

EFFECT OF SURFACTANTS ON THE THERMAL DECOMPOSITION OF $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ CERAMICS POWDER

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Abstract- Ceramics powder of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) was prepared by a sol-gel method from the stoichiometric mixtures of nitrate salt as precursor. The LLZ resin was heated at temperature of 325 °C for 2 hours and at various calcination temperatures between 600-900 °C for 10 hours. The powders obtained were characterized by Thermal Gravimetry Analysis (TGA) and Fourier Transform Infrared (FTIR) to verify the thermal decomposition of the powders and the presence of carbonate group in the compound. TGA results indicate that all the samples were almost completely decomposed at ~800 °C except for sample with CTAB surfactant that showed the lowest thermal decomposition temperature at 733 °C. FTIR analysis showed that the intensity of carbonate group were decreased due to the increasing of temperature. It was found that the different surfactants used lead to the different characteristics of the LLZ powder.

Keywords – LLZ ceramics powder, modified sol-gel method, surfactants, thermal decomposition

INTRODUCTION

Garnet-structure ceramic materials with zirconate based are promising candidate for development of solid electrolytes for batteries, gas sensors and solar cells due to their stability against molten lithium metal ion, moisture and air for several weeks and good ionic conductivity relative to other metal based polycrystalline structure [1,2]. Among the various kinds of solid electrolytes, garnet-structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) is a promising solid electrolyte due to its high lithium ion conductivity, good thermal and chemical stability against reactions with prospective electrode materials, environmental benignity, availability of the starting materials, low cost and ease of preparation and densification [3].

In order to use lower temperature, homogeneous phase distribution, small grain sizes, a low-cost of wet chemical methods (WCMs) is applied in this research. WCMs lead to higher inter-dispersion of metal ions and higher reactivity of the amorphous precursor, assuring enhanced purity of the final product together with better control of the powder morphology [4].

The thermal decomposition of ceramics material depends mainly on the way of combustion propagates of disintegration occurs. The role of surfactants acted as a fuel and the source of carbon, made the dry gel more porous and forced the combustion process to proceed quickly after it was added. Furthermore, the excess fuel might act as a space filling agent, which would leave empty spaces as fuel burns during the reaction. Increasing the fuel content would further cause more gas liberation, which helped to disintegrate to agglomerates into nano- particles and reduce their subsequent growth. The reverse micro emulsions offered a confined micro environment for the formation of nano-powders as a result inhibited their excess growth and agglomeration.

The sol-gel method with the additional of the cationic surfactants has been proven to be efficient method to lowering the thermal decomposition and low agglomeration to fabricate fine nano-powder. Besides the effect of the thermal decomposition, the additional of cationic surfactant with amphiphilic molecules into precursor solution could form the reverse micro emulsions in the sol. Here, we report the effects of surfactants on the formation and the thermal decomposition behavior of the ceramics powder.

MATERIALS AND METHOD

The compound of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ was synthesized by a conventional modified sol-gel method using metal nitrate salts as starting materials. The stoichiometric amounts of lithium nitrate, LiNO_3 (99%, ACROSS), lanthanum nitrate, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, ACROSS), and zirconium nitrate, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99%, ACROSS) was used as starting materials. The citric acid monohydrate, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (99% ACROSS) in powder form and ethylene glycol (99.96% ACROSS) in liquid form were used. Citric acid (CA) acted as complex agent in the sample preparation and ethylene glycol (EG) aided the polymerization process. For the variables, butan-1-ol, propan-2-ol (IPA), sodium didecylsulphate (SDS) and cetyltrimethylaminebromide (CTAB) were used as surface active agents. The molar ratio of CA and ethylene glycol to metal cation was fixed at 4:2:2.

