Analysis Crystal Structure of $La_{0.7}(Ba_{1-x}Sr_x)_{0.3}MnO_3$ by Sol-Gel Method

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Abstrak.
Penelitian tentang struktur kristal bahan $La_{0.7}(Ba_{1-x}Sr_x)_{0.3}MnO_3$ menggunakan metode sol-gel telah berhasil dilakukan. Bahan-bahan dasar yang digunakan dicampur di atas hot plate diaduk sambil ditetesi ammonia solution sehingga mencapai pH 7, selanjutnya didiamkan sampai diperoleh bentuk gel. Gel dikeringkan pada suhu 120°C, selanjutnya dilakukan pra-kalsinasi dengan suhu 650°C selama 6 jam, dilanjutkan dengan kalsinasi pada suhu 1000°C selama 12 jam, dan kemudian disinter pada temperatur 1200°C selama 12 jam. Hasil refinement data XRD memberikan informasi bahwa struktur kristal $La_{0.7}(Ba_{1-x}Sr_x)_{0.3}MnO_3$ adalah rombohedral dengan space grup R-3c. Penambahan substitusi ion Sr$^{2+}$ mengakibatkan terjadinya penurunan intensitas dan pergeseran puncak ke arah sudut yang lebih besar. Hal ini disebabkan karena pengaruh jari-jari ion Sr$^{2+}$ yang lebih kecil dibandingkan dengan jari-jari ion Ba$^{2+}$.

Kata kunci: $La_{0.7}(Ba_{1-x}Sr_x)_{0.3}MnO_3$, metode sol-gel, struktur kristal

Abstract.
In this research, $La_{0.7}(Ba_{1-x}Sr_x)_{0.3}MnO_3$ compound ($x = 0; 0.2; 0.3;$ and 0.5) by sol-gel method has been investigated. The compound used is mixed on a hot plate until reached a pH 7 when dropped ammonia solution, then let stand until turn into a gel. Dehydrated gel at 120°C, pra-calcination at 650°C for 6 hours, calcination at 1000°C for 12 hours, and sintering at 1200°C for 12 hours. The result of refinement XRD pattern shown that samples are single phase with rhombohedral crystal structure with R-3c space group. The intensity decrease and peak list shift to larger angle when Sr-substitution increased, it’s caused ionic radii of Sr$^{2+}$ is smaller than Ba$^{2+}$.

Keywords: $La_{0.7}(Ba_{1-x}Sr_x)_{0.3}MnO_3$, sol-gel method, crystal structure

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INTRODUCTION

LaMnO$_3$ perovskite is one of the most interested engineering materials for researchers because unusual their electrical and magnetic properties. This structure can be modified through doping of divalent ion at La-site and transition ion at Mn-site. Substituted La-site with divalent ion such as Ba, Sr, and Ca can change Mn content from Mn$^{3+}$ to Mn$^{4+}$, this phenomena can be explain with double exchange (DE) effect [1-2], a system by which electron mobility between the nearest Mn ions, preferably, those with aligned spins is preferred [3].

In general, crystal structure of LaMnO$_3$ compound is cubic. Their crystal structure can be change or distortion caused of divalent ions substituted at La-site. Distortion on perovskite structure occurs of different ionic radii or size mismatch at La-site and Jahn-Teller effect. The average size of the A-site cation that modified the Mn-O-Mn bond angle and Mn-O distances can control this distortion [4]. Goldschmidt tolerance factor ($t$) of perovskite compounds ABO$_3$ is commonly used to determine the stability of the geometry and crystal structure distortions. The $t$ is defined by ratios of constituent ionic radii of A, B, and O which expressed by [5]:

$$t = \frac{(r_A + r_O)}{(r_{Mn} + r_O) \sqrt{2}}$$

where $r_A$ are the average ionic radii on site A, $r_{Mn}$ and $r_O$ are the average ionic radii of the manganese and oxygen ions. The ideal perovskite compounds take on a cubic structure with $t=1$. When the ratio of the ionic radii deviates from the ideal value $t \neq 1$, a geometric strain and distortion of crystal occur [5].

In the previous work of Ref. [6], substitutes Ba$^{2+}$ ions to the LaMnO$_3$ compound (La$_{0.7}$Ba$_{0.3}$MnO$_3$) has a rhombohedral structure with R-3c space group. The structure of La$_{1-x}$Sr$_x$MnO$_3$ switch from orthorhombic to rhombohedral when Sr$^{2+}$ concentration is rising [7]. Mcbride et.al. [1] suggested that La$_{0.6}$Ba$_{0.4}$MnO$_3$ and La$_{0.6}$Sr$_{0.4}$MnO$_3$ have a synthesized LaMnO$_3$ rhombohedral structure using the same process. There are several methods have been reported can be used to synthesis of LaMnO$_3$ with substitution divalent ions such as sol-gel method, solid state reaction, solution combustion method, molten salt reaction, and hydrothermal method. Among these methods, the sol-gel method makes it easier to obtain highly crystalline nanoparticles with the smaller size and stoichiometry desired [8-10].

