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Homogeneity of Lithium Metasilicate-Copper Oxide Glass-Ceramics by Weibull Modulus

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Abstract

The work idea is finding out how the homogeneity of dielectric strength property in lithium metasilicate glass-ceramic with addition weight percentage increasing of CuO. It prepared four specimens, one without CuO addition lithium metasilicate glass-ceramic LSGC and consists of Li_2O-SiO_2 binary system glass batch with weight percentages 45 wt% Li_2O and 55 wt% SiO_2. It added to the binary system CuO with different weight percentages to prepare the rest three specimens in front of the Li_2O weight percentage decreasing as 1 wt% LC1S, 2 wt% LC2S, and 3 wt% LC3S. The glass batches for four specimens were mixed and used melting-quenching method at temperature of 1195^{O}C for soaking time 2 hrs. It used platinum crucible (90 Pt-10 Rh) and immediately cooled in the cold water of temperature at 3^{O}C. This process was repeated twice for all specimens and the produced frit was milled by agate mortar. Addition of P_2O_5 and TiO_2 as nucleating agents with weight percentage 3 wt% P_2O_5 and 1 wt% TiO_2 and prepared compact discs with dimensions 18 diameter × 2.58 thickness mm by the used biaxial hydraulic press with 5 tons for 30 s under pressure. The heat treatment was done for all glass batch compact discs of temperature at 950^{O}C for 6 hrs as soaking time and breakdown voltage test was done executed 10 different spots in each specimen and Weibull modulus was used to know the homogeneity of dielectric strength property and coincided with Field Emission Scanning Electron Microscopes (FE-SEM) images. It got a good match between Weibull modulus results and FESEM images which indicating that Weibull modulus is the active tool that can be used for knowing the homogeneity of any property. The high average dielectric strength is 9.116 kV/mm for LC1S while the lower average dielectric strength is 7.101 kV/mm for LSGC and this back to more homogeneity and fewer defects in LC1S than LSGC.

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1. Introduction

Glass-ceramics are consisting of crystalline phases within the amorphous phase representing the glass by controlling the thermal treatment process [1]. Binary Li_2O-SiO_2 system is glass batch for producing lithium metasilicate glass-ceramic with main crystalline phase Li_2SiO_3. The composition percentage 43.7 mol% Li_2O in the glass the lithium metasilicate Li_2SiO_3 is the main crystalline phase with orthorhombic structure which crystallizing at 480^{O}C after 24 hr. It is important characteristic the high electrical resistivity 3×10^9 Ω.cm, low loss factor equal to 0.002 (1 MHz at 25^{O}C), transparent material, good mechanical strength, good fracture toughness, and moderate to high thermal expansion coefficient [2]. This material is attractive for electronic devices, nuclear fusion reactors, sealing joints for electronic and electrical substrates, and batteries [3]. The addition of CuO into a glass is important from a technology viewpoint because it shows semiconducting properties and other potential properties [4]. The atomic number and weight of the copper metal are 29 and 63.546 respectively. It is a transition metal and used as a dopant material for coloring glass with electron configuration $3d^{10}$. $4s^1$and has two different oxidation numbers monovalent Cu^+ and divalent Cu^{2+} electrons. The positions of Cu^+ and Cu^{2+} ions are octahedrally coordinate in the glass network and serve as a modifier in the silicate glasses. The Cu^{2+} ion absorbs the light in the visible region and the glass becomes colouring with blue and green while the Cu^+ does not absorbs the light and colouring the glass in $3d^{10}$. $4s^1$[5]. Introduction the CuO in a glass is changing from dielectric properties of the glass and increasing from carriers in the glass structure. The divalent ion Cu^{2+} lays in s orbital gives the coloring glass and electrical conducive for the glass [6].