The stoichiometric amounts of metal nitrate salts was dissolved in distilled water and continuously stirred by a magnetic stirrer to make a transparent nitrate solution and sample left over a night for homogenous and stabilization. Citric acid was added into the nitrate solution under continuous stirring. Then ethylene glycol was gradually added into the complex mixture and surfactants were added and left over for 24 hours. The ethylene glycol and surfactants was added drop by drop. The pH of the solution

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was maintained at a neutral pH value. The solution was continuously stirred for 2 hours after the pH neutralized. The resulting solution was heated at 120 °C and stirred continuously using a hot plate and a magnetic stirrer. During the process, most of the water-evaporate yielding a viscous clear solution of metal citrate complexes. The solution was heated at this temperature for 2 hours. The gel was dried on a hot-plate overnight at 325 °C and transform into black sponge-like. The sponge-like was continued heated in a furnace at temperature 500 °C as pre-calcination for 2 hours. Then the powder was further calcined at 700 °C, 800 °C and 900 °C for 12 hours to ensure all the organic compounds was eliminated. Heating rate of 10 °C min⁻¹ was used in all calcination process.

Thermogravimetric analysis (TGA) was carried out to the dried powder (T=325 °C) by a TA instrument model SDT Q600. Fifteen miligrams of dried powder was placed in a sample holder and heated from 25 to 1000 °C with a heating rate of 10 °C min⁻¹ under synthetic air (flow rate 100 ml min⁻¹). IR spectra were recorded with a FTIR Spectrophotometer (Nicolet 380) in the range 400 - 4000 cm⁻¹ to identify the IR active functional groups using the KBr pellet technique.

RESULTS AND DISCUSSION

Thermal Analysis

The TG curves of the dried powders prepared with different types of surfactants are shown in Figure 1. All samples exhibit almost similar pattern of LLZ TG profile with four stages of weight loss. In stage 1, the temperature ranging from 30 - 230 °C cause the reduction of weight loss about 5 - 9 % attributed to the decomposition of hydroxyl (OH) group from ethylene glycol and also related to the complete combustion of chelation process (with the losses of NO_x gaseous) [5].

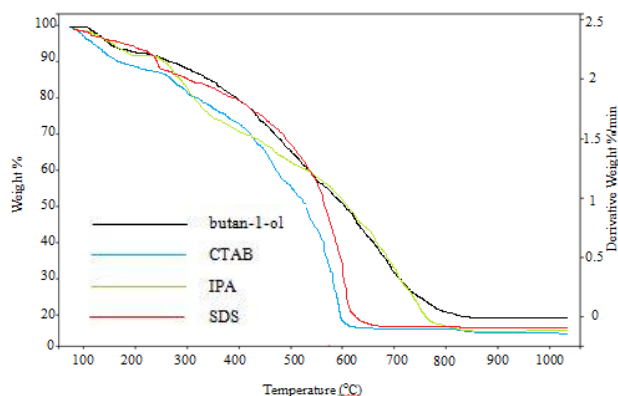


Figure 1. TG spectra for dried powders of LLZ with various surfactants

In stage 2 and stage 3, the temperature ranging from 230 - 780 °C shows major weight loss due to the exothermic reaction between chelating agent, surfactants and nitrate ions (with the released of NH₃, CO₂, CO and NO₂) [6,7]. Finally, at stage 4 with 5% of weight loss at temperature ranging from 560 - 830 °C resulted from the decomposition of trapped carbonaceous residue at the beginning of transformation to

form oxides. Table 1 shows the thermal decomposition data for sample with different surfactants. The sample with CTAB shows the lowest thermal decomposition compared to the others due to the large number of carbon chain present in the surfactant. The carbon chains acted as sources of fuel that helped the sample to be further decomposed [8]. This can be observed by descending order of carbon chain in types of surfactants, CTAB > SDS > butan-1-ol > IPA.

