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Effect of La Doped on the Conductivity of the Perovskite Type $PbZrO_3$

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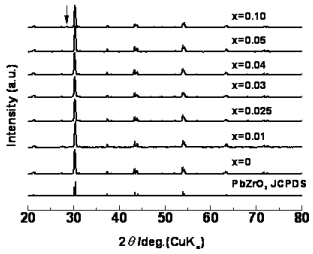
Graphical abstract



Abstract

Electrochemical properties of $Pb_{1-x}La_xZrO_{3+x/2}$ with perovskite structure have been studied. The powdery $Pb_{1-x}La_xZrO_{3+x/2}$ has been prepared by solid-state reaction method. The X-ray diffraction analysis reveals that $Pb_{1-x}La_xZrO_{3+x/2}$ (x = 0.0-0.05) sintered at 900 ˚C was single phase structure. The electrical conductivity of the material has been investigated. By doping La at the lead site, the electrical conductivity of the $Pb_{1-x}La_xZrO_{3+x/2}$ system decreased. The undoped compound showed the highest electrical conductivity of ca. 10^{-3} S/cm. Electromotive Force (EMF) measurements of oxygen concentration cell confirm that the charge carrier of La doped $PbZrO_3$ was the oxide ion.

Keywords: Perovskite; solid solution; interstitial ion; oxide ion electromotive force

Abstrak

Sifat-sifat elektrokimia $Pb1_{-x}La_xZrO_{3+x/2}$ dengan struktur perovskit telah dikaji. Serbuk $Pb1_{-x}La_xZrO_{3+x/2}$ telah disediakan melalui kaedah tindak balas keadaan pepejal. Analisis belauan sinar-X memperlihatkan bahawa $Pb1_{-x}La_xZrO_{3+x/2}$ (x = 0.0-0.05) yang disinter pada 900 ˚C mempunyai struktur fasa tunggal. Kekonduksian elektrik bahan ini telah dikaji. Dengan mendopkan La pada tapak plumbum, kekonduksian elektrik bagi sistem Pb1-xLaxZrO3+x/2 menurun. Bahan yang tidak didop telah menunjukkan kekonduksian paling tinggi iaitu kira-kira 10^{-3} S/cm. Pengukuran daya gerak elektrik (dge) bagi sel kepekatan oksigen mengesahkan bahawa cas pembawa bagi $PbZrO_3$ yang didopkan dengan La ialah ion oksigen.

Kata kunci: Perovskit; larutan pepejal; ion celahan; ion oksigen; daya gerak elektrik

1.0 INTRODUCTION

Fast oxide ion conductor has received an attention because of the potential application in solid oxide fuel cell and oxygen gas sensor. A numerous of study has been focusing on oxygen vacancy, which increased the conductivity of the materials. The most common solid electrolyte material with oxygen vacancy is Sr- and Mg- doped $LaGaO_3$ [1]. Relatively, materials with interstitial ion are less investigated because the mechanism of oxide conduction via interstitial oxide ions in perovskite structure is unclear. Esaka et al. reported that La or Sm doped scheelite type oxide $PbWO_4$ has interstitial oxide ion and the conductivity increased with increasing the concentration of La or Sm. Both are oxide ion conductors. It was found that the conductivity for La or Sm doped $PbWO_4$ is 10^{-2} S/cm at 800 ˚C [2] [3]. Esaka et al also found that perovskite type oxide Zr doped-$LaYO_3$ has an interstitial oxide ion and shows purely oxide ion conductor [4]. $CeTaO_{4+\delta}$ as well reported by Stepen J.Skinner as an interstitial oxide ion conductor with high conductivity [5]. In this work, we synthesized perovskite type $PbZrO_3$. La was doped at Pb site to produce interstitial oxide ions. The formula of doped sample becomes $Pb_{1-x}La_xZrO_{3+x/2}$. Then, electrochemical properties of the samples were investigated in order to discover of new conductor with optimal conductivity, and then will result in a new class of fast ion conductor.

2.0 METHODOLOGY

2.1 Sample Preparation

In this study, all samples were prepared by conventional solid-state reaction method. Reagent grade of PbO, ZrO_2 and La_2O_3 powders were used as the starting materials. In order to determine the solid solubility of the dopant in the materials, samples were prepared with different amount of La. Required amount of oxide powders were mixed in agate mortar. During this process, ethanol was added to the powders as mixing aid. After mixing, the powders were calcined at 750 ˚C in air for 10 hours. The calcined powders then were finely ground and pressed into pellets 5 mm in diameter and 10 mm thick, and disc 13 mm in diameter and 2 mm thick under a pressure of 2 tons/cm^2, and sintered at 900 ˚C in air

for 10 hours. Pellet samples were 5 mm in diameter 10 mm thick for electrical conductivity measurement and disc 13 mm in diameter and 2 mm thick for electromotive for measurement.

