X-ray diffraction studies of low to high temperature synthesis of LiMn$_2$O$_4$

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ABSTRACT   LiMn$_2$O$_4$ is prepared from acetates of lithium and manganese using the sol-gel method. The precursor obtained was annealed at different temperatures for 24 hours and furnace cooled. The materials were then grounded into very fine powder. X-Ray Diffraction measurements are done on the materials and the spectrograms are analyzed for identification, purity and crystallinity studies.

(LiMn$_2$O$_4$, Lithium, Cathode, XRD)

INTRODUCTION

LiMn$_2$O$_4$ is a very promising material for use in the rocking-chair batteries [1-5]. Lithium rocking-chair batteries are second-generation developments of lithium rechargeable batteries employing intercalation materials as electrodes. This type of batteries are safer compared to the first generation rechargeable lithium cells which employed pure lithium metal as anodes.

Sol-gel method is a relatively new synthesis method for obtaining LiMn$_2$O$_4$ [6]. The more conventional method of synthesizing the material is the solid-state method, which uses very high temperatures, that is, from 800 °C to well over 900 °C [6-8]. The sol-gel method is an easier method of obtaining LiMn$_2$O$_4$ and it is believed that the final product has better characteristics compared to that of the solid-state method [6, 7]. The objective here is to synthesize LiMn$_2$O$_4$ using the sol-gel method and to study characteristics of the products obtained in terms of purity, crystallinity and phase.

EXPERIMENTAL

Stoichiometric measurements of lithium acetate and manganese acetate are mixed with ethanol and stirred for several hours to dissolve the materials. The two mixtures are then added together and tartaric acid is slowly added until a pinkish gel is obtained with the pH value between 5.0 and 6.0. The mixture is slow heated at around 100 °C to get rid of the liquid leaving a black precursor material. The precursor material is grinded into fine powder. The precursor is heated at 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C and 850 °C. The heating time is 24 hours. The material is furnace cooled before the grinding process is done. The final products are in the form of fine powders. X-Ray Diffraction spectrograms are taken using the Phillips X'pert employing the Cu K$_\alpha$ line.

