A Comparative Study on Structure La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$MnO$_3$ Prepared by Sol-Gel and Wet-Mixing Methods

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Abstract. Nanocrystalline La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$MnO$_3$ (LSBMO) has been synthesized using two difference method, sol-gel and wet-mixing methods. Both samples were sintered at the same temperature of 900$^\circ$C for 12 hours. Structural investigation using X-Ray Diffraction (XRD) shows that both samples crystallise in the same rhombohedral structure with R$3c$ (167) space group. A slight difference on lattice parameters, unit cell volume and Mn–O bond length was observed. The crystallinity from the sol-gel method was better than that of from wet-mixing method. The average crystallite size was calculated by Scherer formula, namely 32.8568 nm for sol-gel method and 18.3777 nm for wet-mixing method. The electronic bandwidth which was calculated with theoretical approach reveal that the sol-gel method gives larger bandwidth than the wet-mixing method, which can affect the physical properties of the LSBMO.

1. Introduction

Lanthanum Manganite (LaMnO$_3$) has attracted attention as research subject because partial substitution of lanthanum by alkaline earth metal ion resulting in a mix valance system which generate interesting physical properties, such as colossal magnetoresistance (CMR), magneto-caloric effect (MCE) [1–3]. Moreover, partial substitution on mix valance lanthanum manganite and difference synthetic method influences the physical properties, such as a structural parameter, morphology, grain size distribution, which correlate to magnetic and electrical properties [4, 5].

Conventional solid-state is a powerful method for ceramic material synthesis. However, solid state reaction requires a high sintering temperature and long-time duration [5]. Recently, the sol-gel method has been used as an attracting technique for the synthesis of high purity product with lower temperature than the conventional solid-state reaction [3, 6-8].

One of the studied compounds in our work is La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$MnO$_3$ (LSBMO) system. The LSBMO has been successfully synthesized using sol-gel method with sintering temperature of 1200$^\circ$C for 6 hours in previous work [6-7]. The lack of sol-gel method is that it needs additional precursors, such as citric acid, metal ions complexing agent, fuel, and ammonia solution for adjusting pH [8, 9]. Thus, the sol-gel method is costly for mass production. Another work in oxide materials, many researchers have reported superconductor material synthesis using a simple dissolved metal mixing method which can be called wet-mixing method [10-12]. It is a simple and effective way to prepare homogeneous nanomaterials. In this paper, we are reporting LSBMO materials prepared using sol-gel and wet-mixing methods. Comparative studies of the structure and microstructure of both samples are discussed.
2. Experimental

La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$MnO$_3$ were synthesized using two different methods: sol-gel and wet-mixing methods. The powder of both samples was then calcined and sintered at 600°C for 6 hours and 900°C for 12 hours. The structural and purity of both samples were measured using X-ray diffractometer (XRD) with Cu-Kα ($\lambda = 1.5406$ Å) at room temperature. The morphologies of both compounds were investigated by Scanning Electron Microscopy (SEM).

2.1 Sol-Gel Method

In the sol-gel method, the precursors were La$_2$O$_3$, Ba(NO$_3$)$_2$, Sr(NO$_3$)$_2$, Mn(NO$_3$)$_2$·4H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O, and citric acid (C$_6$H$_8$O$_7$·H$_2$O). The precursor used in the sol-gel method is mostly as metal nitrate. The detailed synthesis of sol-gel method is reported in our previous work [6].

2.2 Wet-Mixing Method

In the wet-mixing method, the precursors were La$_2$O$_3$, BaCO$_3$, SrCO$_3$, and MnCO$_3$. The compounds that were used in wet-mixing method are in the form of oxide or carbonate. Each precursor powder was dissolved and stirred in nitric acid (65%) to obtain a clear solution. After that, all solutions were mixed with constant stirring, and then heated at 80°C until the solution was evaporated. Powder obtained from evaporation result was then dehydrated to eliminate water and nitric acid at 120°C for overnight. Finally, the powder was grinded and ready for the calcination.

3. Result and Discussion

Figure 1a shows the comparison of powder XRD pattern of both samples. According to the XRD pattern, both samples have the same diffraction pattern. It showed that there is no change of crystal structure although different synthesis method was used. It is supported by the same Miller indices on the diffraction pattern. The result showed that both samples have a rhombohedral structure with $R\bar{3}c$ (167) space group. The XRD patterns clearly show that the sol-gel method form a single phase, but on wet-mixing method, the presence of La$_2$O$_3$ in the perovskite structure is observed. The presence of La$_2$O$_3$ phase was likely due to the undissolved La$_2$O$_3$ in nitric acid, which is also been reported in the wet-mixing method for other materials [10-12].

![Figure 1](image-url)

**Figure 1.** (a) A comparative of XRD pattern both sample and (b) at the highest intensity at (110) and (104) Miller indices on the diffraction pattern.