Table 1. Summarization of the thermal decomposition data for dried sample (at 325 °C)

Samples	Stages	Temperature ranged (°C)	Weight loss %
butan-1ol	1	130 - 230	~7
	2	230 - 410	~23
	3	410 - 770	~58
	4	770 - 830	~2
CTAB	1	30 - 150	~5
	2	150 - 300	~12
	3	300 - 560	~68
	4	560 - 700	~5
IPA	1	140 - 180	~6
	2	180 - 405	~11
	3	405 - 780	~55
	4	780 - 830	~3
SDS	1	30 - 150	~9
	2	150 - 300	~7
	3	300 - 595	~68
	4	595 - 760	~4

Infrared Spectra Analysis

Figure 2 shows FTIR spectra for LLZ sample at 325 °C. There are six stretching bands observed in the spectra which is 3160 cm⁻¹, 1705 cm⁻¹, 1603 cm⁻¹, 1384 cm⁻¹, 1190 cm⁻¹, and 639 cm⁻¹ that represent different functional group. Broad band at 3160 cm⁻¹ assign to OH group that presence due to the absorption of water in the sample. The band at 1603 cm⁻¹, 1384 cm⁻¹, and 1190 cm⁻¹ respectively for C=O stretch of ester which formed by polymerization of CA and EG [9], nitrate stretch from pre-cursor salt and remaining carbonate (CO₃²⁻) in dried sample. The band 639 cm⁻¹ could be assigned to metal oxide stretching mode from the chelation of CA and metallic ions.

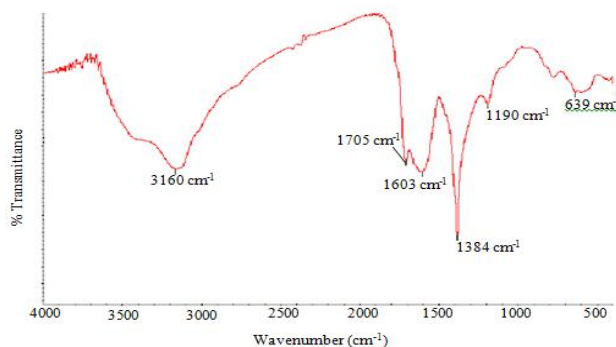


Figure 2. FTIR spectrum of LLZ powders after dried at 325 °C

The LLZ sample then calcinated at various temperatures from 350 °C to 900 °C and the FTIR spectra was shown in

Figure 3. There are several regions of spectroscopic interest involve C=O, C-OH, and metal oxygen bonding (M-O). At T=500 °C, the band at 1439 cm⁻¹ contibuted to COO⁻ stretching in monodentate metallic complex formed between carbonyl group and metallic ions and it still present in the spectra at T=900 °C which shows that the α- hydroxilic acid group of CA provide a strong chelating ability and can stabilized different metal ions simultaneously within one molecule or complex [10].

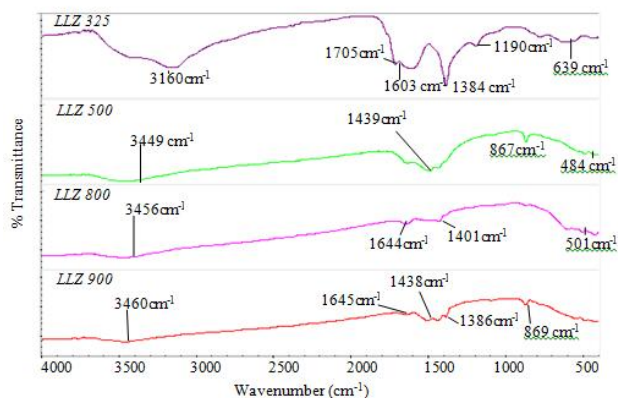


Figure 4. FTIR spectra of LLZ powders at various calcination temperatures

The FTIR pattern of sample LLZ with IPA was shown in Figure 4. Spectra at 850 - 1400 cm⁻¹ related to carboxylate stretch. At 1600 - 1750 cm⁻¹ assigned for C=O stretching, broad band at 3150 - 3500 cm⁻¹ for O-H group due to absorption of moisture in the powder and from the IPA itself, and at 400 - 170 cm⁻¹ for M-O stretching from chelation of CA and metallic ions. It can be concluded that by the addition of surfactant, the intensity peak of CO₃²⁻ ion decrease and disappear in the spectra as the temperature increases. This similar phenomenon also happens to broad band spectra of OH group. While for M-O stretching band, as temperature increase, the intensity increase due to the enrichment of formation LLZ compound in the sample.