RESULTS AND DISCUSSION

The evolution of the X-Ray Diffraction (XRD) spectrograms of LiMn$_2$O$_4$ heated at 100 °C, 200 °C, 300 °C and 400 °C are shown in Fig 1 and those heated at 500 °C, 600 °C and 850 °C are shown in Fig 2. From the XRD's, it can be seen that the 100 °C sample is quite amorphous and the peaks are not very well defined. Samples with annealing temperatures between 200 °C and 400 °C contain residual peaks which shows the presence of impurities such as lithium carbonate (Li$_2$CO$_3$), lithium acetate (C$_2$H$_3$LiO$_2$.2H$_2$O), lithium hydroxide (LiOH) and manganese oxide (Mn$_2$O$_3$). The residual peaks are marked in Fig 1.
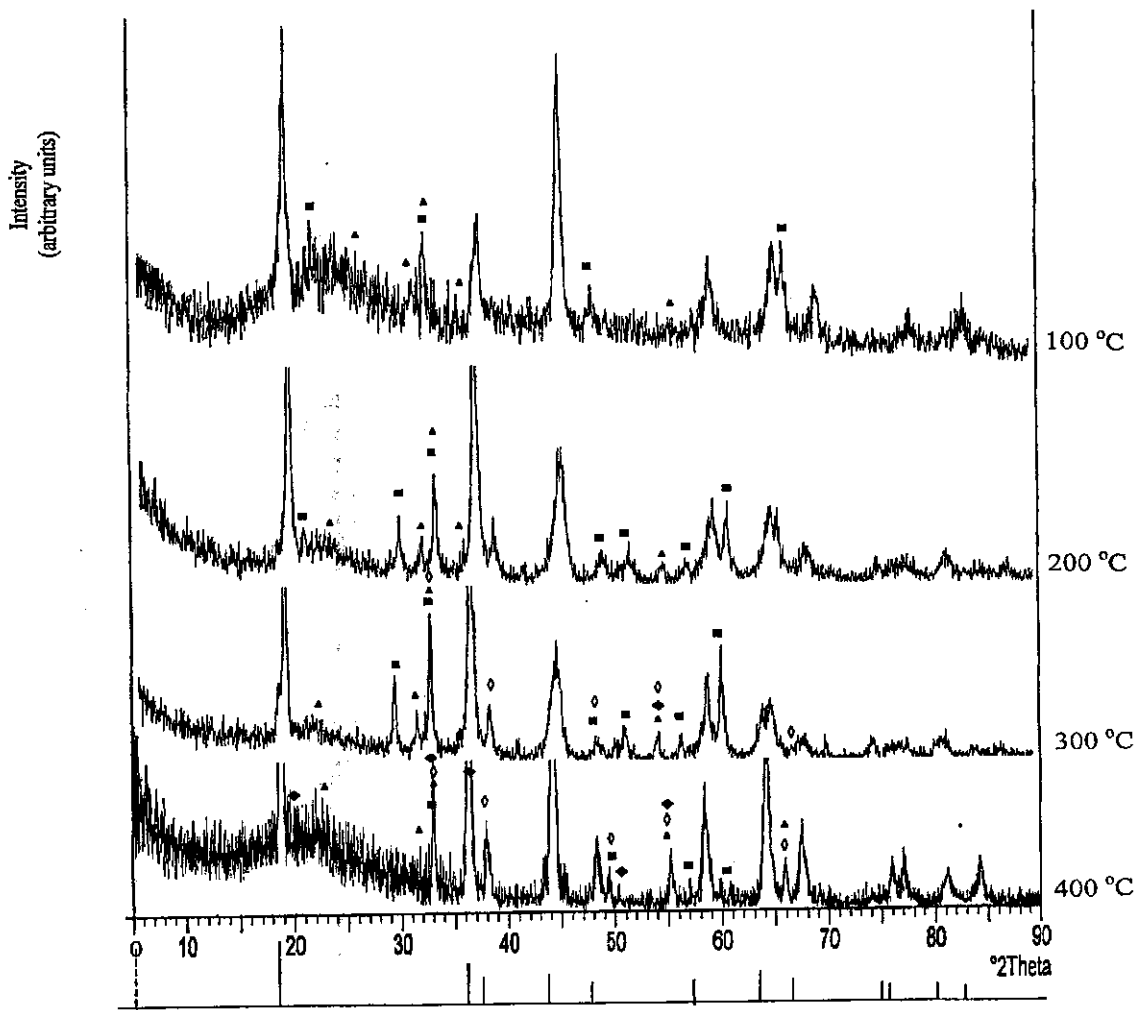
Figure 1. XRD's of $LiMn_2O_4$ annealed at 100 °C, 200 °C, 300 °C and 400 °C. The
bottom lines are the $LiMn_2O_4$ JCPDS pattern no. 35-0782 peaks.
{ ■ indicate peaks assigned to Li_2CO_3 JCPDS pattern no. 22-1141
▲ indicate peaks assigned to lithium acetate JCPDS pattern no. 23-1171
◆ indicate peaks assigned to LiOH JCPDS pattern no. 32-0564
◊ indicate peaks assigned to Mn_2O_3 JCPDS pattern no. 24-0508 }

