Effect of sintering temperature on structure and morphology of \( \text{Ca}_{0.95}\text{La}_{0.02}\text{Bi}_{0.03}\text{MnO}_3 \) perovskite manganite prepared by sol-gel method

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Abstract. The effect of sintering temperature on the structure and morphology of \( \text{Ca}_{0.95}\text{La}_{0.02}\text{Bi}_{0.03}\text{MnO}_3 \) was investigated by X-ray diffraction and Scanning Electron Microscope. The sample was prepared by sol gel method. Their homogeneity was confirmed using X-ray diffraction. Rietveld refinement of X-Ray diffraction results showed that the sample sintered at 1100 °C for 12 h are single phase and have an orthorhombic structure with \( Pnma \) space group. While, the samples were sintered at 900 °C and 1000 °C did not show a single phase due to another peak is found. For the lattice parameter, crystal volume increases with increasing sintering temperature. The largest crystal volume was reached at sintering temperature 1100 °C which is equal to 208.7319 Å. For the angle of the Mn-O-Mn bond, the sample was sintered at 1100 °C has the largest value obtained 157.6695° while at 1000 °C is 157.1440° and 900 °C is 157.3655°. For the average Mn-O bond length shows relatively the same value for all sintering temperature. The sample was sintered at 1100 °C had the largest grain size. Sintering temperature does not change the crystal structure of \( \text{Ca}_{0.95}\text{La}_{0.02}\text{Bi}_{0.03}\text{MnO}_3 \) samples

1. Introduction

Material that has quite interesting and promising properties to be used as n-type thermoelectric material is Calcium Manganite. The performance of the thermoelectric material is determined by the value of the ZT merit figure, which is defined as \( S^2T/\rho\kappa \) where \( S, \rho, \kappa, \) and \( T \) are Seebeck coefficients, electrical resistivity, thermal conductivity, and temperature, respectively [1]. \( \text{CaMnO}_3 \) has the attention of a possible n-type oxide thermoelectric material for use in energy conversion. When Bi, Y, La, Ce, and Rare Earth Elements (Nd, Tb, Ho, Yb, Lu) were substituted in \( \text{CaMnO}_3 \) at the Ca site, the electrical conductivity increased considerably, while the Seebeck coefficient decreased slightly [2].

Some researchers are trying to develop this material in order to have a good thermoelectric performance, one of which is to doping with certain elements. The sample was prepared using the sol-gel method, sintering is carried out in the synthesis process to grow crystals and densification process in the material. The basic principle of sintering is the achieving rate of desired particles in powder compacts. The sintering temperature and holding time for controlling the microstructure and porosity that determines the degree of particles bonding. In solid-state sintering, the bonding among particles requires transport by volume diffusion material, grain-boundary diffusion, and surface diffusion [3]. The temperature of sintering holds an important influence in the structure and morphology of the material produced.
Furthermore, it has been reported that the thermoelectric properties of the Thermoelectric-based CaMnO₃ depended strongly on its crystal structure and microstructure. As a result, in the present work, in an attempt to increase the thermoelectric properties of CaMnO₃, we studied the effects of sintering temperature on structure and morphology of Ca₀.₉₅La₀.₀₂Bi₀.₀₂MnO₃.

2. Experimental

The sample Ca₀.₉₅La₀.₀₂Bi₀.₀₂MnO₃ was synthesized using the sol-gel method. The precursors used were Ca(NO₃)₂·4H₂O (Merk 99%), Mn(NO₃)₂·4H₂O (Merk 98.5%), La₂O₃ (Merk 99.5%), Bi₂O₃ (99.8% Fluka) and citric acid C₆H₈O₇·H₂O (Merk 99.5%) which is used as fuel combustion in sol-gel synthesis. In the sol-gel method, nitrate-based precursors are used to be easily dissolved in aquabidest before the mixing process is carried out.

