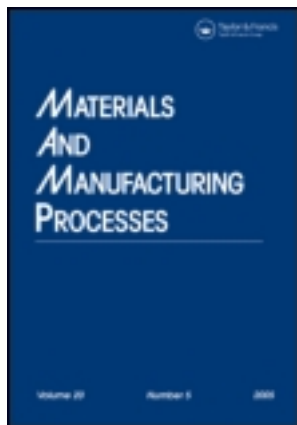


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## Materials and Manufacturing Processes

Publication details, including instructions for authors and subscription information:

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Available online: 24 May 2011

To cite this article: M. Helan & L. John Berchmans (2011): Low-Temperature Synthesis of Lithium Manganese Oxide Using LiCl-Li<sub>2</sub>CO<sub>3</sub> and Manganese Acetate Eutectic Mixture, *Materials and Manufacturing Processes*, 26:11, 1369-1373

To link to this article: <http://dx.doi.org/10.1080/10426914.2010.536932>

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# Low-Temperature Synthesis of Lithium Manganese Oxide Using LiCl-Li<sub>2</sub>CO<sub>3</sub> and Manganese Acetate Eutectic Mixture

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Fine crystalline LiMn<sub>2</sub>O<sub>4</sub> powders have been prepared by molten salt synthesis (MSS) at 500°C, using an eutectic mixture of lithium chloride, lithium carbonate, and manganese acetate salts. Thermogravimetric and differential thermal analysis (TGA/DTA) measurements are performed to investigate the thermal decomposition behavior of the precursor salts. The single-phase cubic structure of LiMn<sub>2</sub>O<sub>4</sub> is confirmed by X-ray powder diffraction analysis. The lattice parameter is found to be 8.1967 Å. The molecular structure of the compound is studied using FT-IR and Raman spectroscopy. The chemical composition and the purity of the synthesized powders are determined using atomic absorption spectroscopy (AAS), energy-dispersive X-ray spectroscopy (EDAX), and carbon hydrogen nitrogen sulfur (CHNS) analyses. The magnetic behavior of the compound is examined using electron paramagnetic resonance (EPR) spectroscopy. The morphology of the powders is assessed by scanning electron microscopy (SEM). The average particle size of the powders is ranging between 10–20 μm. This investigation shows that pure crystalline lithium manganese oxide powders can be conveniently synthesized by molten flux method.

**Keywords** Characterization; Diffusion; EPR; LiMn<sub>2</sub>O<sub>4</sub>; XRD.

## INTRODUCTION

Rechargeable lithium-ion batteries have become a commercial reality in recent years. They are used in a multitude of mobile electronic equipments and transport systems. The global projections for the marketing of portable electronic devices with extraordinary capabilities create a driving force for the fabrication of an efficient, environmentally friendly and cheap rechargeable lithium-ion battery. Lithium cobaltate-LiCoO<sub>2</sub> is used as the cathode material in most of the commercial lithium batteries. However, the high cost and toxicity along with the safety problems have hindered the usage of LiCoO<sub>2</sub> in large-scale applications. In recent years, considerable efforts have focused on the development of alternate cathode materials to replace LiCoO<sub>2</sub>. Lithium manganate-LiMn<sub>2</sub>O<sub>4</sub> is one of the candidate materials, which crystallizes in the spinel structure with the space group of Fd3m. The oxygen atoms form a cubic-close packed array in which the Li atoms occupy one-eighth of the 8a tetrahedral sites and the Mn atoms occupy half of the 16d octahedral sites. The unoccupied 16c sites form a three dimensional network that facilitates the transport of Li<sup>+</sup> cations [1].

