

Effect of Metal Chloride Pre-Cursor on the Structure of Yb-Doped Ba(Ce, Zr)O₃ Ceramics Electrolyte: A Comparative Study with Different Metal Salts

(Kesan Bahan Pelopor Logam Klorida ke atas Struktur Yb Terdop Ba(Ce, Zr)O₃ Elektrolit Seramik: Suatu Kajian Perbandingan antara Garam Logam yang Berbeza)

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ABSTRACT

This paper discusses the effect of a metal chloride pre-cursor on the phase formation of Yb-doped Ba(Ce, Zr)O₃ solid electrolyte derived from a sol-gel method via acetate and chloride salts. The use of metal chloride as a pre-cursor showed the increased in thermal decomposition temperature ($T_{td} \approx 1360^\circ\text{C}$) compared to the metal nitrate pre-cursor ($T_{td} \approx 1280^\circ\text{C}$) and (b) leading to the formation of impurity phases. At calcination temperature of 1500°C , the sample prepared from metal chloride did not form a single-phase of Ba(Ce, Zr)O₃. Impurity phases of BaCl₂, BaCO₃ and (Ce, Zr)O₂ were detected in the sample as proven by XRD result. A high purity compound at relatively lower temperature ($T=1400^\circ\text{C}$) was only obtained for the sample that prepared from metal nitrate compared to acetate and chloride ($T>1500^\circ\text{C}$) and carbonate and oxide ($T=1500^\circ\text{C}$) pre-cursors.

Keywords: Ceramics; perovskites; thermal properties; X-ray technique

ABSTRAK

Kertas ini membincangkan kesan bahan pelopor logam klorida ke atas fasa pembentukan Yb terdop Ba(Ce, Zr)O₃ elektrolit pepejal yang disediakan secara kaedah sol-gel menggunakan garam berasaskan asetat dan klorida. Penggunaan logam klorida sebagai bahan pelopor menunjukkan peningkatan suhu penguraian terma ($T_{td} \approx 1360^\circ\text{C}$) berbanding dengan logam nitrat sebagai bahan pelopor ($T_{td} \approx 1280^\circ\text{C}$) dan menjana ke arah pembentukan fasa bendasing. Pada suhu pengkalsinan 1500°C , sampel yang disediakan daripada logam klorida tidak membentuk fasa tunggal Ba(Ce, Zr)O₃. Fasa bendasing seperti BaCl₂, BaCO₃ dan (Ce, Zr)O₂ telah dikesan di dalam sampel seperti disahkan oleh keputusan sinar-X. Sebatian yang berketulenan tinggi diperolehi pada suhu pengkalsinan yang secara relatifnya rendah ($T=1400^\circ\text{C}$) adalah sampel yang disediakan daripada bahan pelopor berasaskan logam nitrat dibandingkan dengan bahan pelopor berasaskan asetat dan klorida ($T>1500^\circ\text{C}$) dan karbonat dan oksida ($T=1500^\circ\text{C}$).

Kata kunci: Ciri terma; perovskite; seramik; teknik pembelauan sinar-X

INTRODUCTION

Studies on solid electrolyte based on cerate-zirconate ceramics that combine the high conductivity of cerates and the high chemical stability of zirconates have been widely reported in literature (Azad & Irvine 2007; Shimada et al. 2004; Zhang et al. 2008). The compound was prepared by various physical and chemical methods to substitute zirconium at cerium-sites or vice-versa to form cation B⁴⁺ in perovskite ceramics ABO₃. We noticed that generally two types of metal inorganic salts have been used by many researchers in synthesizing the modification of cation B structure. The first type, carbonate and oxide precursors was used in the solid-state reaction (SSR) method (Azad & Irvine 2007; Ricote et al. 2009; Shimada et al. 2004) while the second type, nitrate precursors, was used in the wet chemical methods (WCMS) (Azimova & McIntosh 2009; Zhang et al. 2008; Zhong 2007). In this work, we used the SSR, sol-gel and Pechini methods to prepare a solid electrolyte of

Ba(Ce_{0.8}Zr_{0.2})_{0.95}Yb_{0.05}O_{2.975} using various inorganic salts. The effect of metal inorganic salts on the structure of Yb doped Ba(Ce,Zr)O₃ has been investigated and discussed.