Fig 2: XRD's of LiMn$_2$O$_4$ annealed at 500 °C, 600 °C and 850 °C. The
bottom lines are the LiMn$_2$O$_4$ JCPDS pattern no. 35-0782 peaks.
{ ▲ indicate peaks assigned to lithium acetate JCPDS pattern no. 23-1171
♦ indicate peaks assigned to LiOH JCPDS pattern no. 32-0564
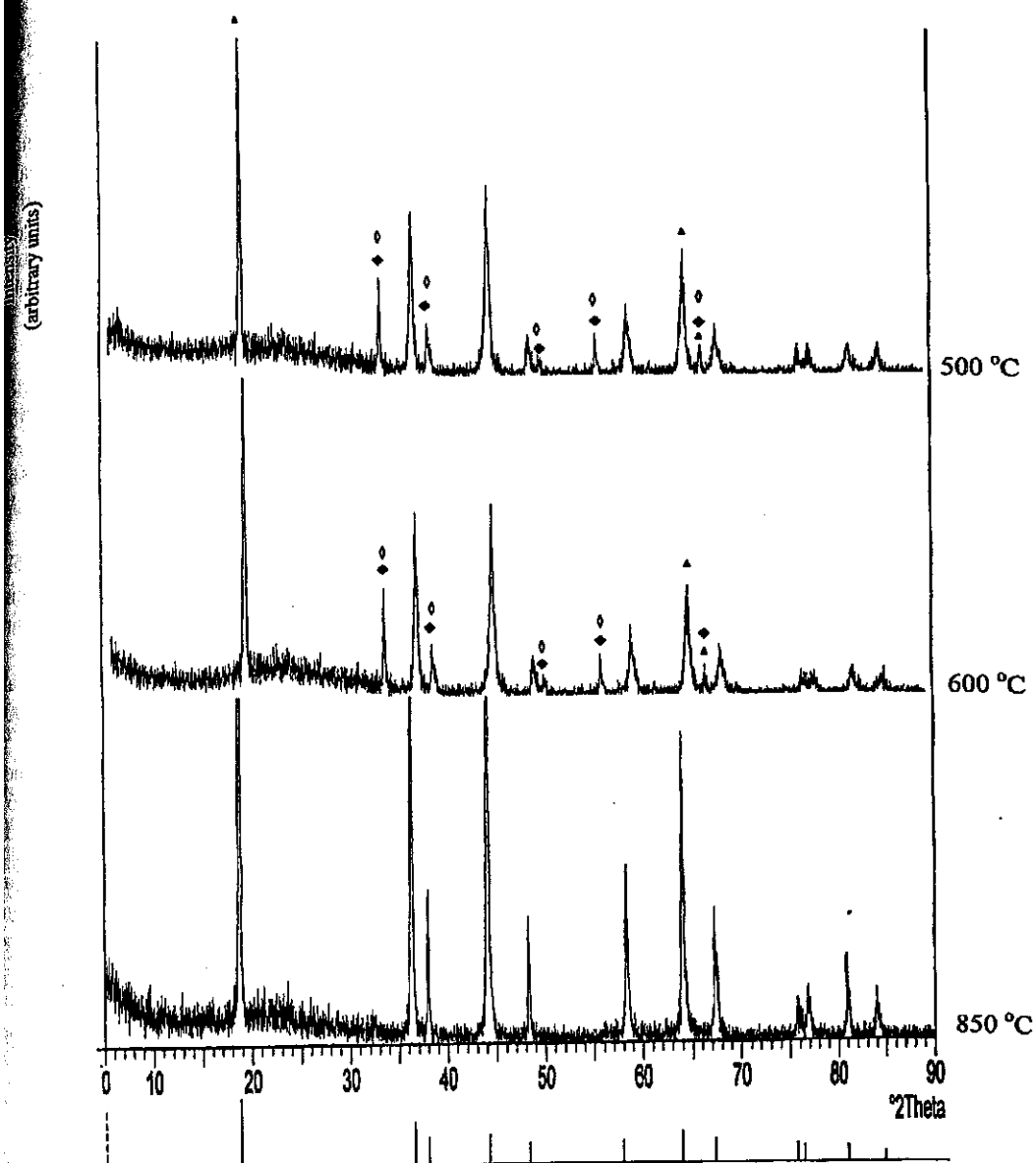◊ indicate peaks assigned to Mn$_2$O$_3$ JCPDS pattern no. 24-0508 }

is observed that as the annealing temperature is raised, the impurities present in the samples decreased. In the 500 °C and 600 °C samples the impurities present are only lithium acetate and manganese oxide. The XRD spectrogram for the 850 °C sample compares very well with the JCPDS data (pattern no. 35-0782) and indicates pure, single phase LiMn$_2$O$_4$ spinel obtained by the sol-gel method. No other residual peaks are observed. Thus, from the results

obtained, it can be said that XRD is a very useful tool for the identification of the material and the determination of the impurities contained in the samples.

Table 1 shows the analysis of the crystallinity of the samples. The analysis is done using the Scherer equation for powder samples. The coherent length calculations are done for the 3 main peaks of the XRD's, that is, for 2θ values of $18.6°$, $36.1°$ and $43.9°$ corresponding to peaks 1, 2 and 3 in Table 1 respectively. Generally, it is observed that the coherent length increases as the annealing temperature progresses higher. This means that the sample materials become more crystalline as the annealing temperature is raised. This result confirms the expected behaviour of an inorganic compound.