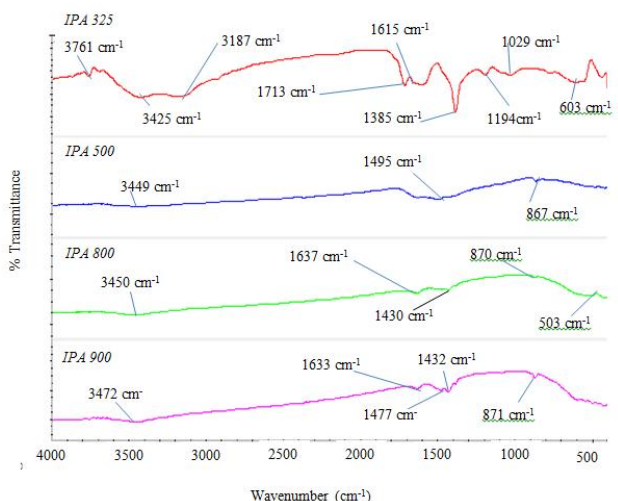


Figure 5. FTIR spectra of LLZ powders with propan-2-ol (IPA) at various calcination temperatures

For LLZ sample with butan-1-ol, C=O stretching mode appear at 1604 cm⁻¹, 1714 cm⁻¹, COO⁻ at 1192 cm⁻¹, 1386 cm⁻¹, respectively and O-H stretch from 2700 - 3500 cm⁻¹ as shown in Figure 5. M-O stretching band can be assigned at 637 cm⁻¹ and below from the chelation of CA and metallic ions. As temperature increase, the intensity of stretching band of carboxylate ion decreases but for metal oxide band increases. This is due to the decomposition of compound and formation of LLZ compound respectively. While for O-H stretching band also decreases which shows that water are being removed from the sample.

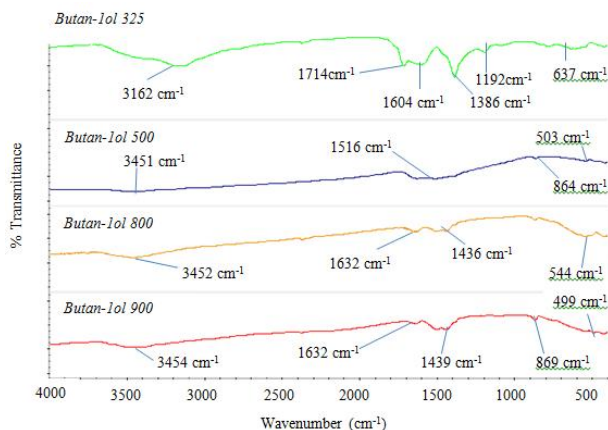


Figure 3. FTIR spectra of LLZ powders with butan-1-ol at various calcination temperatures

When LLZ compound was treated with SDS, strong adsorption bands appear at 1384 cm⁻¹ and can be assigned to carbonate ions in the dried powder. At higher calcination temperature, small absorption bands in region of 1619 - 1638 cm⁻¹ attributed to C=O stretching mode of ester. The IR bands at 3422, 3449, 3451, 3407 cm⁻¹ shows the presence of O-H group. The broad band for O-H group diminished as the temperature increase. Small peaks at 490 - 550 cm⁻¹ are mainly due to the formation of metal oxides. The FTIR spectra are shown in Figure 6.