All precursors are weighed according to stoichiometric calculations. The ratio of molar ion metal with citric acid is 1: 1.2 [4]. All nitrate and citric acid-based precursors, which are in the form of powder, are dissolved with sufficient aquabidest until dissolved. Non-nitrate-based precursors such as La₂O₃ and Bi₂O₃ are dissolved first with 65% nitric acid solution and sufficient aquabidest until the solution appears clear, with the following reaction:

\[ \text{La}_2\text{O}_3 + 6 \text{HNO}_3 \rightarrow 2 \text{La(NO}_3)_3 + 3 \text{H}_2\text{O} \]
\[ \text{Bi}_2\text{O}_3 + 6 \text{HNO}_3 \rightarrow 2 \text{Bi(NO}_3)_3 + 3 \text{H}_2\text{O} \]

Then, all the dissolved precursors are mixed in the beaker glass and then stirred and heated on a hot plate. After mixing, the dissolved citric acid is then poured into the precursor mixture, thus fulfilling the reaction as follows:

\[ 0.95 \text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O} + 0.02 \text{La(NO}_3)_3 + 0.03 \text{Bi(NO}_3)_3 + \text{Mn(NO}_3)_2 \cdot 4\text{H}_2\text{O} + \beta \text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O} \rightarrow \text{Ca}_{0.95}\text{La}_{0.02}\text{Bi}_{0.02}\text{MnO}_3 + \delta \text{N}_2 + \gamma \text{H}_2\text{O} + \alpha \text{CO}_2 \]

After that the solution is stirred and heated on a hot plate then the solution temperature is maintained at around 80 °C. After the solution reaches 80 °C, ammonium solution is added to the solution until the pH solution reaches 7. The homogeneous solution is stirred to form a gel. The obtained viscous gel was dehydrated at 120 °C for 6 hours to remove the moisture content in the sample [5]. The obtained dried gel was crushed to a powder, after which the powder was calcined 600 °C for 6 hours to remove organic components which were still present in the sample. After calcining, the sample was crushed again to produce a fine powder. The obtained fine powder is then sintered with 3 different temperatures of 900 °C, 1000 °C, and 1100 °C for 12 hours, respectively. X-Ray Diffraction (XRD) for structural characterization and Scanning Electron Microscopy - Electron Dispersive Spectroscopy (SEM-EDS) for morphology and composition analysis.

3. Results and discussion

XRD pattern of Ca₀.₉₅La₀.₀₂Bi₀.₀₂MnO₃ for sintered temperature at 900°C, 1000°C, and 1100°C for 12 h showed the characteristic peaks of the compound as can be seen in Figure 1. The diffraction peaks were indexed to an orthorhombic perovskite structure having Pnma space group. Stability of the structure can be determined by Goldschmidt’s tolerance factor (τ) [6]. The value of τ can be calculated by using the equation:

\[ \tau = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \]  

(1)

When τ is close to 1, perovskite structure showed cubic structure. As \( r_A \) decreases, induce τ also decreases, the lattice structure shift to the rhombohedral structure (0.96 < τ < 1). If τ gets lower, then the lattice structure shift to orthorhombic structure (τ < 0.96). This also shows the bending of Mn–O–Mn bond and the deviating of the bond angle from 180° increase [7]. The crystal structure was further refined.
by a standard Rietveld refinement technique. The unit cell parameters, Mn–O–Mn bond angle and Mn–O bond length were obtained using the Rietveld refinement technique presented in Table 1.

![Figure 1](image-url)

**Figure 1.** XRD pattern for samples Ca$_{0.95}$La$_{0.02}$Bi$_{0.03}$MnO$_3$ were sintered at 900 °C, 1000 °C, and 1100 °C for 12h.

From the XRD refinement results, samples with sintering temperatures of 900 °C and 1000 °C show a secondary peak. However, the samples were sintered at 900 °C and 1000 °C contained small amounts of additional phases. The weak diffraction peaks at 2θ = 33,166° correspond to the very small amount of CaMn$_3$O$_4$ phase [8]. While samples with sintering temperature of 1100 °C showed a single-phase result. The difference in sintering temperature affects the change in the lattice parameter value, unit cell volume, the length of the Mn–O bond, the angle of the Mn–O–Mn bond, which value affects electronic bandwidth (W).