Various methods have been tried to synthesise LiMn<sub>2</sub>O<sub>4</sub> powders. It is reported that the preparation of pure crystals of LiMn<sub>2</sub>O<sub>4</sub> is found to be difficult below 700°C using conventional solid-state method. It involves repeated crushing-calcining cycles to obtain pure phase of LiMn<sub>2</sub>O<sub>4</sub> compound [2, 3]. It also consumes a large

amount of energy and the powders have relatively irregular morphology. In recent years, attention is focused on the development of a simple and reproducible low temperature synthesis route. Wet chemical methods such as co-precipitation [4], modified citrate gel process [5], and hydrothermal method [6] have been attempted to synthesize this compound. These methods need high temperature calcination and special autoclaves to achieve required properties. The above-mentioned difficulties induced us to explore new routes for the bulk-preparation of LiMn<sub>2</sub>O<sub>4</sub> powders.

Molten salt synthesis (MSS) provides a way to overcome these problems that can result in the formation of stoichiometric compounds with good control over the chemistry, purity, morphology etc., of the crystals. Recently, the molten salt (MS) method is widely used for the preparation of unitary oxides, electrode materials, and multicomponent oxides [7–16]. MSs such as LiCl, LiNO<sub>3</sub>, Li<sub>2</sub>SO<sub>4</sub>, LiOH do not only act as solvents but also take part in the reaction [16–18].

Advantages of MSS are as follows: (1) the temperature of synthesis can be lowered and the duration of reaction can be reduced because of high diffusivities, strong dissolving capability, large interfacial tension, and quick crystallization process; (2) the molten medium facilitates a better reaction condition with a high ion concentration of reactants; and (3) by using this technique, the large furnaces can be replaced with small ones, which can reduce the capital cost of the process. It means that this method is ideally convenient for a large-scale production of materials [19–25].

In MSS generally, two reaction sequences are considered for the product formation. In the first case, the reactants are dissolved in the MS, followed by the formation of the product in the molten medium and finally precipitate the

Received July 30, 2009; Accepted October 30, 2010

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product above its solubility limit. In the second case, one of the reactants dissolves in the MS and the dissolving component is transported to the outer surface of the other reactant and the product is formed on the latter surface [26, 27].

Tang et al. have tried the "Li-containing flux method" to prepare lithium manganese oxides, using LiCl-MnOOH salts [16]. Fine crystals of  $\text{LiMn}_2\text{O}_4$  were synthesized using LiCl as the flux [28]. Spinel-type lithium manganese oxides were prepared at 400°C using  $\text{LiNO}_3$ ,  $\gamma\text{-MnOOH}$ ,  $\beta\text{-MnO}_2$ , and birnessite ( $\text{Na}_{0.3}\text{Ca}_{0.1}\text{K}_{0.1}$ )  $(\text{Mn}^{4+}, \text{Mn}^{3+})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$  as the precursors [21].

In our previous communications, we reported the synthesis of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiSm}_{0.01}\text{Mn}_{1.99}\text{O}_4$  compounds using LiCl-MnO<sub>2</sub> and LiCl-MnO<sub>2</sub>-SmCl<sub>3</sub> · 6 · H<sub>2</sub>O as the precursor salts [29, 30]. In the present work, we have made an attempt to synthesize this compound using manganese acetate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) as one of the precursor salts with 0.6M LiCl and 0.4M Li<sub>2</sub>CO<sub>3</sub> as the eutectic mixture. Various characterization techniques such as thermogravimetric and differential thermal analysis (TGA/DTA), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), atomic absorption spectroscopy (AAS), CHNS, EDAX, electron paramagnetic resonance (EPR), and scanning electron microscopy (SEM) were used to identify the synthesized compound. The results on our investigation are presented in this article.

#### EXPERIMENTAL

$\text{LiMn}_2\text{O}_4$  powders were synthesized using high purity LiCl and Li<sub>2</sub>CO<sub>3</sub> (99% purity, Merck) salts in the molar ratio of 0.6:0.4 (eutectic mixture) with Mn-acetate salt (98% purity, Aldrich). The molar ratio of the eutectic mixture and the transition metal acetate was fixed at 1:2. The chloride, carbonate, and acetate salts were ground using a mortar and pestle. Then the mixed salts were dried at 110°C for 8h. The dried powders were placed in a high-density alumina crucible and then heated in a muffle furnace at 500°C for 5h. The resulting mass was then cooled to ambient temperature. The residual flux was removed from the product by washing with 1M acetic acid followed by triple distilled water and dried at 120°C for 2h.

