3rd International Seminar on Chemistry 2014

Synthesis of the Bi-doped apatite-type phases La$_{10-x}$Bi$_x$Si$_6$O$_{27}$ (x= 0.5, and 1) by hydrothermal method

Atiek Rostika Noviyanti*, Diana Rakhmawaty Eddy, and Annisa Anshari

Department of Chemistry, Faculty of Mathematic and Natural Science, Universitas Padjadjaran
Jl. Raya Bandung-Sumedang Km. 21, Jatinangor 45363, Indonesia

Abstract

Lanthanum silicate apatites are attracting due to their considerable interest as an electrolyte of solid oxide fuel cells. In this paper, we reported synthesis of two Bi-doped apatites and one undoped one. Apatite were synthesized by hydrothermal at 200 °C for 3 days from La$_2$O$_3$, Na$_2$SiO$_3$, and Bi$_2$O$_3$ (for Bi-doped). Le Bail refinement of X-ray data showed that all apatites have a hexagonal cell ($P 6_3/m$ space group). The lattice parameters of La$_9.5$Bi$_0.5$Si$_6$O$_{27}$ and La$_9$Bi$_1$Si$_6$O$_{27}$ are $a = b = 9.718(1)$ Å, $c = 7.190(1)$ Å, and $a = b = 9.724(1)$ Å, $c = 7.189(1)$ Å, r. There is increase in lattice parameters with increasing content of Bi.

Keywords: Lanthanum silicates apatites, oxygen ion conductivities; Bi-doped Apatite; Le Bail refinement, hexagonal cell.

1. Introduction

Apatite-type lanthanum silicates with high oxide ion conductivity offers potential use as electrolyte, particularly in the area of solid oxide fuel cell (SOFC)$.^1,2$ Apatite has general formula of M$_{10}$(XO$_4$)$_6$O$_2$, where M is a metal such as rare-earth or alkaline, and X is a p-block element such as P, Si or Ge. The typical crystal structure of apatite is shown in Figure.1, consisting of isolated XO$_4$ tetrahedral with the M cation located in two cavities, one with 7 coordination numbers (4f) and the other with 9 coordination numbers (6h). The extra oxygen atoms occupy channels throughout the structure and these channels are responsible for the high oxygen ion conduction.

Another key feature of these apatite-type oxide is its wide ranges of doping possibilities within the structure, which can be utilized to improve their conductivity. Previous studies have suggested that for oxygen stoichiometric samples, doping onto the Si site with small levels of lower valent ions such as B, Al, Ga, Fe, Mn and Co on the La site resulted in a general reduction in conductivity$.^3$. Apatite with containing either cation vacancies, La$_{9.33}$(SiO$_4$)$_6$O$_2$, or oxygen excess, La$_9$Sr(SiO$_4$)$_6$O$_{2.5}$, have high conductivities and low activation energies$.^4$. The modeling studies also predicted the presence of an energetically favorable oxygen interstitial position located at the periphery of the channels (sansom, 2004). It is important to note that relaxation of [SiO$_4$]$^4$ substructure play role to increase conductivity in apatite system samples, doping onto the Si site with small levels of lower valent ions such as B, Al, Ga, Fe, Mn and Co on the La site resulted in a general reduction in conductivity$.^3$.

* Corresponding author. Tel.: +62-22-7794391; fax: +62-22-7794391
  E-mail address: atiek.noviyanti@unpad.ac.id

doi:10.1016/j.proche.2015.12.111
In general, silicates are prepared by solid state reaction using La$_2$O$_3$ and SiO$_2$ as precursors, with high temperature (about 1500 °C). In addition, it is very difficult to remove trace amounts of La$_2$SiO$_5$ impurity when these apatite are prepared by solid state reaction. In this report, we synthesized undoped and two Bi-doped apatite in order to further investigate the effect doping to cell parameter of apatite by using a lower temperature synthesis (hydrothermal method).