Table 1: $LiMn_2O_4$ samples with the corresponding coherent length values

Sample	Peak	Coherent Length, L/nm
100 °C	1	16.6
	2	16.3
	3	10.0
200 °C	1	20.7
	2	19.5
	3	11.0
300 °C	1	20.8
	2	4.46
	3	11.0
400 °C	1	20.8
	2	16.3
	3	27.8
500 °C	1	20.7
	2	19.8
	3	36.5
600 °C	1	27.7
	2	24.4
	3	36.5
850 °C	1	41.5
	2	32.4
	3	54.8

CONCLUSION

It can be concluded here that using the XRD results, pure spinel phase $LiMn_2O_4$ is obtainable with the sol-gel method at the annealing temperature of 850 °C. The crystallinity of the samples also increases with annealing temperature.

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Application of XRD and TEM analysis for phase observation on doped PSZ

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ABSTRACT   XRD and TEM techniques were used to analyse tetragonal phase stabilization with addition of SrO in CaO-ZrO$_2$ system. Improvements in tetragonal phase stabilization of calcia-stabilized zirconia are obtained by the addition of 3 mol% SrO. There were evidences, which indicated that the added SrO effectively neutralized the accumulation of SiO$_2$ containing grain boundary phases which results in high tetragonal phase in the sintered body.

(SrO, Calcia, Zirconia ceramic, Phase transformation)

INTRODUCTION

Zirconia has excellent refractory properties, but its use in bulk form is restricted by the disruptive tetragonal (*t*) to monoclinic (*m*) phase transformation which occurs at 1000 °C [1]. Thermal cycling through the transformation range (800 $\leftrightarrows$ 950°C) causes cracking and sometimes complete disintegration of sintered specimens [2] because volume change of 3 % accompanies transformation [3]. Therefore, interest has centered on alloys of ZrO$_2$ with other oxides such as calcia, magnesia, yttria or ceria primarily because these oxides can form stable solid solutions with the cubic fluorite structure [4-5]. Fully stabilized cubic zirconia is not particularly resistant to thermal shock but partially stabilized zirconia (PSZ) can be both stronger and more resistant to thermal shock than fully stabilized [6-7] and unstabilized bodies. The origin of these improved properties is still under investigation [8-9], although Garvie [10] has suggested that the improved properties of PSZ may result from metastable *t* particles in the sintered body. In the presence of a propagating crack the tetragonal particles are induced to transform to monoclinic. The volume change and the shear strain developed during the phase transformation are recognized as opposing the opening of the crack and therefore increase the resistance of the ceramic to crack propagation. However, less desirable changes in tetragonal phase stabilization also can occur in PSZ as a result of contamination, which originates from the starting powders or fabrication process. The major contaminations present in zirconia are hafnia (HfO$_2$) and silica (SiO$_2$). Removal of impurities from the starting powders can increase the cost of the final product. This paper shows how addition of SrO can nullify the detrimental effects of SiO$_2$ and improve the tetragonal phase stabilization of calcia-zirconia system.

EXPERIMENTAL PROCEDURE

Materials used were ZrO$_2$ (83.91%), CaCO$_3$ (99.28%) and SrCO$_3$ (98.59%). The hafnia content was 15.54% whilst silica was 0.11% in ZrO$_2$. These materials were used for preparing the samples. The powder was prepared by wet ball milling in a plastic container for 8 hours using ZrO$_2$ balls. These compositions were uniaxially pressed at 100MPa to form a compact of 13mm diameter and 2 mm thick pellets. These pellets were than fired at 2°C/min up to 700°C followed by 5°C/min up to sintering temperature (1450°C) and soaked for 3 hours. Samples were cooled to room temperature at 10°C/min. The microstructure observation was conducted using transmission electron microscopy (TEM). Quantitative measurement of phase was based on X-Ray Diffraction (XRD).

RESULTS AND DISCUSSION

XRD Analysis

Phases of the sintered sample are shown in Figure 1. No other phases were observed except of the monoclinic and tetragonal zirconia. Generally the tetragonal phase was high in SrO-CaO-ZrO_2 system as compared to CaO-ZrO_2 system. For example, sample 7CZ contain 31.53 % of t-ZrO_2 but with addition of SrO (sample 3S7CZ) contain 41.90 % of t-ZrO_2. More tetragonal phase was retained in the sample, which SrO had been added.