The thermal behavior of the precursor salts was studied by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a thermal analyzer (model number STA 1500 PL Thermal Sciences, version V4.30 analyzer). The TGA/DTA curves were recorded from room temperature to 1000°C in air at a heating rate of 10°C/min. The purified product was characterized by XRD using philips 8030 X-ray diffractometer. The unit cell lattice parameters were determined using least-square fitting method of the d spacing and the hkl values. FT-IR spectroscopy was used to study the structure coordination of the calcined powders using Perkin Elmer UK paragon-500 spectrometer. To record the spectra, each sample was mixed with KBr and thoroughly ground in to fine powder and examined in the wave number ranging between 400–4000cm<sup>-1</sup>. Raman spectral analysis was performed using a Renishaw InVia Microscope. The Raman system is equipped with a charge-coupled device (CCD) detector,

which gives the best spectral data. AAS analysis was done using a spectrophotometer (Varian Spectra 220). CHNS analysis was carried out using an instrument Elementar Vario EL III-Germany make. EPR was done using a Bruker Bio Spin GmbH EPR spectrometer. The measurement was performed at microwave frequency 9.857403GHz with fields corresponding to about 6500.000G sweep width. The morphology and the elemental composition of the synthesized powders were determined using a scanning electron microscope JEOL-JSM-3.5 CF-Japan make fitted with the EDAX facility.

#### RESULTS AND DISCUSSION

Figure 1 shows the TGA and DTA curves for the precursor salts on the synthesis of  $\text{LiMn}_2\text{O}_4$ . The TGA curve exhibits four distinct weight loss steps. The first weight loss occurs between 81.01°C to 151.86°C is ascribed to the dehydration of water molecules. The loss in weight between 151.86°C to 266.58°C is mainly due to the decomposition of carbonate and acetate salts. The weight loss between 266.58°C and 372.30°C shows a sharp incursion, which is mainly due to the transformation of reactants into the product. The final weight loss of about 2.63wt% is noticed from 372.30°C to 1000°C, and is attributed to the evaporation of the melt at high temperature zone. The endothermic peak noticed at 136.12°C, is due to the evaporation of water molecules. The exothermic peak at 248.18°C is assigned to the decomposition of carbonate and acetate salts. A sharp exothermic peak at 369.48°C indicates the initiation of the compound formation.

The XRD spectrum of  $\text{LiMn}_2\text{O}_4$  sample is presented in Fig. 2. All the XRD peaks are indexed for cubic structure of  $\text{LiMn}_2\text{O}_4$  (space group:  $\text{Fd}3\text{m-O}_h^7$ ). The lattice constant value is determined by an iterative least-square refinement using "h, k, l" values. The lattice constant value for the cubic system  $a = 8.1967 \text{ \AA}$  (JCPDS data card no. 88-1026), which is in good agreement with the reported value [31].

The FT-IR spectrum of  $\text{LiMn}_2\text{O}_4$  synthesized at 500°C is shown in Fig. 3. The high-frequency bands, located around 610 and 519cm<sup>-1</sup> are associated with the asymmetric stretching modes of the MnO<sub>6</sub> group [32–35]. It is reported that the resonant frequencies of alkali metal cations in their

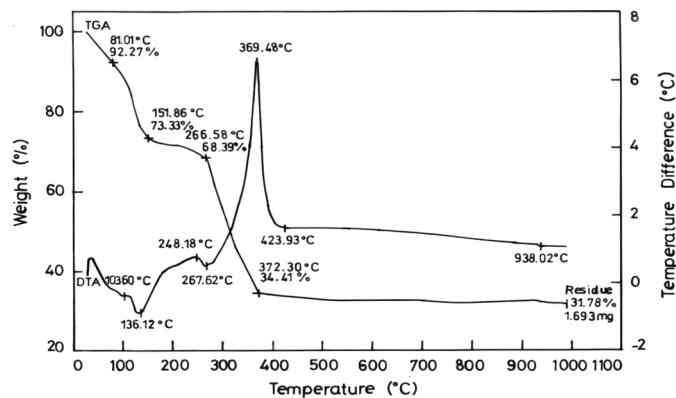


FIGURE 1.—TGA and DTA curves for  $\text{LiMn}_2\text{O}_4$  synthesized by molten salt route.

