The influence of calcination temperature on the structural properties of La$_2$FeMnO$_6$ double perovskite materials

Yunida and D Triyono
Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia

Corresponding author’s email: djoko.triyono@sci.ui.ac.id

Abstract. The double perovskite compound, La$_2$FeMnO$_6$ (LFMO), has been synthesized using the sol-gel method. Structural properties were characterized by X-ray diffraction (XRD), and X-ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and Raman scattering spectroscopy. Rietveld refinement of calcination powder from X-ray data indicates the compound was a single-phase formation of double perovskite with 750 °C and 900 °C calcination temperatures. XRF showed the weight and atomic ratio of the compound are suitable with double perovskite stoichiometric, respectively. The result of structural analysis confirmed that the La$_2$FeMnO$_6$ has a cubic structure with space group $Pm-3m$ at both temperatures. Lattice parameters, volume and crystallite size of the samples become larger as higher calcination temperatures. Raman scattering spectroscopy and FTIR have been used to study the peak vibrational modes and various bond formations of the prepared samples.

Keywords: Double perovskite, LFMO, sol-gel method, structural properties

1. Introduction
Single perovskites are the most intensely studied materials in solid-state chemistry and physics in recent years. These materials with ideal cubic compound formula $ABX_3$ exhibit several fundamentally interesting chemical and physical properties [1]. LaFeO$_3$ is one of kind single perovskite oxide/rare earth orthoferrite which is significant because it is potential to be applied in data storage media, multiple stage memories and sensors [2]. Jung-Hoon et al reported that Mn-doped LaFeO$_3$ nanofibers were prepared using the electrospinning technique have a single phase without any trace impurity from XRD analysis [3]. The single perovskite LaFeO$_3$ and LaMnO$_3$ are well known as antiferromagnets (AFM) materials with Néel temperatures (TN) 740 K and 140 K.

Perovskite with substitution of $A'$ for $A$ (or $B'$ for $B$) cations will take on a disordered arrangement which rises a compound generally labelled as double perovskite, $A_2B'B''X_6$ [4]. La$_2$FeMnO$_6$ (LFMO) is a double perovskite that has gained popularity, where $A$ is Alkaline earth or Rare earth element and $B'$ & $B''$ is a $3d$ transition metal [5]. Lanthanum oxide has an attractive characteristic such as structural, magnetic and electrical properties as a base compound in double perovskite. In La$_2$FeMnO$_6$ double perovskite, La$^{3+}$ occupies site A with the ionic radius (1.06 Å) whereas Fe$^{3+}$ (0.64 Å) and Mn$^{3+}$ (0.58 Å) cation occupy site $B'$ and $B''$, respectively.

Recent work has been focused on the synthesized method, characterization and magnetic behavior of double perovskite [6]. Hence, this paper has been focused on the influence of calcination
temperature towards the structure of double perovskite Mn substituted LaFeO$_3$ compounds (La$_2$FeMnO$_6$).

2. Experimental
The La$_2$FeMnO$_6$ (LFMO) materials were synthesized by the sol-gel method at ambient atmosphere. The composition of lanthanum (III) oxide, iron (II) nitrate nonahydrate, and mangan (II) nitrate tetrahydrate were measured using double perovskite stoichiometric with citric acid and aquadest as a solvent. All precursors were mixed and stirred at 120 °C to remove water and citric acid. The stirring process is also to obtain a gel phase of the sample with a magnetic stirrer. The mixture was dried at temperature 200 °C for 5 hours to get a sample in the form of a sponge, then calcined at 900 °C for 6 h and 750 °C for 5 h. X-ray diffraction type *X’Pert PRO PANalytical* diffractometer with Cu K$_α$ radiation ($λ = 1.5405$ Å) and range of angle 20°-90° was used for phase and impurity identification whereas the X-Ray Fluorescence (XRF) was used for determining the composition. Raman scattering spectroscopy and FTIR have been employed to study the vibrational modes and various bond formations of LFMO.