2.2 Characterization

In order to identify crystal phase of the sintered powder, we analyzed the samples using X-ray diffraction (XRD) with Cu K_α. The electrical conductivity of the samples was measured using two-probe ac method. Both flat surfaces of the sample were painted with platinum paste, and fired at 850 ˚C for 2 hours, which is function as the electrodes. In order to investigate the charge carriers in the sample, electromotive force (EMF) measurements were conducted using the disc sample as the electrolyte. The anode and cathode gas was 1 atm oxygen and air, respectively.

3.0 RESULTS AND DISCUSSION

The XRD patterns of samples sintered at 900 ˚C are shown in Figure 1. It is confirmed that samples with x = 0.0 – 0.05 have a single phase which is tetragonal phase. XRD patterns were analyzed based on JCPDS (no. # 35-0739). This is in agreement with C.Puchmark et al. who also found that single phase of $PbZrO_3$ was obtained when sintered at 775 to 900 ˚C [6]. For sample with x = 0.10, additional peak was observed nearly 28 ˚. This result shows solubility of La in the sample is x < 0.10. This result shows that excess oxygen can exist in $PbZrO_3$ but with a very limited amount.

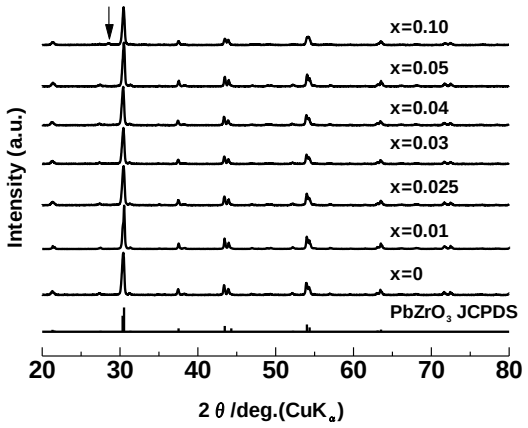


Figure 1 X-ray diffraction patterns of $Pb_{1-x}La_xZrO_{3+x/2}$

Figure 2 shows the electrical conductivity of $Pb_{1-x}La_xZrO_{3+x/2}$ as a function of temperature. In the range of temperature, pure $PbZrO_3$ shows the highest conductivity, which is 10^{-3} S/cm. However, for samples with La-doped, conductivity decrease to 10^{-6} – 10^{-4} S/cm. Although the conductivity decreased when doped with La, it increased with increasing the La content. The conductivity of all samples decreases with decreasing temperature, and no gradient change was observed; indicate that there is no structure change of the samples in the range of temperature. It is necessary to investigate the localized position of excess oxygen and carrier diffusion in this structure.

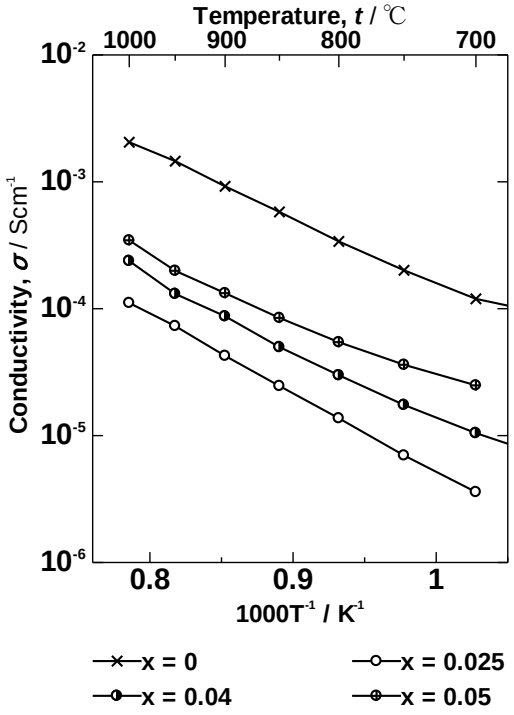


Figure 2 Arrhenius plots of conductivity of $Pb_{1-x}La_xZrO_{3+x/2}$

The EMF of the samples was measured to determine the charge carrier in the samples. Samples were used as the electrolyte of the oxygen concentration cell, and both flat surfaces of the samples were coated with the Pt paste which serves as the electrode.
The oxygen concentration cell is

$$Pt, O_2\ (0.21\ atm) \mid Pb_{1-x}La_xZrO_{3+x/2} \mid Pt, O_2\ (1.0\ atm)$$

The reactions at both electrodes are

$$\text{Cathode } O_2 + 4e^- = 2O^{2-}$$
$$\text{Anode } 2O^{2-} = O^2 + 4e^-$$

According to Nerst equation,

$$E = (RT/4F) \ln (P_{O2}/P'_{O2}),$$

E equals to 1 when all charge is carrier ion [7].