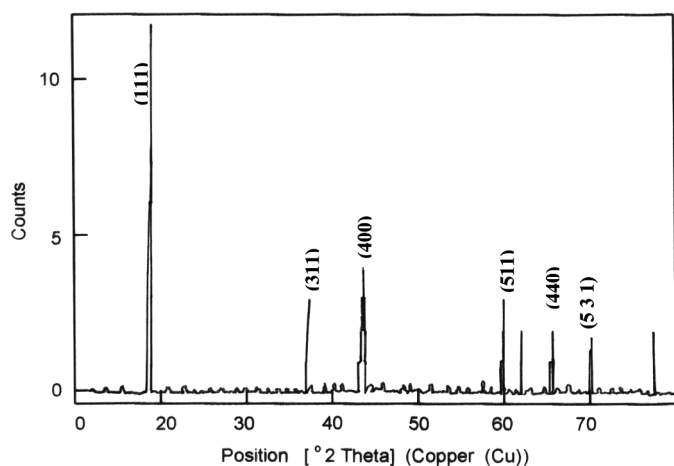


FIGURE 2.—X-ray powder diffraction pattern of the  $\text{LiMn}_2\text{O}_4$ .

octahedral interstices ( $\text{LiO}_6$ ) in inorganic oxides are located in the frequency range of  $200\text{--}400\text{ cm}^{-1}$ . The present study is restricted to the assignment of various vibrational modes of transition metal oxides within the frequency range of  $400\text{--}1000\text{ cm}^{-1}$ . These observations are quite similar to those given in earlier reports [36, 37].

Figure 4 shows the Raman spectrum of  $\text{LiMn}_2\text{O}_4$  powders measured between  $100\text{--}1000\text{ cm}^{-1}$ . The spectrum mainly consists of strong bands between  $600\text{--}700\text{ cm}^{-1}$  and several weak bands in the range of  $150\text{--}400\text{ cm}^{-1}$ . The strong band located at  $662\text{ cm}^{-1}$  may be assigned to  $A_{1g}$  mode, corresponding to the symmetric Mn-O stretching vibration of  $\text{MnO}_6$  groups. The weak bands may be assigned to three modes of  $t_{2g}$  phonons as reported in the literature. Further analysis of the spectrum is found to be complicated and the assignments are difficult to predict, since they are sensitive to the laser excitation [33, 38–40].

The concentration of Li and Mn ions is determined by AAS. An aliquot quantity of the sample is dissolved in 1N HCl solution, and the concentrations of Li and Mn ions are assessed. The determined values are presented in Table 1. It is found that the concentrations of Li and Mn ions

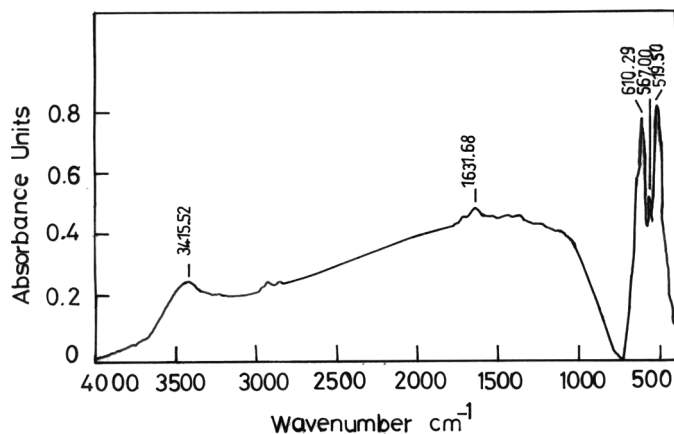


FIGURE 3.—FT-IR spectrum of  $\text{LiMn}_2\text{O}_4$ .

