Synthesis of Y^{3+} Doped $BaZrO_3$ Nanopowders via A Pechini Method with Different Molar Ratios Citric Acid

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Abstract: Sample of $BaZr_{0.85}Zn_{0.05}Y_{0.1}O_{2.95}$ (BZY10) was prepared by a Pechini method with different molar ratios of citric acid (CA) to metal ions (M^+) using metal nitrate-salts. Metal organic complexes were obtained from the polymerization process between metal nitrate, citric acid and ethylene glycol. After heated at 120 °C, a clear viscous solution or polymer resin containing metal in solid solution was formed. The resin was annealed at 3 different temperatures to remove the organic materials and produce the desired oxide powder. After calcined at 1000°C, all the samples almost formed perovskite-like phase with cubic structure. The present of small amount carbonate traces was proved by FTIR and XRD. The primary particles are spherical in shape and here diameter in the range 20-100 nm. However, agglomerates seem to dominate a bulk sample.

Key words: Nanopowders · Complexing Agent · $BaZrO_3$ · Pechini Method

INTRODUCTION

Protons conducting solid electrolytes have got significant attention due to their wide range of technological applications, especially in solid state ionics devices [1]. Alkaline-earth zirconate-based conductors such as $BaZrO_3$ show enhance chemical stability and high proton conductivity compare to cerate-based conductors [2-3]. Recently, in terms of sample preparation, the compounds have been widely prepared by wet chemical methods (WCMs) such as Pechini method in order to overcome the drawback of solid state reaction (SSR) method [4]. In the Pechini process, α-hydrocarboxylic acid such as CA was used to form metal complexes. These complexes will form metal organics polymer network after heated with polyhydroxyl alcohol such as EG, prior the formation of intermediate resin. The process can produce a single-phase ceramics powder a lower temperature than that used in SSR [5]. Furthermore, the properties of the synthesized product for electrode material were also reported affected by different amounts of CA or/and EG to M^+ [6]. This work was carried out to study the influence of different CA^+ to M^+ on the phase formation and morphology for doped $BaZrO_3$.

Experimental: $Ba(NO_3)_2$ (RandM Chemicals, 99.0%), $Y(NO_3)_3 \cdot 6H_2O$ (Aldrich, 99.9%), $Zn(NO_3)_2 \cdot 6H_2O$ (Fluka, 99.0%), and $ZrO(NO_3)_2 \cdot xH_2O$ (Acros Organics, 99.5%), $x = 4.83$, were used as starting materials. Three different molar ratios of citric acid (CA) to ethylene glycol (EG) and metal cations (M^+) was prepared, which is 3:1:1 (denoted as S1), 2:1:1 (S2) and 1:1:1 (S3) were prepared. A detail procedure in obtaining sol and gel was reported in Osman *et al.* [7]. The gel was heated at temperature of 120 - 260°C until it became a dark brown viscous gel. The viscous gel was dried at 300°C overnight and then further heated at T=500°C for 10h and 1100°C for 30h. The determination of IR vibration bands for carbonate species in S1, S2, and S3 was carried out using a Fourier Transform Infra Red (FTIR) analyzer model Nicolet 380 (Thermo Electron Corporation). Phase identification of the calcined powder was determined using a X-ray diffractometer (XRD) Bruker D8 Advanced (Cu-Kα; $\lambda = 1.5418$ Å from 20° to 80° in steps of 0.025°. Morphology of the calcined powder was observed using a field emission scanning electron microscope (FESEM) model Supra 55 VP.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra for S1, S2 and S3 after the powders were calcined at 1100°C for 30 h. A broad absorption band around 3670 cm^{-1} is due the absorbed water or hydroxyl group in alcohol. A twin peaks at 2350 cm^{-1} is attributed to the artefact from

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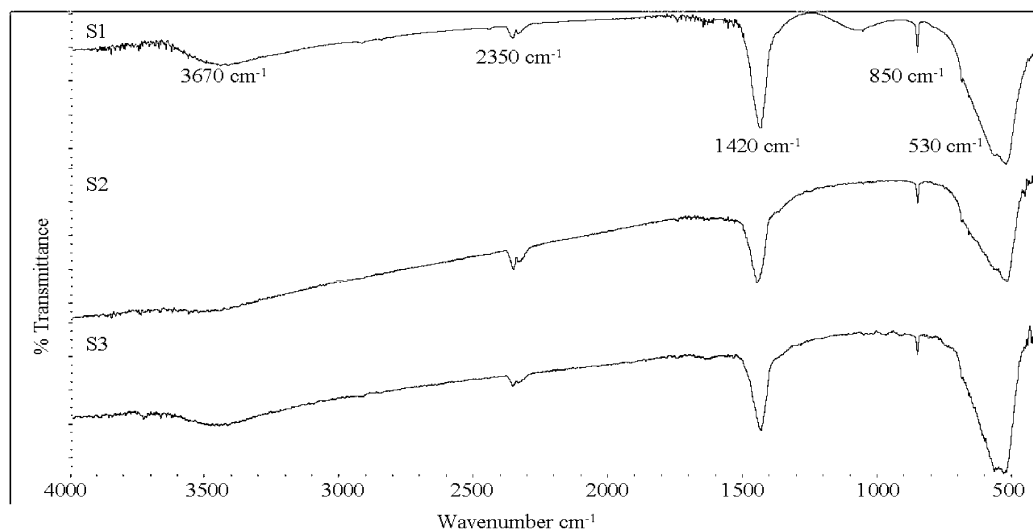
Fig. 1: FTIR spectra of BZY10 powders prepared from different molar ratios of CA to M^+ after calcined at 1100°C
for 30 h