EXPERIMENTAL DETAILS

Synthesis of the powders was carried out by the SSR method using precursors based on carbonate and oxides, sol-gel method via acetate and chloride route and Pechini method using metal nitrate salt as reported in our previous works (Osman et al. 2010, 2009). Table 1 summarizes the denomination of samples with different metal inorganic salts. The compound was characterized by a thermogravimetric analysis (TGA, model SDT-Q600), a Fourier transform infrared spectroscopy (FTIR, Thermo Electron Corporation - Nicolet 380) and X-ray diffraction (XRD, Siemens D5000, Cu-K_α radiation $\lambda=1.5418 \text{ \AA}$) from 20 to 80°.

TABLE 1. Summary of the samples with different type of metal inorganic salt and method of sample preparation

Sample preparation method	Types of precursor	Denomination
Solid state reaction (SSR)	Carbonate and oxide	BCZYb-1
Sol-gel (SG)	Acetate and chloride	BCZYb-2
Pechini (PM)	Nitrate	BCZYb-3

RESULTS AND DISCUSSION

THERMOGRAVIMETRIC ANALYSIS (TGA)

Figure 1 shows the thermal decomposition of the BCZYb-1 powder (manually grounded at room temperature), dried powders of BCZYb-2 (pretreated at 550°C) and BCZYb-3 powder (dried at 350°C). There are three stages of weight loss in the TG signal for all the samples. The weight loss in stage A is mainly due to the loss of absorbed moisture and low boiling organic species. Weight loss in stage B is attributed to the vaporization of high boiling organic residues. Weight loss in stage C is due to the liberation of CO and CO₂ gasses. Clearly seen, thermal decomposition temperature (T_{td}) for BCZYb-3 ($T_{td} \approx 1280^\circ\text{C}$) is lower than BCZYb-1 ($T_{td} \approx 1340^\circ\text{C}$) and BCZYb-2 ($T_{td} \approx 1360^\circ\text{C}$). It shows that the acetate and chloride-based precursors need a high temperature for complete decomposition of intermediate compounds to yield an oxide material.

Generally, metal carbonate, oxide, acetate and chloride salts require higher T_{td} than metal nitrate salt. For example, in our previous work with BaCe_{0.95}Yb_{0.05}O_{2.975} (Toop et al. 2009), it was found that the T_{td} for carbonate-based was higher than acetate-based and the T_{td} for acetate-based is higher than that of nitrate-based. Therefore, the higher T_{td}

in sample BCZYb-2 than BCZYb-1 could be due to the used of chloride precursor. In the reaction, the zirconyl chloride (the source of Zr ions) decomposed into Zr⁴⁺ and Cl⁻. The anion of Cl reacted with Ba²⁺ (from barium acetate) to form BaCl₂ in the sample. The existence of this phase may affect the formation of the secondary phases in the BCZYb-2 sample.

X-RAY DIFFRACTOGRAM (XRD)

X-ray diffraction patterns of the BCZYb-1, BCZYb-2 and BCZYb-3 samples are shown in Figure 2. The XRD spectrum shows that a single-phase perovskite structure was obtained only for BCZYb-1 (calcined at 1500°C) and BCZYb-3 (calcined at 1400°C) (Figure 2(a) and 2(b)). The peaks slightly shift to higher 2θ values compared to those of the BaCeO₃ (JCPDS # 22-0074). It was attributed to a slight change in the unit cell volume of BaCeO₃ as zirconium element was introduced into the compound and also due to the partial substitution of Yb³⁺ ($R^{IV}=0.868 \text{ \AA}$) into Ce and Zr ions. However, four additional peaks at $\approx 28.6^\circ$, 33.1° , 47.6° and 56.4° that correspond to the fluorite structure of (Ce,Zr)O₂ were present in the BCZYb-2 sample (calcined at 1500°C for 5 h). Even after the sample was calcined at a longer time (10 h), the intensity of the four