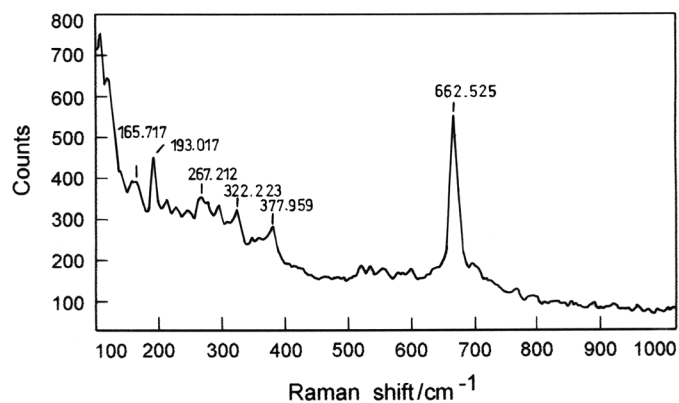


FIGURE 4.—Laser Raman spectrum of  $\text{LiMn}_2\text{O}_4$ .

TABLE 1.—Atomic absorption spectroscopy (AAS) analysis of synthesized  $\text{LiMn}_2\text{O}_4$  product.

| Concentration of Lithium (%) | Concentration of Manganese (%) |
|------------------------------|--------------------------------|
| 3.1                          | 58.77                          |

TABLE 2.—Chemical analysis of synthesized  $\text{LiMn}_2\text{O}_4$  product.

| Compound                  | C     | H     | N     | S     |
|---------------------------|-------|-------|-------|-------|
| $\text{LiMn}_2\text{O}_4$ | 0.191 | 0.030 | 0.025 | 0.000 |

are in stoichiometric ratio, which confirms the compound  $\text{LiMn}_2\text{O}_4$ . These values are in good agreement with the reported data [28].

The results on CHNS analysis are given in Table 2. From the table, it is noticed that the compound has minor impurities such as C, N, and H.

Figure 5 shows the EDAX profile of the synthesized  $\text{LiMn}_2\text{O}_4$  compound. The EDAX spectrum shows the wt% of Mn and O in the product. The values are shown in Table 3. The results reveal that the absence of other impurities in the product.

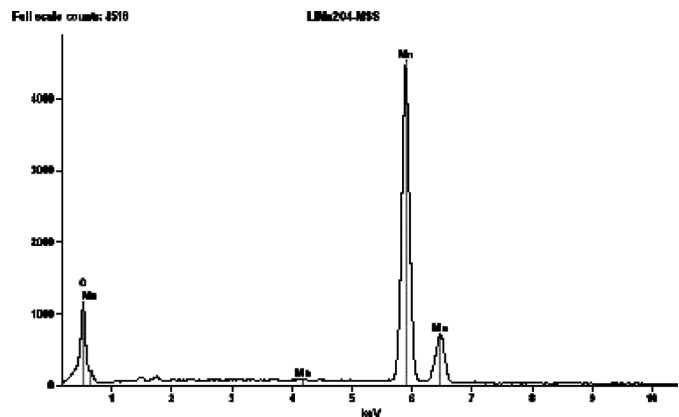


FIGURE 5.—EDAX profile of synthesized  $\text{LiMn}_2\text{O}_4$ .

TABLE 3.—EDAX analysis of synthesized  $\text{LiMn}_2\text{O}_4$  product.

| Weight of Oxygen (%) | Weight of Manganese (%) |
|----------------------|-------------------------|
| 23.06                | 76.94                   |