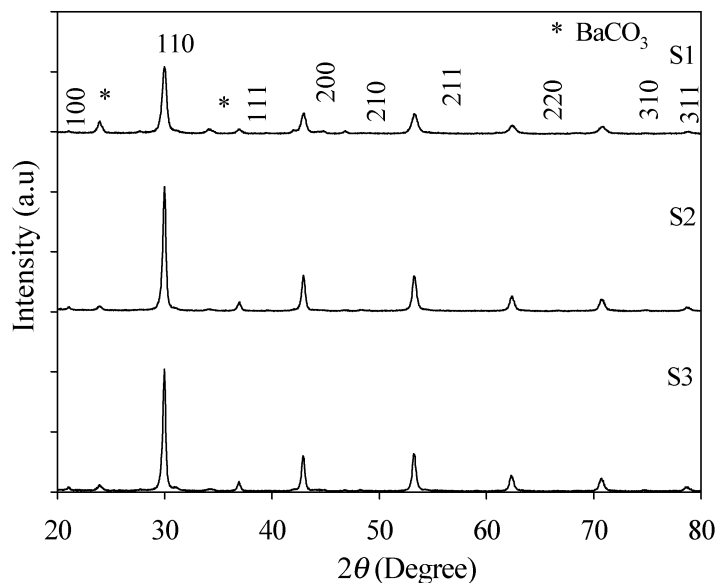
Fig. 2: XRD spectra of BZY10 powders prepared from different molar ratios of CA to M^+ after calcined at 1100°C
for 30 h

instrument [5]. The of absorption bands at 1420 cm^{-1} and 850 cm^{-1} indicate that a secondary phase of carbonate species present as impurity in the samples. The presence of carbonates residue might be due to the incomplete combustion of the excessive organic matters during heat treatment. The large vibration band around 530 cm^{-1} is due to Zr-O vibration in the perovskite structure.

Figure 2 shows XRD spectra for S1, S2 and S3 after the samples were calcined at 1100°C for 30 h. All the peaks are matched to $BaZrO_3$ (JCPDS card no. 06-0399) except

for the small peaks at 2è ? 23.9 and 34.1. These two peaks are associated to the remaining carbonate species as also prove by FTIR results. Figure 2 shows the peak due to perovskite phase is getting intense and sharper as the molar ratio of citric acid decreases, indicating that an increases in the degree of long-range order in the perovskite lattice.

Figure 3 shows the FESEM micrographs for the S1, S2 and S3 samples. The particles are spherical in shape and have sizes in range 20-100 nm whereas diameters for
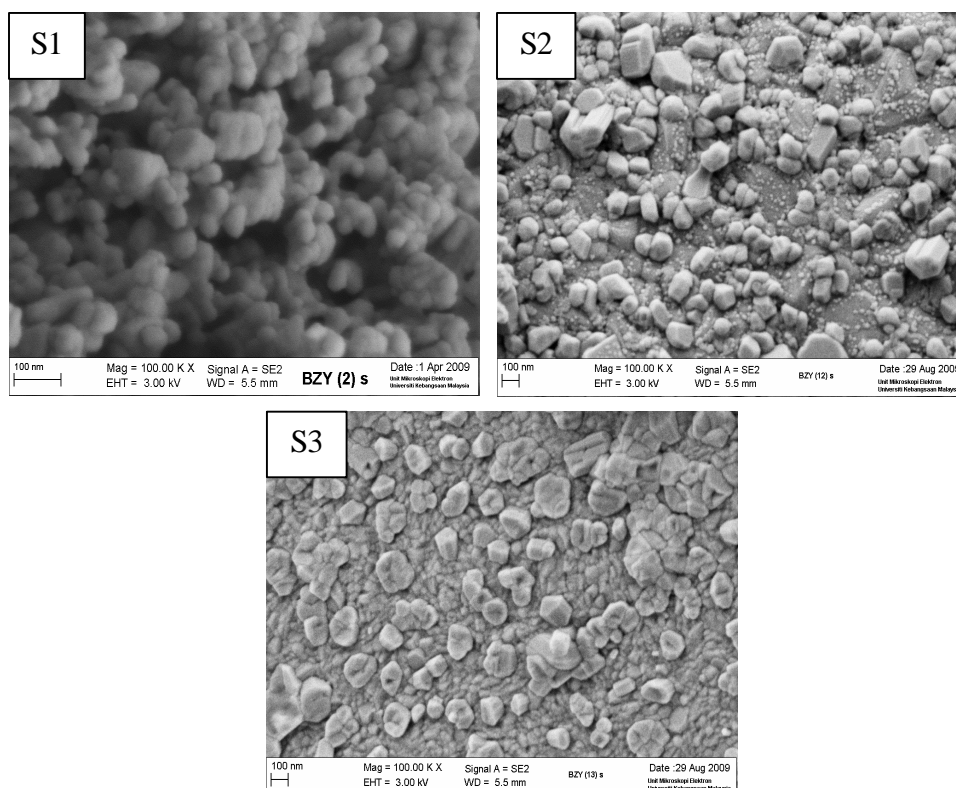
Fig. 3: FESEM images of BZY10 powders prepared from different molar ratios of CA to M^+ after calcined at 1100°C for 30 h

the agglomerates are 100-300 nm. For S1, its particles are smaller than S2 and S3 but have more agglomerates. It can be explained that the higher molar ratio of CA to M^+, the particles become smaller and tend to form large and hard agglomerates due to the COOH (carbonyl acid group) reacted with hydroxyl from ethylene glycol [5].

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