Dielectric strength (dielectric breakdown voltage) is a dielectric failure of electrically insulating material by exerting potential difference when a material is located between two electrodes [7]. The dielectric strength of glass-ceramic depends on the frequency, the rate of voltage increasing, the glass-ceramic composition, and test conditions. The dielectric strength is increasing with decreasing the glass-ceramic sample thickness and the most type of breakdown voltage occurred is heat breakdown which increases the temperature and electrical conductivity in the material. This type is considering the main breakdown mechanism that happens in most materials under testing [8].

2. Theoretical Part

The dielectric strength is calculating according to the formula below in unit kV/mm [7]:

$$\sigma_{V\,max} = \frac{V_b}{t} \quad \text{.................} (1)$$

Where σ_{Vmax} is maximum dielectric strength in kV/mm, V_b is voltage breakdown reading from the test in kV and t is the thickness of sample in mm. The Weibull modulus is a parameter without units of the Weibull distribution using to attributive the difference of measured strength for brittle materials. The maximum measured stress in a brittle material to withstand before failure may vary from one material to another even under identical test conditions [9]. The survival probability Ps at any stress as [10]:

$$\mathbf{1} - Ps = \exp\left[-\left(\frac{\sigma_{V\,max}}{\sigma_o}\right)^w\right] \quad \text{..................} (2)$$

Where survival probability Ps is 0.37(1/e) so either $\sigma_o=\sigma_{oE}$ electrical strength or $\sigma_o=\sigma_{oM}$ mechanical strength, σ_{max} is the maximum strength which represents maximum mechanical or electrical strength, σ_o is characteristic strength. It must take a natural logarithm for both sides of equation (2) to calculating the Weibull modulus [10]:

$$\ln\left(-\ln\left|\frac{\mathbf{1}}{PS}\right|\right) = w \ln \sigma_{V\,max} - w \ln \sigma_o \quad \text{....................} (3)$$

Plot ln(-ln|1/Ps|) versus $\ln\sigma_{V\,max}$ will get a straight line of slope w. The higher Weibull modulus is relating to the lower variability of strength [10].

3. Experimental Procedure

3.1. Glass batch preparation

The weight of the glass batch was 18 g consist of a binary Li_2O-SiO_2 system, Li_2O of 8.1 g and SiO_2 of 9.9 g according to weight percentages 45 wt% Li_2O and 55 wt% SiO_2. The carbonate and oxides used for glass batch preparation were Li_2CO_3 BDH Chemicals Ltd, England, quality 99.5%, SiO_2 Thomas Baker Chemicals Ltd, India, quality 99%, and CuO BDH Chemicals Ltd, England, quality 99.5%. The oxides used as nucleating agents were P_2O_5 Fluka AG, Buchs SG, quality 99% and TiO_2 BDH Chemicals Ltd, England, quality 98%. The weight percentages of prepared glass- ceramics are showing in the table (1).

Table 1: The ingredients of prepared glass-ceramics with weight percentages.

Glass-ceramic	Li_2O	SiO_2	CuO	P_2O_5	TiO_2
LSGC	45	55	0	3	1
LC1S	44	55	1	3	1
LC2S	43	55	2	3	1
LC3S	42	55	3	3	1

Every glass batch was mixed in mortar for 30 mins and put in a laboratory beaker with distilled water as slurry and heating mixer was used with moderate speed and low heat for 1:30 hr. After almost evaporating the distilled water, the glass mixture was put in a crucible and pre-calcined was made for every glass mixture at $700^{O}C$ for 1 hr. A platinum crucible (90% Pt-10% Rh) was used in the melting process at $1195^{O}C$ for 2 hrs. The melting-quenching method is used to produce glass powders (frits) by pouring the glass melton directly into cold water at $3^{O}C$. The produced frits were milling in an agate mortar to get more fine grains and homogenous frits. The above steps were repeated one from melting to milling in an agate mortar to more homogeneity in the glass-ceramic structure.

3.2. Specimen preparation

The produced frits were mixed with P_2O_5 and TiO_2 with percentages shown in table (1-1) as nucleating agents in these frits in the agate mortar. It is compacting to discs under exerting pressure 5 ton with biaxial compression and prepared 5 specimens for each glass batch and selected the best of them. The frit discs with dimensions 18 mm diameter × 2.58 mm thickness was undergone for heat treatment with a moderate rate of $10^{O}C$/min at $950^{O}C$ for 6 hrs.