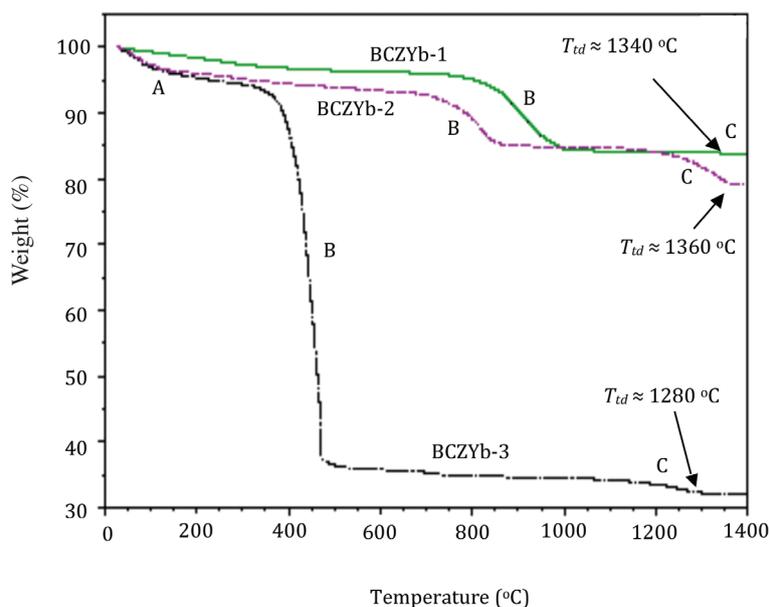


FIGURE 1. Comparative TG signal of the powders BCZYb-1, BCZYb-2 and BCZYb-3

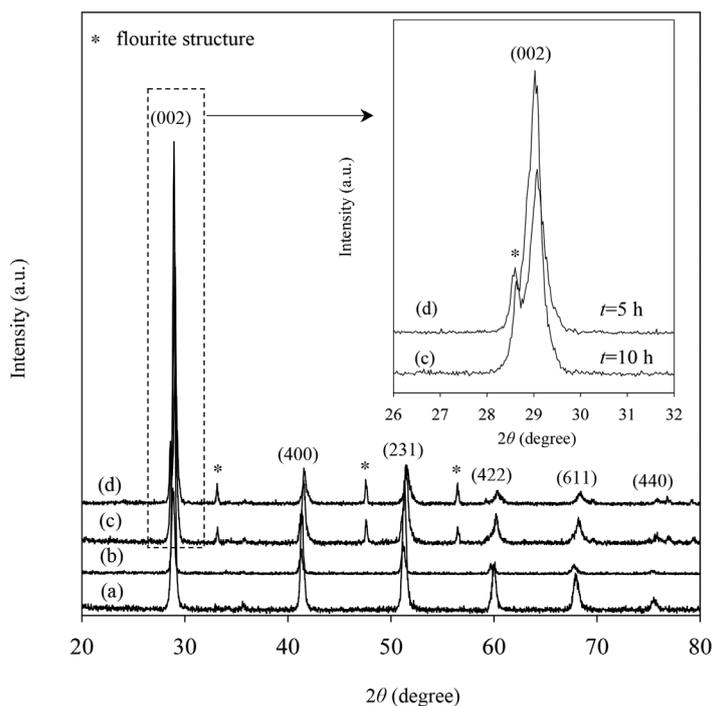


FIGURE 2. XRD patterns for the (a) BCZYb-1 and (b) BCZYb-3 samples, (c) and (d) are for the BCZYb-2 sample at different calcination time

peaks did not change, indicating that the prepared sample was not a single-phase of BaCeO_3 (Figure 2(c) and 2(d)).