| Table 1. Structural parameters from Rietveld refinement analysis for all samples. |
|---------------------------------|----------------|----------------|----------------|
| Parameter | 900°C | 1000°C | 1100°C |
| a (Å) | 5.2984 | 5.2980 | 5.2983 |
| b (Å) | 7.4586 | 7.4601 | 7.4643 |
| c (Å) | 5.2735 | 5.2746 | 5.2779 |
| V (Å) | 208.4021 | 208.4730 | 208.7319 |
| Structure | Orthorhombic | Orthorhombic | Orthorhombic |
| d$_{Mn-O}$ (Å) | 1.903 | 1.904 | 1.903 |
| <$Mn-O-Mn>$ (degrees) | 157.3655 | 157.1440 | 157.6695 |
| $\alpha = \beta = \gamma$ (degrees) | 90 | 90 | 90 |
| Mean Crystallite Size (nm) | 39.6258 | 42.5134 | 44.5532 |
By using the Scherrer equation [9], the sample mean crystallite size is obtained:

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)

Where K is crystallite shape factor a good approximation is 0.9, \(\lambda\) is wavelength of X-ray, in the case for CuK\(\alpha\) is 1.5406 nm, \(\beta\) is the full width at half the maximum (FWHM) in radians, and \(\theta\) is diffraction angle.

For thermoelectric applications, electrical conductivity is a considerable factor, many researchers are trying to increase the electrical conductivity from several factors, one of them is the effect of grain size [10]. The grain size and density have an influence on the electrical conductivity. the electrical conductivity of the material decreases as the mean grain size decreases due to the enhanced electron scattering at the grain boundaries. It clearly indicates that the sample with largest grain size, the interconnectivity between the grain is better those of smaller grain size samples.

The relative contribution of the insulating region connecting the grains is smaller in the sample with a bigger grain size [11]. Figure 2 shows Scanning Electron Microscope (SEM) with secondary electron mode for samples were sintered at 1000 °C and 1100 °C for 12h. This result was used to study morphology of the materials Ca\(_{0.95}\)La\(_{0.02}\)Bi\(_{0.03}\)MnO\(_3\). By increasing the sintering temperature, the mean grain size of sample increases.

**Figure 2.** SEM secondary electron mode images for sample sintered at a) 1000 °C, b) 1100 °C.

Figure 3. EDS results for sample sintered at a) 1000 °C, b) 1100 °C.
Table 2. The composition of Ca_{0.95}La_{0.02}Bi_{0.03}MnO_3 for stoichiometry calculation and EDS results.

| Element | Calculated (At %) | Measured (At %) 1000 °C | Measured (At %) 1100 °C |
|---------|-------------------|--------------------------|--------------------------|
| Ca      | 25.4              | 24.2                     | 25.7                     |
| La      | 1.8               | 2.1                      | 2.5                      |
| Bi      | 4.2               | 9.1                      | 3.7                      |
| Mn      | 36.6              | 40.3                     | 38.0                     |
| O       | 32.0              | 24.3                     | 30.1                     |
| Total   | 100               | 100                      | 100                      |

Figure 3 shows the EDS results to confirm the composition of the sample Ca_{0.95}La_{0.02}Bi_{0.03}MnO_3 at sintering temperatures of 1000 °C and 1100 °C. From the results of the EDS spectrum, it shows all the peaks of the sample components, which are Ca, La, Bi, Mn, and O. Both samples show good impurity values because no other components are found. The peak of the dopant elements in this sample is La and Bi element seen in the EDS spectrum. This shows that La^{3+} and Bi^{3+} ions successfully substitute the Ca site. For EDS analysis by observing the three dominant grain regions of SEM results, then the composition values of the three spectrums were averaged so that the composition results were obtained based on EDS measurements. The EDS composition has a similar value to the stoichiometry calculation for the sintered temperature of 1100 °C. When temperature sintering is 1000 °C, there is a significant difference for the Bi element, but this value is not an absolute value because the EDS measurement is a semi-quantitative measurement. The comparison between the composition of the EDS results and the stoichiometry calculation was seen in Table 2.

4. Conclusion
In conclusion, all samples Ca_{0.95}La_{0.02}Bi_{0.03}MnO_3 with different sintering temperature were found to crystallize in the orthorhombic structure belonging to the Pnma space group. Different sintering temperature does not change crystal structure, but affect lattice parameter, crystallite size, and morphology of sample. The sample was sintered at 900 °C and 1000 °C for 12 h each did not show single phase, A small amount of CaMn_2O_4 is detected as secondary phase. While sample was sintered at 1100 °C for 12 h show single phase, as well the largest lattice parameter and mean crystallite size.

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