3.3. Testing methods and measurements

The testing of dielectric strength was done with high voltage supplier Baur-PGO-S-3 (Germany) with a voltage range from 0 kV to 60 kV and a frequency of 50 Hz. 10 points voltage breakdowns were made for each glass-ceramic specimen with a voltage increasing rate of 5 kV/s and paraffin liquid was used as voltage insulator media. SEM images were taken for each specimen of the glass batches by MIRA3, LMU, Tescan field emission scanning electron microscope (FESEM) made in the Czech Republic.

4. Results and Discussion

In same every specimen, 10 times voltage breakdown was made in different positions and dielectric strength was determined from equation (1) which represented 10 probabilities. It started from 1to 10 and every probability substituting in ln(-ln|1/Ps|), probability 1 takes the lowest dielectric strength value while probability 10 takes the highest dielectric strength value. To know the extent of the closeness or divergence of the dielectric strength values in the same specimen. Figure (1) a shows ln(-ln|1/Ps|) versus ln σ_{Vmax} to determined Weibull modulus as slope and indication homogeneity of the LSGC specimen. It can see from the figure, a large disparity between the probabilities of dielectric strength values leading to Weibull modulus with sharp slope and frequently low homogeneity for LSGC specimen. This back to the particle size is not same size and particle shape is changing from one to another particle. It can see from the figure (1) b the random directions of the particles (1) and indirection toward one (2), existence the micro-cracks (3), and a lot of pores with different sizes (4). These defects resulted from the addition of P_2O_5 and TiO_2 as nucleating agents before the heat treatment which were made these micro-cracks and pores and random of the particle size and shape during the heat treatment [11].

