particles having 20, 140, 160 and 180nm sizes. The ED pattern (Fig. 6 (a)) illustrates the crystalline nature of the particles as white spots are obtained. Amorphous materials do not exhibit white spots (Fig. 6 (b)). The variation of resistivity with temperature obtained using the four-probe technique shows that the $\text{La}_{0.9}\text{MnO}_3$ is a semi conductor but it was not possible to obtain the semi conductor-to-metal transition for this

sample at the temperature range of 50-300K studied.

It is necessary to re-emphasize that it has been possible to synthesize nanopolycrystalline orthorhombic $\text{La}_{0.9}\text{MnO}_3$ with a semi conductor-like behavior from the acetylacetonate complexes of La and Mn for the first time via the combustion method. The combustion method is a very effective method that precludes any danger and has all the advantages of the wet chemical methods such as atomic level doping of the desired dopants.

CONCLUSION

The $\text{La}_{0.9}\text{MnO}_3$ has been synthesized from lanthanum acetylacetonate, manganese acetylacetonate and urea via the combustion method for the first time. The synthesized $\text{La}_{0.9}\text{MnO}_3$ is a semi conducting nanopolycrystalline material crystallizing in the orthorhombic geometry.

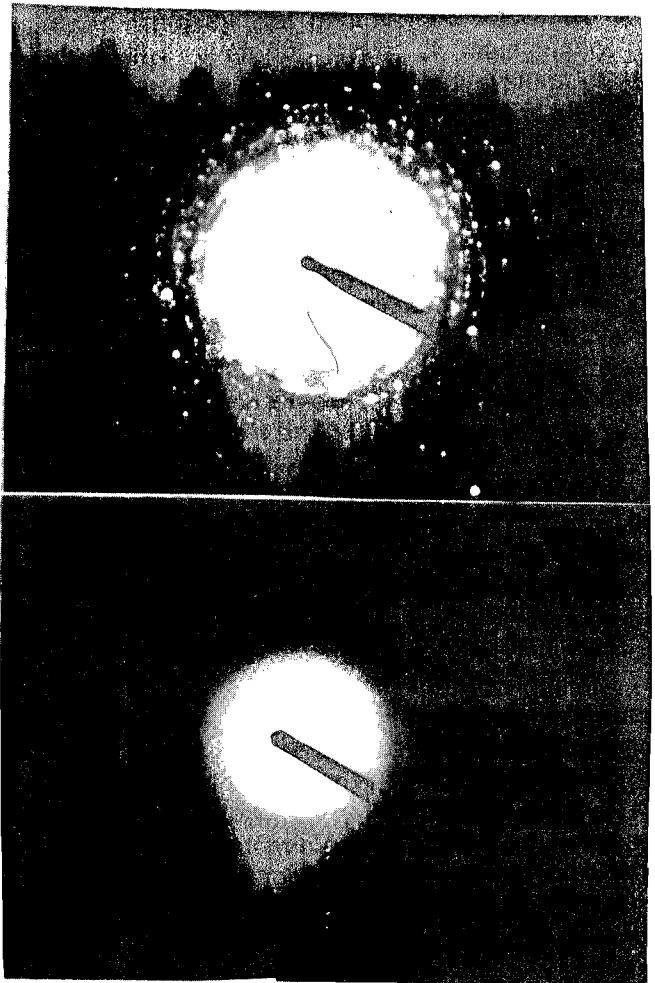


Fig.6 The ED pattern of the $\text{La}_{0.9}\text{MnO}_3$ nanopolycrystals obtained by combustion method: (a) Crystalline (b) Amorphous.

ACKNOWLEDGEMENT

The author (BII) is thankful to TWAS for a fellowship to India. He is also grateful to Prof. C. N. R. Rao at JNCASR, Bangalore, India for the provision of facilities for this work.

REFERENCES

- Arulraj, A., Mahesh, R., Subbanna, G. N., Mahendiran, R., Raychaudhuri, A.K. and Rao, C.N.R., 1996. Insulator-metal transitions, giant magnetoresistance and related aspects of the cation-deficiency $\text{La}_{0.9}\text{MnO}_3$ compositions $\text{La}_{1-\delta}\text{MnO}_3$ and $\text{LaMn}_{1-\delta}\text{O}_3$. *J. Solid State Chem.* 127:87-91.
- Ita, B. I., 1998. Synthesis and characterization of some semi conducting oxides-perovskites and spinels. Ph.D Thesis, University of Calabar, Calabar; Nigeria.
- Ita, B. I., 2000. Combustion synthesis of nanocrystalline LaFeO_3 . *ICIT-Models in Chemistry*. 137-671-676.
- Ita, B. I., 2000. Synthesis and characterization of nanocrystalline LaMnO_3 . *J. Chem. Soc. Nigeria*. 25: 58-60.
- Mahindiran, R., Tiwary, S. K., Raychandhuri, A. K., Ramakrishnan, T. V., Mahesh, R., Rangavittal, N. and Rao, C. N. R., 1996. Structure, electron-transport properties and giant magnetoresistance of hole-doped LaMnO_3 systems. *Phys. Rev. B*. 53: 3348-3358.
- Maignan, A., Michel, C., Hervieu, M. and Raveau, B., 1997. A monoclinic manganite, $\text{La}_{0.9}\text{MnO}_{3-\delta}$, with colossal magnetoresistance properties near room temperature. *Solid State Comm.* 101: 227-281.
- Rao, C. N. R. and Raveau, B., 1995. *Transition metal oxides*, VCH Publishers Inc., New York.
- Ravindranathan, P., Karmaneni, S. and Roy, R., 1993. Synthesis of lithium aluminate, mullite and colored zirconia by a combustion process. *J. Mater. Sci. Lett.* 12: 369-371.
- Troyanchuk, I. O., Samsonenko, N. V., Shepvalova, E. F., Szymezak, H. and Nabialek, A.; 1997. Synthesis and characterization of $\text{Ln}(\text{Ba}_{0.5}\text{Mn}_{0.5})\text{O}_3$ (Ln Lanthanoid; B = Ni, Co) perovskites. *Mater. Res. Bull.* 32: 67-74.