Further work on the BCZYb-2 sample with higher concentrations of zirconium ($x=0.25, 0.30, 0.35$ and 0.40)

also showed that the intensity of the secondary phases that match the $(\text{Ce,Zr})\text{O}_2$ and BaCO_3 became more intense as the Zr content increased as shown in Figure 3. Small peaks of BaCl_2 could also be observed in the XRD spectrum and

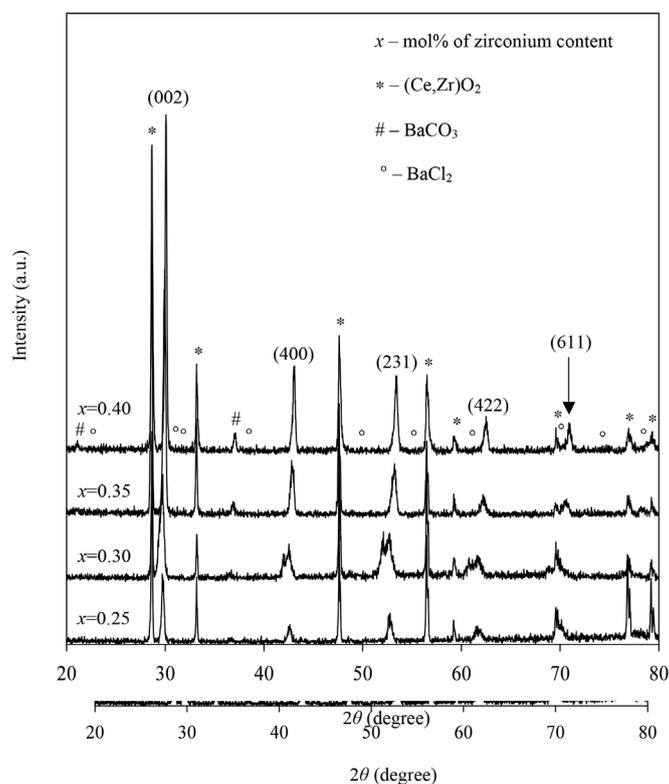


FIGURE 3. XRD patterns of the BCZYb-2 sample at different Zr-content

the presence of Cl element was also proven by EDX analysis as previously reported (Osman et al. 2006). BaCl_2 is a very stable compound and it will decompose at temperature of 1560°C (Material Safety Data Sheet, CAS no 10361-37-2). Therefore, the use of metal chloride salt as a precursor should be avoided in the sample preparation. Even when it was used in small amounts, it was difficult to produce a single-phase of cerate-zirconate compound.

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The absence of a carbonate residue in the BCZYb-3 sample annealed at 1400°C was proven by FTIR as shown in Figure 4(a). For comparison, we also included the FTIR spectrum for the dried sample (at 550°C) and calcined sample (at 1100°C). The existence of absorption bands at 1450 and 850 cm^{-1} in Figure 4(b) and 4(c), respectively, indicates that the residue of the carbonate species still remains in the samples. A small twin peak at around 2350 cm^{-1} is an artifact caused by the spectrometer (Nafisah 2010). It was found that the purity of Yb-doped $\text{Ba}(\text{Ce}, \text{Zr})\text{O}_3$ strongly depends on the types of metal salts precursor.

CONCLUSION

The use of metal chloride is not recommended in the synthesizing of $\text{Ba}(\text{Ce}, \text{Zr})\text{O}_3$. It tends to form BaCl_2 during the chemical reaction that leads to the formation of others impurity such as BaCO_3 and $(\text{Ce}, \text{Zr})\text{O}_2$. Once BaCl_2 formed, high temperature is needed to decompose this compound. Therefore, the metal nitrate precursor seems to exhibit an optimum condition for sample preparation than others. It has better decomposition character and phase formation than acetate and chloride or carbonate and oxide metal salts. The results from XRD and FTIR confirmed that there were no traces of organic species such as BaCO_3 in the BCZYb-3 sample.