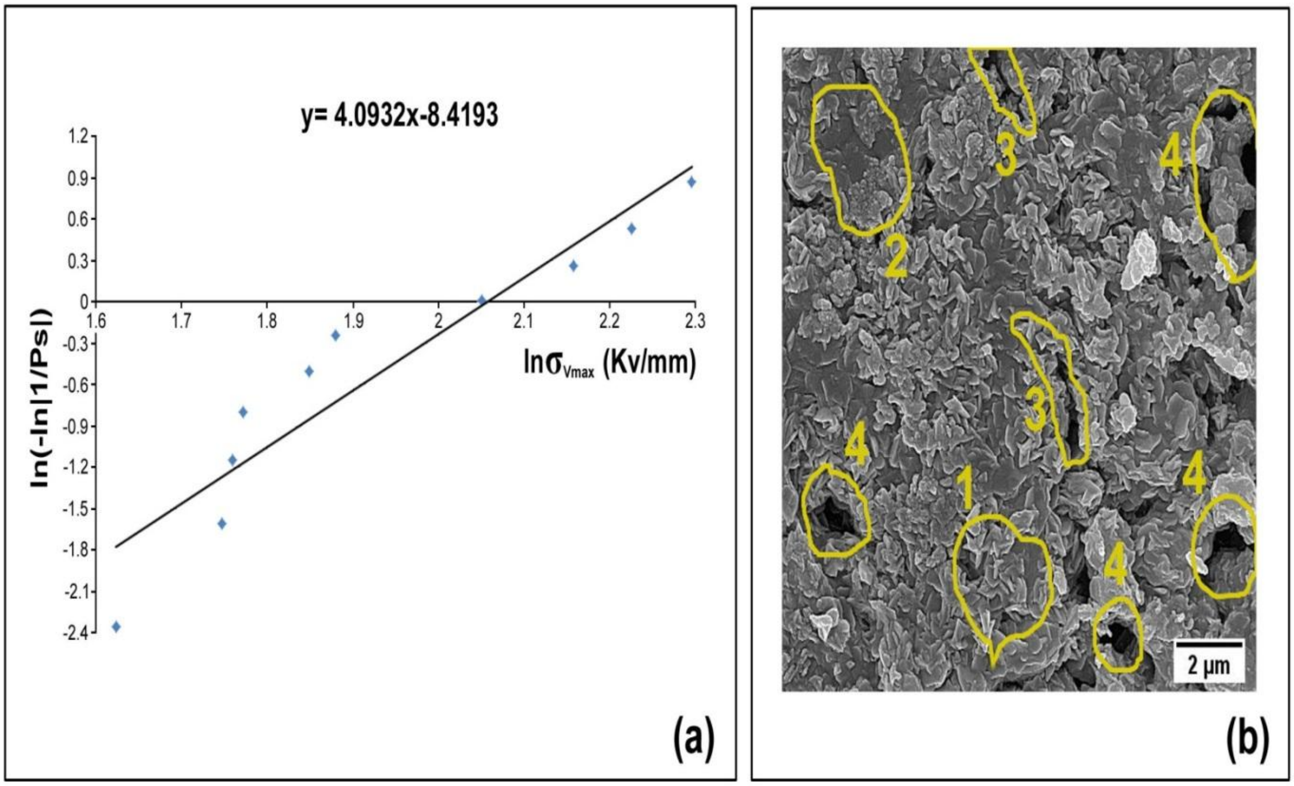

Figure 1: (a) Weibull modulus determination for LSGC as homogeneity indicator. (b) FESEM image for LSGC microstructure 2 µm.

The values of ln σ_{Vmax} in LC1S specimen are more converge than the values in LSGC specimen and frequently the Weibull modulus with a less sharp slope as shown in figure (2) a. This indicated LC1S specimen is more homogeneity than LSGC specimen and cause is back to addition 1wt% CuO and dissolved within glass network take octahedral positions Cu^{2+} and interstitial sites Cu^{+} and Cu^{0} between the glass network lead to decrease the transition glass temperature T_g because the ionic exchange had happened between Li^{+} and Cu^{+}, $Si^{4\pm}$ and Cu^{2+}. The valence of copper ions is become regulate in the glass structure and increases from the density glass network by crosslinking with fewer defects, micro-cracks, and pores. It helps to increase the crystalline phase formation during the heat treatment by carriers and vacancies abundance in the glass network [4,6]. Figure (2) b shows there are little micro-cracks (1), pores (2), and more order for particle size and shape (3), and this why give the value of Weibull modulus high with a less sharp slope for LC1S specimen and this indicating on a good homogeneity.