3. Results and discussion
Figure 1 shows the XRD pattern of La$_2$FeMnO$_6$ powder with calcined 900 °C for 6 h and 750 °C for 5 h (figure 1). The refinement was done by *Highscore Plus* software and the Le-bail fitting was plotted using *Crystallography Open Database* (COD) of LaFeO$_3$ with number COD 96-154-2145. The Le-bail fitting material plotted confirmed that both of samples were the single-phase without any trace of impurities. Sample A has a peak intensity higher than sample B and a smaller full width at half maximum (FWHM). It is due to an enhanced crystallization of perovskite phase as the increasing calcination and the grain size become larger than one on the FWHM [7]. The Rietveld refinement results confirm that both of the prepared LFMO material into a cubic structure with *Pm-3m* (221) space group.

![Figure 1. Rietveld refinement of XRD patterns of La$_2$FeMnO$_6$ double perovskite with A: calcination of 900 °C and B: calcination of 750 °C.](image-url)
3.1. Structural analysis

Table 1 shows the crystallography and geometric parameters of LFMO powders. Sample A and B have Goodness of fit ($\chi^2$) 1.60 and 1.44 respectively. It is indicated that the comparison between Rwp (weighted profile) and Re (expected) from XRD fitting, as a result, Rietveld refinement was suitable to be used [8]. The different crystallite sizes at both samples are due to the diffusivity of the individual grains, sintering temperature and porosity [9].

Table 2 shows the weight and atomic ratio of the La$_2$FeMnO$_6$ comparison between experimental and calculation by X-Ray Fluorescence. From the table, it is known that the composition of the sample is a slight different between experimental and calculation results. The weight percentage of Fe and Mn in experimental is less than the one from calculation result. It is due to the deficient mass along the calcination process and correlates to the both components’ melting point which is lower than La.

3.2. Raman scattering analysis

Figure 2 shows the Raman spectral analysis of La$_2$FeMnO$_6$ with wavenumber 100–2000 cm$^{-1}$. The peak position was determined by fitting the peak with the Lorentzian function for structure and phase purity analysis. Only a few report mentioning the lattice dynamical calculations and

| Parameter                             | La$_2$FeMnO$_6$ | La$_2$FeMnO$_6$ |
|---------------------------------------|-----------------|-----------------|
| **La$_2$FeMnO$_6$**                  | Calcination of 900 °C | Calcination of 750 °C |
| Phase                                | Cubic           | Cubic           |
| Space group                          | $Pm-3m$ (221)   | $Pm-3m$ (221)   |
| Lattice parameters                   |                 |                 |
| a (Å)                                | 3.89            | 3.90            |
| b (Å)                                | 3.89            | 3.90            |
| c (Å)                                | 3.89            | 3.90            |
| Volume (Å$^3$)                       | 59.30           | 59.33           |
| Crystallite size (nm)                | 235.20          | 382             |
| Density g/cm$^3$                      | 6.79            | 6.79            |
| Geometrical parameters               |                 |                 |
| R factor (%)                         |                 |                 |
| $R_e$ (expected)                     | 7.07            | 6.74            |
| $R_p$ (profile)                      | 6.58            | 6.20            |
| $R_{wp}$ (weighted profile)          | 8.97            | 8.10            |
| Goodness of fit ($\chi^2$)           | 1.60            | 1.44            |

| La$_2$FeMnO$_6$ | Calcination temperature | (%) experimental | (%) calculation |
|-----------------|--------------------------|-------------------|-----------------|
| Weight 900 °C   | 78.67                    | 11.50             | 9.83            |
| Atomic ratio    | 2.76                     | 1                 | 0.86            |
| Weight 750 °C   | 74.52                    | 13.79             | 11.69           |
| Atomic ratio    | 2.17                     | 1                 | 0.86            |
assignment of LFMO materials, but the Raman Spectra of double perovskite is mostly below the value of 1000 cm$^{-1}$ [10]. Table 3 is the list of the observed Raman active modes. The peak positions are in good agreement with the report in the literature. The peak at 503.72 cm$^{-1}$ and 499 cm$^{-1}$ correspond to $A_g$ vibrational mode and the resonance peak at 653.53 cm$^{-1}$ and 659.89 are attributed to $E_1$ mode of vibration [11]. The resonance peak at 1325.76 and 1379.29 are the double energy values of $E_1$. The strong reduction (2$E_2$) is correlated to the existence of magnetic ordering in these materials [12]. It is also shown that the vibrational mode in which appearance at peaks influences the anti-ferromagnetic ordering [13].