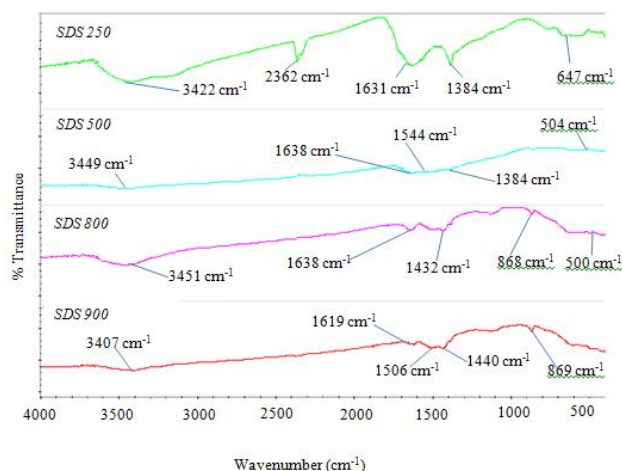


Figure 6. FTIR spectra of LLZ powders with sodium didodecylsulphate (SDS) at various calcination temperatures

Figure 7 shows the FTIR spectra pattern for LLZ with cetyltrimethylammonium bromide (CTAB). At the $T=325\text{ }^{\circ}\text{C}$, a small sharp peak at 1385 cm^{-1} corresponds to carbonate ions group. The IR adsorption bands at 1493 , 1441 , 1439 cm^{-1} suggested to be the methyl ($-\text{CH}_3$) group from the polymeric network of CTAB structure. Higher calcinations temperature revealed $\text{C}=\text{O}$ stretching mode at 1629 , 1658 cm^{-1} for ester that formed from CA and EG polymerization.

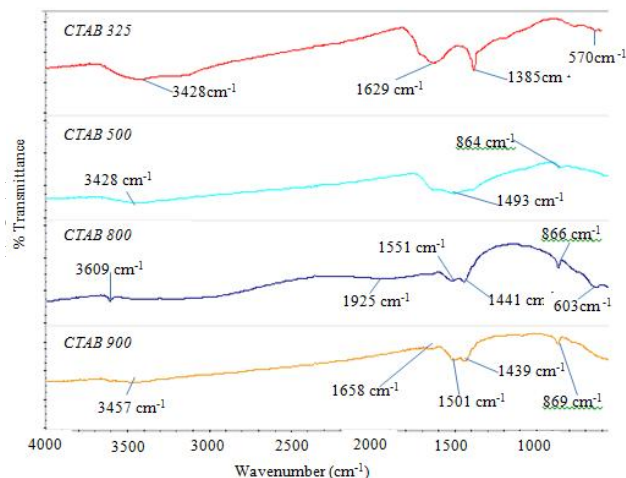


Figure 7. FTIR spectra of LLZ powders with cetyltrimethylammonium bromide (CTAB) at various calcination temperatures

CONCLUSIONS

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramics powder was successfully prepared by a sol-gel method using butan-1-ol, IPA, CTAB and SDS as the surfactants. TGA studies showed that the lower thermal decomposition temperature ($T_{td} = 733^{\circ}\text{C}$) was obtained for the sample added with CTAB with heating rate $10\text{ }^{\circ}\text{C min}^{-1}$. All the samples added with surfactant showed four stages of weight loss. First stage is loss of moisture and impurities and the second stage is vaporization of high boiling organics compound. At the temperature $> 900\text{ }^{\circ}\text{C}$ the intensity of the medium stretching band around $1300 - 1400\text{ cm}^{-1}$ almost disappeared in IR spectrum signifying that the absence of carbonate in the compound.

The metal oxides peak at $490 - 550\text{ cm}^{-1}$ is gradually enhanced as calcination temperature increased. Thus, the ceramics based on garnet types oxides, calcination temperature played an important rule to ensure the absence of carbonate and formation of garnet structure in the final product.

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