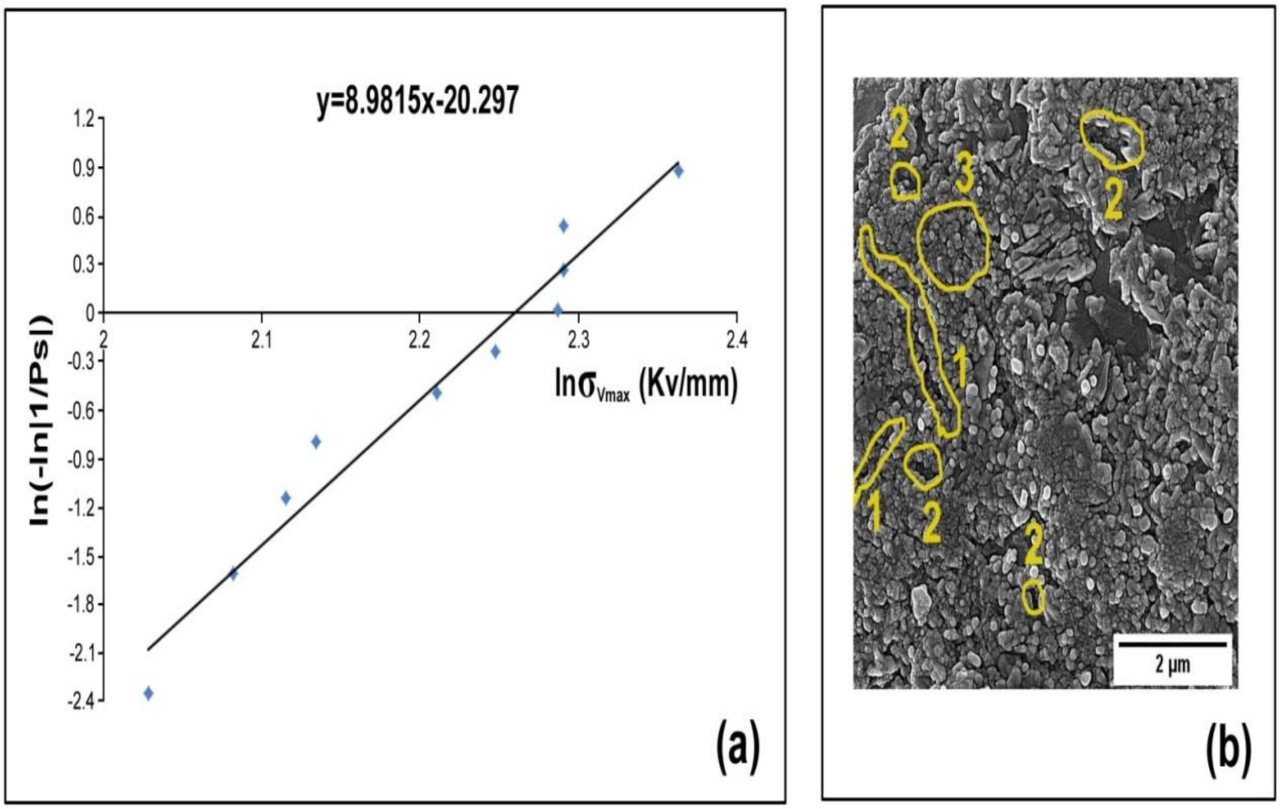

Figure 2: (a) Weibull modulus determination for LC1S as homogeneity indicator. (b) FESEM image for LC1S microstructure 2 µm.

The Weibull modulus is a sharper slope in LC2S specimen than LC1S specimen and this indicating less homogeneity in LC2S specimen. This back to the values of dielectric strength is more spacing than the values in LC1S specimen as shown in figure (3) a. The addition of CuO with a weight percentage of 2wt% means more CuO dissolved in the glass network in the front decreasing the weight percentage of Li_2O. More amount of Cu^{2+} takes octahedral positions in the glass network. More abundance of Cu^{+} in the glass network leading to accelerating the movement of the ions and made the glass structure more order but facing the high viscosity of glass molten so small order regions in the front disorder regions creating defects like micro-cracks, dislocations and vacancies defects which are lead to less homogeneity in LC2S specimen [6]. Plus, pores and other micro-cracks are forming during the heat treatment by melting P_2O_5 as nucleating and making vapor pressure into LC2S specimen as well as TiO_2 as nucleating agent work as a center to growing the crystalline phases. Because differences in the thermal expansion coefficient among these oxides led to rising the micro-cracks [11]. Figure (3) b shows numerous pores (2) and clear micro-cracks (1) into LC2S specimen lead to decreasing of the value Weibull modulus and the reasons causing this state was explained above.