2. Experimental

2.1 Synthesis and Characterization of apatite phase La$_{9.33}$Si$_6$O$_{26}$, La$_{9.5}$Bi$_{0.5}$Si$_6$O$_{27}$ and La$_{9}$Bi$_{1}$Si$_6$O$_{27}$

To prepare the composite materials, three composition apatites were designed (noted as La$_{9.33}$Si$_6$O$_{26}$, La$_{9.5}$Bi$_{0.5}$Si$_6$O$_{27}$ and La$_{9}$Bi$_{1}$Si$_6$O$_{27}$, respectively). The starting materials were high purity La$_2$O$_3$ (Aldrich, 99.99%), Na$_2$SiO$_3$ (Sigma, 97%) and (Bi$_2$O$_3$; Aldrich 99.99%) powders. The La$_2$O$_3$ powder was precalcinated at 1100 °C for 10 hours in order to achieve complete decarbonation and dehydroxylation. The starting materials were weighed in the appropriate ratios as shown in Table 1 and mixed with the NaOH solution, after which the mixtures were transferred into a stainless steel autoclave (302 AC Bombs Parts 105 mL) until 60% volume of the autoclave was occupied. After being heated at 240°C for 3 days, the precipitate was collected by filtration and washed with demineralized water. The resulting powder was dried at 120°C.

| Target Material | La$_2$O$_3$ (g) | Na$_2$SiO$_3$ (g) | Bi$_2$O$_3$ (g) |
|-----------------|----------------|-----------------|----------------|
| La$_{9.33}$Si$_6$O$_{26}$ | 0.8197 | 0.1953 | - |
| La$_{9.5}$Bi$_{0.5}$Si$_6$O$_{27}$ | 0.7644 | 0.3618 | 0.0575 |
| La$_{9}$Bi$_{1}$Si$_6$O$_{27}$ | 0.7118 | 0.3557 | 0.1131 |

2.2 Characterization of apatite phase La$_{9.33}$Si$_6$O$_{26}$, La$_{9.5}$Bi$_{0.5}$Si$_6$O$_{27}$ and La$_{9}$Bi$_{1}$Si$_6$O$_{27}$

Phase identification was performed by using X-ray diffraction (PW 3373 PANalytical using Cu-Ka radiation using Cu-Ka radiation ($\lambda$=1.5406 Å) at room temperature. XRD data were analyzed using the Le Bail method to evaluate cell parameter of apatite. Fourier transform infrared spectra (FTIR) of powdered samples suspended in KBr pallets were acquired between 400 and 4000 cm$^{-1}$ using FTIR – 8400 SHIMADZU.
3. Results and Discussion

Fig. 2 shows XRD diffraction pattern of apatite phases of undoped apatite $La_{9.33}Si_6O_{26}$ and two Bi-doped apatite, $La_{9.5}Bi_{0.5}Si_6O_{27}$ and $La_9Bi_1Si_6O_{27}$) after heating at 120ºC. The diffraction pattern of Bi-doped apatites and Bi-doped apatite are similar. This means that doping of $Bi^{3+}$ ion at the La position on the apatite structure can be synthesized. All the doped apatite diffractogram show a secondary phase $La_2SiO_5$ (peak at around 20 15º and 44º), as is often reported in previous studies. The presence of secondary phases $La_2SiO_5$ almost appear at the lanthanum silicate apatite resulted from the synthesis, as well as Bi-doped apatite.

![XRD diffraction pattern of (a) $La_{9.33}Si_6O_{26}$ (b) $La_{9.5}Bi_{0.5}Si_6O_{27}$ and (c) $La_9Bi_1Si_6O_{27}$) after heating at 120 ºC.](image)

**Table 2.** Cell Parameter of undoped apatite ($La_{9.33}Si_6O_{26}$) and Bi.doped apatites ($La_{9.5}Bi_{0.5}Si_6O_{27}$ and $La_9Bi_1Si_6O_{27}$).

| Composition       | $a = b$ (Å) | $c$ (Å)   | Cell Volume (Å³) | Doping site |
|-------------------|-------------|-----------|------------------|-------------|
| $La_{9.33}Si_6O_{26}$ | 9.722(1)    | 7.188(1)  | 588.458(2)       | -           |
| $La_{9.5}Bi_{0.5}Si_6O_{27}$ | 9.718(1)    | 7.190(1)  | 588.402(1)       | La          |
| $La_9Bi_1Si_6O_{27}$ | 9.724(1)    | 7.189(1)  | 588.727(1)       | La          |

As for the shift in cell parameter of apatite, complicated lattice distortion was observed in the X-ray pattern with increasing content of Bi. This may result from the small large $Bi^{3+}$ (0.120 nm) and that of $La^{3+}$ (0.115 nm), this result is in agreement with previous studies.