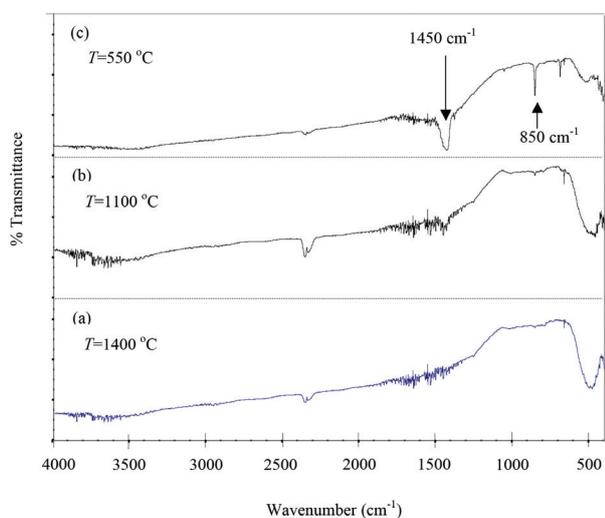


FIGURE 4. FTIR spectra of BCZYb-3 for (a) precalcined powder at 550°C and calcined powders (b) at 1100°C and (c) at 1400°C

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REFERENCES

- Azad, A.K. & Irvine, J.T.S. 2007. Synthesis, chemical stability and proton conductivity of the perovskites $\text{Ba}(\text{Ce}, \text{Zr})_{1-x}\text{Sc}_x\text{O}_{3-\delta}$. *Solid State Ionics* 178: 635-640.
- Azimova, M.A. & McIntosh, S. 2009. Transport properties and stability of cobalt doped proton conducting oxides. *Solid State Ionics* 180: 160-167.
- Nafisah Osman. 2010. Kajian pencirian bahan elektrolit pepejal berasaskan $\text{Ba}(\text{Ce}, \text{Zr})\text{O}_3$ yang didopkan dengan Yb^{3+} sebagai konduktor proton pada suhu pertengahan, ($400 \leq T \text{ } ^\circ\text{C} \leq 750$), Tesis Ijazah Doktor Falsafah. Universiti Kebangsaan Malaysia (unpublished).
- Osman, N., Jani, A.M. & Talib, I.A. 2006. Synthesis of Yb-doped $\text{Ba}(\text{Ce}, \text{Zr})\text{O}_3$ ceramic powders by sol-gel method. *Ionics* 12: 379-384.
- Osman, N., Talib, I.A. & Hamid, H.A. 2009. Effect of stoichiometric composition and different metal salts on the phase formation of cerate-zirconate ceramics. *Sains Malaysiana* 38(3): 401-405.
- Osman, N., Talib, I.A. & Hamid, H.A. 2009. Preparation and characterization of Yb-doped $\text{Ba}(\text{Ce}, \text{Zr})\text{O}_3$ nanopowders with high sinterability. *Ionics* 16: 561-569.
- Ricote, S., Bonanos, N., Marco de Lucas, M.C. & Caboche, G. 2009. Structural and conductivity study of the proton conductor $\text{BaCe}_{(0.9-x)}\text{Zr}_x\text{Y}_{0.1}\text{O}_{3-\delta}$. *Journal of Power Sources* 193: 189-193.
- Shimada, T., Wen, C., Taniguchi, N., Otomo, J. & Takahashi, H. 2004. The high temperature proton conductor $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{In}_{0.2}\text{O}_{3-\alpha}$. *Journal of Power Sources* 131: 289-292.
- Toop, M.R.M., Hamid, H.A., Osman, N., Hassan, Z.R. & Talib, I.A. 2009. The decomposition of $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ prepared by different preparation routes. *Solid State Science and Technology* 17(2): 89-95.
- Zhang, J., Wen, Z., Huang, S., Wu, J., Han, J. & Xu, X. 2008. High-temperature proton conductor $\text{Sr}(\text{Ce}_{0.6}\text{Zr}_{0.4})_{0.9}\text{Y}_{0.1}\text{O}_{3-\alpha}$. *Ceramics International* 34: 1273-1278.
- Zhong, Z. 2007. Stability and conductivity study of the $\text{BaCe}_{0.9-x}\text{Zr}_x\text{Y}_{0.1}\text{O}_{2.95}$ systems. *Solid State Ionics* 178: 213-220.

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