Analysis crystal structure and crystallographic characterization generally used X-ray diffractometer (XRD), this is non-destructive analytical technique [11]. The properties of polycrystalline materials depend on several things, such as the crystalline size. Using Scherrer equation, we can calculated the crystalline size expressed by [12-13].

$$D = \frac{k \lambda}{B \cos \theta}$$

where $D$ is crystalline size, $k$ have value 0.9, $\lambda$ is wavelength of X-ray ($\lambda = 1.5406$ Å), B is FWHM, and $\theta$ is Bragg angle.

In this work, La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ where ($x = 0; 0.2; 0.3$; and 0.5) have been synthesized by sol-gel method. Using Rietveld refinement of X-ray diffraction data the structural parameters (unit cell volume, crystalline size, bond length, bond angle, and tolerance factor ($t$)) were refined.

METHOD

La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ ($x = 0; 0.2; 0.3$; and 0.5) was prepared using the sol-gel reaction method, La$_2$O$_3$ (99.99%), Mn(NO$_3$)$_2$.4H$_2$O (98.5%), Ba(NO$_3$)$_2$ (99%), Sr(NO$_3$)$_2$ (99%), and CaH$_2$O$_7$.H$_2$O (99.5%). The compounds were mixed and stirred on the hot plate, then added ammonia solution during the stirring process and resulted in brown colloid, after that oven at 120°C for 3 hours. After drying, pra-calcined at 650 °C for 6 hours and then calcined at 1000°C.
for 12 h. The black powder obtained was pressed at 10 tons and sintered at 1200°C for 12 h. XRD Panalytical X’pert Pro MPD identified the crystal structure and phase information of the samples with Fast Detector X’celerator using CuKα (λ = 1.5406 Å) radiation in the range 10°-90° with step size of 0.02°. The X-ray diffraction data were analyzed by Rietveld refinement using HighScore Plus software.

RESULT AND DISCUSSION

XRD character trends in Fig. 1 shown the single phase of LBSMO where all samples have rhombohedral structure with R-3c space group. XRD results also indicated that the intensity decreased when Sr²⁺ substitution increased. The sample’s unit cell parameters, other fitting parameter and Goldschmidt tolerance factor are shown in Table 1 using the refined crystallography data. Fig. 2 shown the peak LBSMO shifted to the right when substitution Sr²⁺ increased. The higher value of 2-θ indicates that LBMO (x = 0) have larger d-spacing compared to substituted with Sr²⁺ so d-spacing decreased, which is caused by the ionic radii of Sr²⁺ (1.44 Å) is smaller to replaces of Ba²⁺ (1.61 Å).

Table 1. Structure parameter La₀.₇(Ba₁₋ₓSrₓ₀₃,MnO₃)

| Lattice Parameters | x = 0   | x = 0.2 | x = 0.3 | x = 0.5 |
|--------------------|--------|---------|---------|---------|
| a = b (Å)          | 5.538  | 5.544   | 5.540   | 5.543   |
| C (Å)              | 13.501 | 13.465  | 13.475  | 13.425  |
| Discrepancy Factors|        |         |         |         |
| Rp                 | 6.0042 | 6.0145  | 6.1213  | 6.336   |
| Wrp                | 7.852  | 8.067   | 8.121   | 8.392   |
| GoF                | 1.18   | 1.204   | 1.31    | 1.35    |
| Goldschmidt tolerance factor | 0.9885 | 0.9848 | 0.9832 | 0.9794 |

Figure 1. LBSMO XRD pattern
Figure 2. Shifting of peak LBSMO

Beside the result of refinement in table 1, substituted Sr$^{2+}$ also caused a decrease of volume cell crystal shown fig. 3, it’s occurred that ionic radii of Sr$^{2+}$ smaller than ionic radii of Ba$^{2+}$ so the d-spacing is decreased. The different ionic radii also affected Goldschmidth tolerance factor ($t$) as a result distortion of LaMnO$_3$ structure caused mismatch between ionic radii which is substituted with the ionic radii of La. The ionic radii of Ba$^{2+}$ (1.61 Å) and Sr$^{2+}$ (1.44 Å) too large to occupied site La (1.172 Å). Substitution increased causes the value of Goldschmidth tolerance factor decreased. This occurred when substituted increased, the value of ionic radii at site A from La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ decreased from 1.435 Å to 1.4025 Å. Fig. 4 shown the crystalline size of La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ calculated using the Eq.(2).

Figure 3. Volume cell of La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$
Sr$^{2+}$ substituted on La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ not change crystal structure of LBSMO compound, but changed the lattice parameter and caused MnO$_6$ distortion. Bond length $d_{\text{Mn-O}}$ and bond angle $<\text{Mn-O-Mn}>$ of La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ shown in fig 5. The increased substitution caused bond length increased and bond angle decreased.

As the result refinement and Goldscmidt tolerance factor, crystal structure La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ is rhombohedral with R-3c space group. Using VESTA software, the visualization of La$_{0.7}$(Ba$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ shown at fig. 6.
CONCLUSION

Analysis of $\text{La}_{0.7}(\text{Ba}_{1-x}\text{Sr}_x)_{0.3}\text{MnO}_3$ crystal structure was studied using sol-gel method. All samples have rhombohedral structure with R-3c space group. Volume cell, crystalline size, and tolerance factor ($t$) are decreased with increasing Sr$^{2+}$ substituted. On the other, the increased substitution of Sr$^{2+}$ caused bond length $d_{\text{Mn-O}}$ increased and bond angle $\theta_{\text{Mn-OMn}}$ decreased.

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