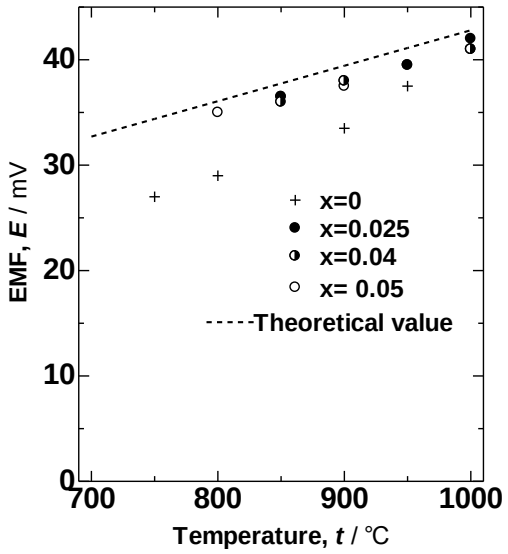


Figure 3 EMF versus temperature relations for the following cell; O_2 (0.21 atm), Pt | $Pb_{1-x}La_xZrO_{3+x/2}$ | Pt, O_2 (1.0 atm)

The result of the EMF measurement is shown in Figure 3. The dashed line indicates E = 1, which shows the electrolyte is a purely ionic conductor. From this figure, undoped $PbZrO_3$ shows only 80 – 90 % of ionic transference number. This means, the undoped sample also has electron as the carrier which contributes to the conductivity. For all the La-doped samples show that the ionic transference number is almost 100 %. The contribution of the electron carrier explains why the conductivity of the undoped sample is higher than the La-doped samples.

4.0 CONCLUSION

$Pb_{1-x}La_xZrO_{3+x/2}$ with perovskite structure showed single phase when La-doped at Pb site below than 10 %. The conductivity decreased when La was doped into the sample. The charge carrier of pure sample was identified as mixed oxide ion and electron, meanwhile for the La-doped sample it is confirmed that the charge carrier is oxide ion. Further work is required to investigate that the sample has that interstitial ions or cation vacancy.

References

[1] Tatsumi Ishihara, Hideaki Matsuda, Yusaku Takita. 1994. Doped $LaGaO_3$ Perovskite Type Oxide as a New Oxide Ionic Conductor. *J.Am. Chem. Soc*. 116. 3801–3803.

[2] Takao Esaka, Tetsuo Mina-ai, Hiroyasu Iwahara. 1992. Oxide Ion Conduction in the Solid Solution Based on the Scheelite-type Oxide $PbWO_4$. *Solid State Ionics*. 57: 319–325.

[3] Takao Esaka, Ryouchi Tachibana, Shigeomi Takai. 1996. Oxide Ion Conduction in the Sm-substituted $PbWO_4$ Phases. *Solid State Ionics*. 92: 129–133.

[4] Takao Esaka, S. S Che Abdullah. 2010. Oxide Ion Conduction in the Perovskite-type $LaYO_3$ doped with ZrO_2. *Electrochemistry*. 78(11): 907–911.

[5] Stephen, J. Skinner. 2002. $CeTaO_{4+\delta}$ ($0.06 \leq \delta \leq 0.17$) as an Interstitial Oxide Ion Conductor. *Solid State Ionics*. 154–155: 325–329.

[6] C. Punchmark, S. Jiansirisomboon, G. Rujijanagul, T. Tunkasiri. 2004. Effect of Sintering Temperatures on Phase Transition of Lead Zirconate Ceramics. *Current Applied Physics*. 4: 179–181.

[7] Hiroshi Okamoto, Go Kawamura, Tetsuichi Kudo. 1983. Interpretation of the Electromotive Forces of Solid Electrolyte Concentration Cells During Carbon Monoxide Oxidation on Platinum. *Journal of Catalysis*. 82: 322–331.