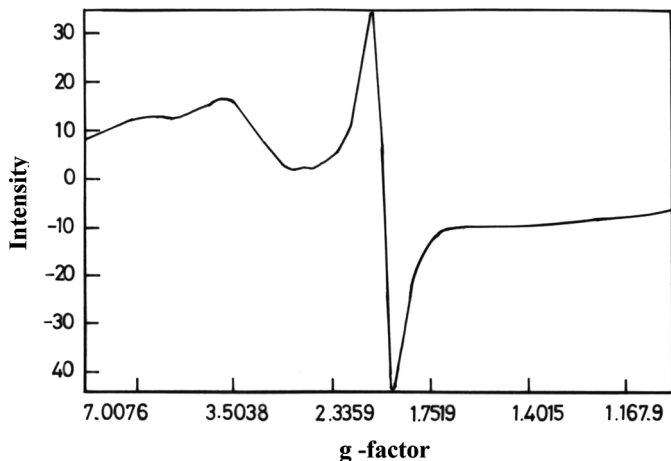
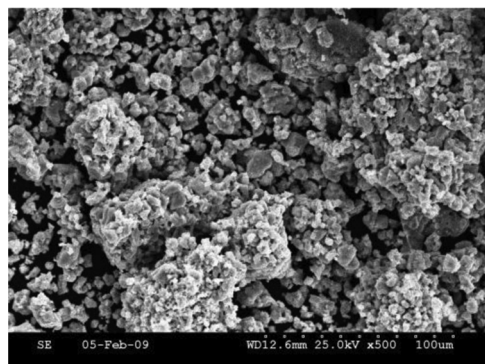
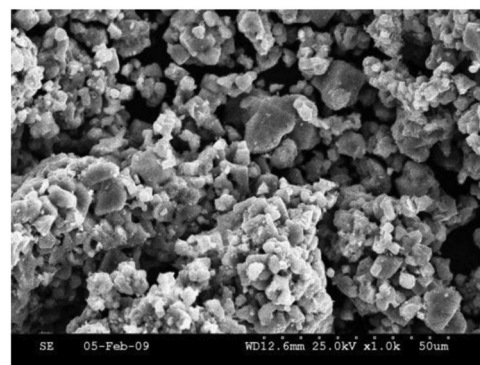


FIGURE 6.—EPR spectrum of  $\text{LiMn}_2\text{O}_4$ .



(a)



(b)

FIGURE 7.—SEM micrographs of synthesized  $\text{LiMn}_2\text{O}_4$  at different magnifications.

The paramagnetic behavior of the synthesized  $\text{LiMn}_2\text{O}_4$  is determined using EPR studies. The EPR spectrum is shown in Fig. 6. It is noticed that the value of  $g$  factor is found to be 1.88, which is in good agreement with the reported value for  $\text{LiMn}_2\text{O}_4$ . The  $\text{Mn}^{4+}$ - $\text{Mn}^{4+}$  as well as the  $\text{Mn}^{4+}$ - $\text{Mn}^{3+}$  dipolar interactions are responsible for the broadening of the signal. The EPR signal corresponds to the collective motion of the total magnetic moment of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  spin system [41–43].

The scanning electron micrographs of  $\text{LiMn}_2\text{O}_4$  powders are shown in Fig. 7(a) and (b). The particle morphology is dominated by the nucleation and growth process. The SEM images reveal that the particles have assorted morphology with the average particle size of 10–20  $\mu\text{m}$ .

#### CONCLUSIONS

Pure fine crystalline  $\text{LiMn}_2\text{O}_4$  powders were synthesized using MS method. The XRD data confirm the cubic spinel structure of the compound with lattice constant value  $a = 8.1967 \text{ \AA}$ . FT-IR spectrum reveals the high-frequency bands, located around 610 and 519  $\text{cm}^{-1}$ , are associated with the asymmetric stretching modes of the  $\text{MnO}_6$  group. Raman spectrum shows a strong band located at 662  $\text{cm}^{-1}$  may be assigned to  $A_{1g}$  mode, responsible for the symmetric Mn-O stretching vibration of  $\text{MnO}_6$  groups. The EPR spectrum shows a broad signal at  $g = 1.88$  and corresponds to the collective motion of the total magnetic moment of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  spin system. From the above investigation, it has been concluded that pure phase of Li-Manganese oxide powders can be easily prepared using simple salts by the low-temperature MSS route.

#### ACKNOWLEDGMENTS

The authors sincerely thank the Director, CECRI, for his kind permission and the staff of Electroprometallurgy Division for their support and encouragement to carry out this study.

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