3.3. Fourier transform infrared spectra (FTIR) analysis

Figure 3 shows the Fourier Transform Infrared Spectra (FTIR) of LFMO materials with range wave number 500–4000 cm$^{-1}$. The vibration mode at 502 cm$^{-1}$ is noted and assigned to Fe-O stretching in these materials [14]. The one sharp vibration mode at 569 cm$^{-1}$ is noted due to the internal movement of length change of the bounds Mn-O-Mn. This vibration corresponds to the octahedron MnO$_6$ which is related to the vibration property of perovskite structure ABO$_3$ [15]. Sample A has two vibrations evident at 1740 cm$^{-1}$ and 1201 cm$^{-1}$. The vibration appearance around 1115 cm$^{-1}$ indicates the presence of C-O groups and a strong vibrational band of water (H-O-H) appearance at 1740 cm$^{-1}$ [16].

![Figure 2. Raman Scattering of La$_2$FeMnO$_6$ double perovskite with calcination of (a) 900 °C and (b) 750 °C.](image)

![Table 3. Raman shift (cm$^{-1}$) of La$_2$FeMnO$_6$ double perovskite with calcination of 900 °C and 750 °C.](table)

| Raman shift (cm$^{-1}$) | Assignment of modes |
|------------------------|---------------------|
| Calcination of 900 °C  | Calcination of 750 °C |
| 120.82                 | 119.49              |
| 503.72                 | 499.27              | Ag |
| 653.53                 | 659.89              | $E_1$ |
| 1325.76                | 1379.29             | 2$E_2$ |
| 1758.61                | 1830                | - |
4. Conclusion
Double perovskite La$_2$FeMnO$_6$ has been synthesized by sol-gel method at ambient condition. The XRD pattern confirmed that all of the samples have a cubic structure with $Pm-3m$ space group. The crystallite size decreases with the increase temperature of calcination. The sample was single phase at both calcination temperatures. The composition of La$_2$FeMnO$_6$ was suitable for double perovskite stoichiometric formula. The vibration mode of Raman Spectra and Fourier Transform Infrared Spectra (FTIR) confirms the phase purity of La$_2$FeMnO$_6$.

Acknowledgments
This work was financially supported by Ministry of Research and Technology (KEMRISTEK/BRIN) Republic of Indonesia under research grant Hibah Penelitian Tesis Magister (PTM) 2020 with contract number NKB-493/UN2.RST/HKP.05.00/2020.

References
[1] Vasala S and Karppinen M 2015 Prog. Solid State Chem. 43 1–36
[2] Mahmood A, Warsi M F, Ashiq M and Ishaq M 2013 J. Magn. Magn. Mater. 327 64–70
[3] Jeong J –H, Song C –G, Kim K –H, Sigmund W and Yoon J –W 2018 J. Alloys Comp. 749 599-604
[4] Xu X, Zhong Y and Shao Z 2019 Trends in Chemistry 1 410-24
[5] Punitha J S, Philip M, Anbarasu V nd Kumar K S 2019 AIP Conf. Proc. 2115 030468
[6] Qian Y et al. 2013 J. Appl. Phys. 114 063713
[7] Sun Y et al. 2014 Sustain. Energy Techn. 8 92-8
[8] Toby B H 2006 Powder Diffr. 21 67–70
[9] Haque M M, Maria K H, Choudhury S, Bhuiyan M and Hakim M 2013 J. Ceram. Process. Res. 14 82-6
[10] Dhipl M, Devi N A, Punitha J S 2019 Vacuum 167 16-20
[11] Iliev M N et al. 1998 Phys. Rev. B 57 2872–7
[12] Hien N T M et al. 2009 J. Raman Spectrosc. 41 983–8
[13] Massey M J, Bailer U, Merlin R and W H Weber 1990 Phys. Rev. B Condens. Matter. 41 7822–7
[14] Romero M, Gomez R W, Marquina V, Perez-Mazariego J L and Escamilla R 2014 *Physica B* **443** 90–4
[15] Moghadam L N and Ranjbar Z R 2019 *J. Alloys Compd.* **785** 117–24
[16] Frost R L, Kristof J, Paroz G N and Kloprogge J T 1998 *J. Colloid Interf. Sci.* **208** 216–25.