TEM Analysis

TEM analysis provided further information regarding the phase stabilization. Microstructural features are important in understanding the influence of SrO on calcia stabilized zirconia. Figure 2 shows TEM micrographs taken from a region within the bulk sample. When no SrO had been added, triple points were clearly visible in the sintered body (Figure 2a) but with the addition of 3 mol % of SrO, no triple points were observed (Figure 2b). There was no triple point with addition of SrO because SrO reacts preferentially with SiO_2 forming compound, which was ejected from the bulk sample during the sintering but without SrO, the affinity of SiO_2 for calcia results in formation of grain boundary phases, which was indicated as triple point in the microstructure.
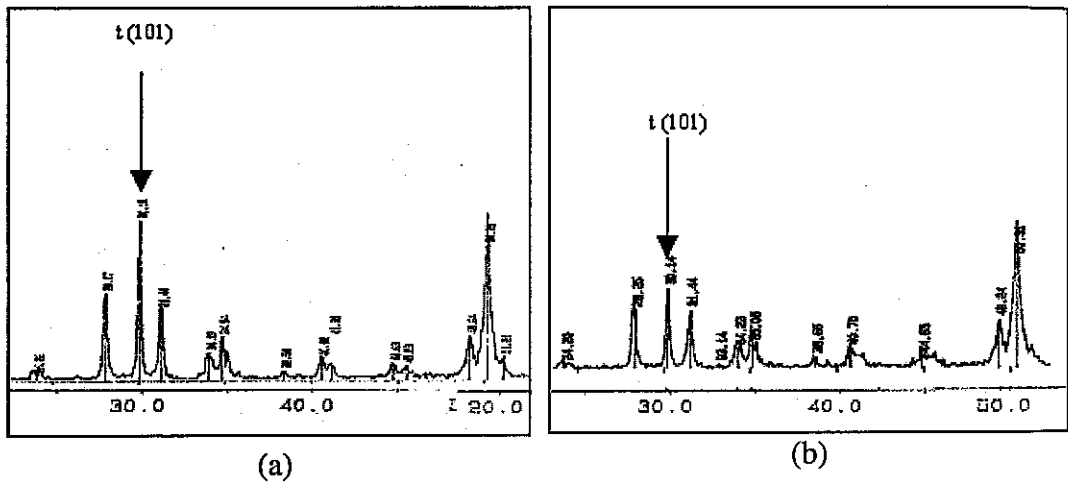

Figure 1. XRD analysis (a) high *t* (101) peak for material with SrO (b) small *t* (101) peak for material without SrO.
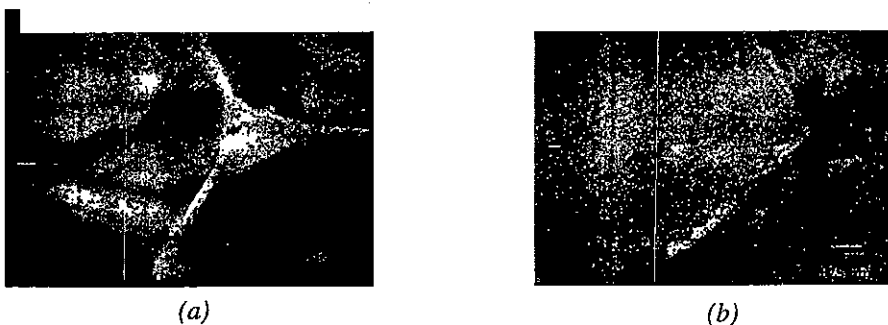

Figure 2. TEM micrograph of calcia-stabilized zirconia (a) without SrO (b) with 3 mol% SrO

the preferential reaction of SiO_2 with SrO as compared to CaO in $SrO-CaO-ZrO_2$ system can be explained with simple thermodynamic calculations. The calculated standard free energies of formation, at 298K for various compounds in the $SrO-SiO_2$ and $CaO-SiO_2$ system, are shown in Table 1. Clearly the stability of the $SrO-SiO_2$ compound is much greater than the corresponding $CaO-SiO_2$ compound.

Table 1: Free energy formation for various compounds

Compounds	ΔG (kJ/mol)
$SrSiO_3$	-130.3
Sr_2SiO_4	-208.4
$CaO.SiO_2$	-38.37
$2CaO.SiO_2$	-67.94

Therefore, more *t* phase was retained in the sample with SrO because SrO prevents $CaO-SiO_2$ formation, thus minimizing the loss of calcia from the material and consequently enhancing the *t* phase stabilization in zirconia system [11].

CONCLUSION

Addition of 3 mol% SrO in calcia stabilized zirconia eliminates $CaO-SiO_2$ grain boundary phases. Therefore the loss of calcia from the material to form grain boundary phases was minimized. As a result, there are more calcia for tetragonal phase stabilization in sintered body.

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