In order to get further proof of the apatite structures, FTIR spectra were undertaken and Fig. 3 showed the spectrum of $La_{9.33}Si_6O_{26}$ sample which are very similar to that of previously reported rare earth silicate apatite materials. The spectrum of lanthanum sample exhibits bands at: 634, 9 cm$^{-1}$ can be assigned as lanthanum silicate apatite (Savignat, 2007). The broadband between 3660 cm$^{-1}$ arises from the O–H bond stretching modes and indicates hydrous species. Fig. 3, show FTIR spectrum of apatites resulted by hydrothermal synthesis.
The slight difference between the undoped and Bi-doped lanthanum silicate that was shown in the XRD diffraction, was also shown in the FTIR spectrum. The Intensity of absorbance at about 643 cm$^{-1}$ in the Bi-doped apatite higher than that of undoped apatite, it was suggested that the spectral differences between the two silicates was caused by partly replacement of La-O by Bi-O. The difference in strength between the La-O vibrations of Bi-O will contribute to the intensity of absorbance FTIR spectrum at about 643 cm$^{-1}$.

**Conclusion**

Bi-doped apatite phase of La$_{9.5}$Bi$_{0.5}$Si$_{6}$O$_{27}$ and La$_{9}$Bi$_{1}$Si$_{6}$O$_{27}$ have been successfully synthesized by using hydrothermal at 200 °C for 3 days. The lattice parameter refinement results Bi$^{3+}$ doped apatite decreased slightly when compared to non-doped apatite lattice parameters La$_{9.33}$Si$_{6}$O$_{26}$. However the decrease was not significant.

**Acknowledgements**

The authors would like to express sincerely thank to PUPT Project No. 2002/UN6.RKT/KU/2013 (DIKTI, Indonesia) for financial support of this research.

**References**

1. Kendrick, E., M.S. Islam, and P.R. Slater, Investigation of the structural changes on Zn doping in the apatite-type oxide ion conductor La$_{9.33}$Si$_{6}$O$_{26}$. A combined neutron diffraction and atomistic simulation study. *Solid State Ionics*, 2007b. 177(39-40), 3411-3416.
2. Sansom, J.E.H., et al., Synthesis and structural characterisation of the apatite-type phases La$_{10-x}$Si$_{6}$O$_{26+z}$ doped with Ga. *Solid State Ionics*, 2004, 167(1-2): p. 17-22.
3. Sansom, J.E.H., et al., A comparison of the effect of rare earth vs Si site doping on the conductivities of apatite-type rare earth silicates. *Journal of Solid State Electrochemistry*, 2006a. 10, 562-566.
4. Sansom, J.E.H., Solid state $^{29}$Si NMR studies of apatite-type oxide ion conductors. *Journal of Materials Chemistry*, 2006b. 16, 1410-1413.
5. Islam, M.S., J.R. Tolchard, and P.R. Slater, An apatite for fast oxide ion conduction. *Chemical Communications*, 2003, 1486-1487.
6. Kendrick, E., M.S. Islam, and P.R. Slater, Developing apatites for solid oxide fuel cells: insight into structural, transport and doping properties. *Journal of Materials Chemistry*, 2007a. 17, 3104-3111.

7. Kim, D.-Y. and S.-G. Lee, Fabrication and electrical properties of Si-based La$_{10-x}$Bi$_x$(SiO$_4$)$_6$O$_3$ apatite ionic conductor. *Materials Research Bulletin*. 2012. 47, 2856-2858.

8. Sansom, J.E.H., P.A. Sermon, and P.R. Slater, Synthesis and conductivities of the Ti doped apatite-type phases (La/Ba)$_{10-x}$(Si/Ge)$_6$Ti$_y$O$_{26-z}$. *Solid State Ionics*, 2005. 176 (19-22), 1765-1768.

9. Savignat, S.B., et al., Oxide ion conduction in Ba, Ca and Sr doped apatite-type lanthanum silicates. *Journal of Materials Chemistry*. 2007. 17, 2078-2087.