The results of the Rietveld refinement are given in Table 1. Figure 2 illustrates the observed, calculated and difference profiles for both samples. A slight difference in lattice parameters, cell unit volume, and Mn–O bond length.
Figure 2. Rietveld refinement of LSBMO obtained from (a) sol-gel and (b) wet-mixing.

Figure 3. SEM images mode BSE of LSBMO (a) sol-gel and (b) wet-mixing, in 1000x magnification.

Figure 3 reveals SEM image both samples with 1000 times magnification. Its uniform colour is indicating a homogeneity level. The yellow circle shows a single powder obtained from grinding the sample. The crystallinity of sol-gel is better than that of wet-mixing; this can be seen from higher intensity and smaller full width at half maximum (FWHM) as shown in Figure 1(b). This indicates the difference in crystalline size from both samples. The average crystalline size \( D_s \) can be calculated by the Scherer equation:

\[
D_s = \frac{K \lambda}{\beta_{HKL} \cos \theta}
\]  

(1)

Where \( \lambda \) is the wavelength of the XRD \( (\lambda_{Cu} = 1.5406 \text{ Å}) \), \( \beta \) is the FWHM of the strongest intensity diffraction peak, and \( \theta \) is the corresponding diffraction angle. The calculated average crystalline size by Eq. 1 are 32.8568 nm for sol-gel method and 18.3777 nm for wet-mixing method. This is in accordance with the results of SEM analysis which reveal that the wet-mixing method has smaller microstructure size of LSBMO than that of sol gel. The images reveal similar shape, but in different size. The size from SEM image seems to be several times larger than those calculated by XRD because each particle observed by SEM consists of several crystalline grains [2].
Figure 4. SEM images mode SE of LSBMO (a) sol-gel and (b) wet-mixing were taken in 10000x magnification.

Table 1. The structural parameter from Rietveld analysis.

| Parameter | Sol-Gel | Wet-Mixing |
|-----------|---------|------------|
| $a = b$ (Å) | 5.51436 | 5.1906 |
| $c$ (Å) | 13.4226 | 13.3991 |
| $V$ (Å$^3$) | 353.4705 | 353.1757 |
| $d_{\text{Mn-O}}$ (Å) | 1.962 | 1.964 |
| Angle of Mn-O-Mn (°) | 164.059 | 164.041 |
| $W$ ($10^{-2}$) | 9.3613 | 9.3278 |
| Crystalline size (nm) | 32.8568 | 18.3977 |
| **Discrepancy factor** | | |
| $R$ Profile (%) | 4.4316 | 3.8649 |
| $R_{wp}$ (%) | 5.6081 | 4.9172 |
| Goodness of Fit | 1.1417 | 1.1978 |

In mix valance lanthanum manganite, the structural parameters are sensitive to their properties. Some of them is the average Mn–O–Mn bond angle and Mn–O distance that influences electronic bandwidth ($W$) which affects the double exchange interaction [3-5]. The increase of $d_{\text{Mn-O}}$ and the decrease of Mn–O–Mn angle causes the weakening of double-exchange interactions. This is due to the decrease in $W$ will reduce the overlap between the manganese 3$d$ and oxygen 2$p$ orbitals and the mobility of $e_g$ electrons [2-4]. It can be evaluated with the equation (where $\gamma$ is the Mn–O–Mn angle):

$$W = \frac{\cos[\frac{1}{2}(\theta - \gamma)]}{(d_{\text{Mn-O}})}$$

The calculation of $W$ is 9.3613 for sol-gel and 9.3278 for wet-mixing. It will affect the material properties, one of which is the Curie temperature ($T_c$). Some studies show that the average decrease in bond angle is followed by an increase in the average bond angle and can cause a decrease in Curie temperature [3-5]. Ayadi et al. reported that the effect of the synthetic method on La$_{0.7}$Sr$_{0.2}$Ag$_{0.1}$MnO$_3$ caused a difference in Curie temperature in which the $T_c$ solid-state method has lower value than the sol-gel, followed by a lower $W$ [5]. From the calculations, it is suggested that $T_c$ value for wet-mixing will be lower than the $T_c$ value for sol-gel, for LSBMO material.
4. Conclusion
LSBMO was synthesized using sol-gel and wet-mixing methods with the same sintering temperature of 900°C for 12 hours. Structural investigation by XRD shows that both samples crystallised in the same rhombohedral R3c space group with a slight difference on lattice parameters, unit cell volume and Mn–O bond length. The LSBMO crystallinity from sol-gel method was better than from wet-mixing method. The average crystalline size based on Scherer formula were 32.8568 nm for sol-gel method and 18.3777 nm for wet-mixing method. The results of SEM reveal identical shape but the size of LSBMO obtained by wet-mixing was smaller than that of from sol-gel. The electronic bandwidth was evaluated with theoretical approach, in which the sol-gel method gives larger bandwidth than the wet-mixing method.

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