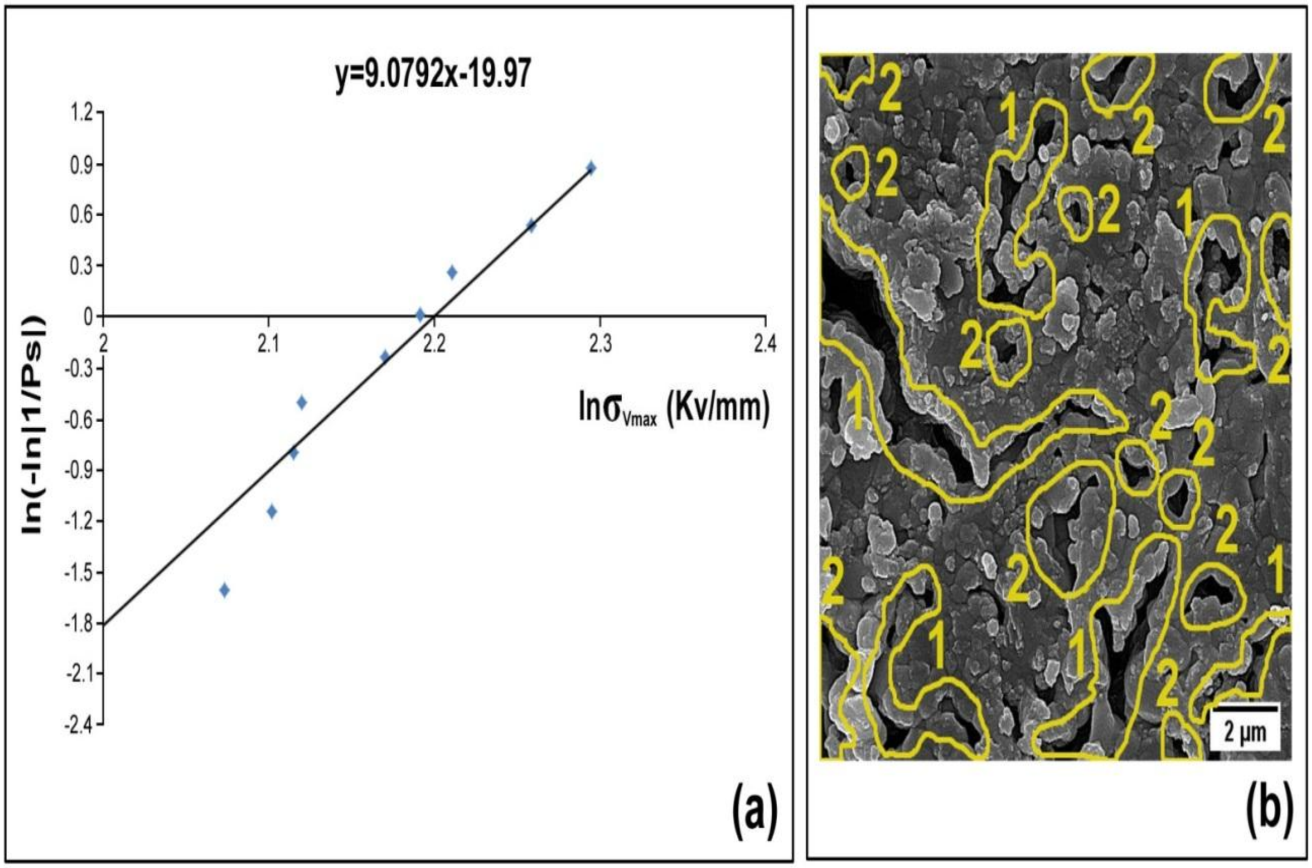

Figure 3: (a) Weibull modulus determination for LC2S as homogeneity indicator. (b) FESEM image for LC2S microstructure 2 µm.

The addition weight percentage of CuO is 3wt% with decreasing weight percentage of Li_2O in LC3S specimen and this meaning more quantity dissolved of Cu^{2+} in the glass network, more Cu^+ in the interstitial sites which makes more non-bridge oxygen (NBO) were formed into the glass network which permits more ions non-bonding with the glass network and change the transition glass temperature T_g to lower value [5]. It can see the larger spacing among the values of dielectric strength in LC3S specimen the rest of specimens in figure (4) a. This back to more crystalline phases was formed by P_2O_5 and TiO_2 as nucleating agents and help of CuO during the heat treatment within the glass structure but without uniform order. So the dielectric strength values were appeared different from spot to other in the LC3S specimen and the Weibull modulus appeared as a sharp slope which indicated less homogeneity. Figure (4) b shows a combination of the micro-cracks with pores that look like deep grooves (1) caused by dislocations that came from a bit different of the thermal expansion coefficient among the ingredients. As well as P_2O_5 and TiO_2 as nucleating agents were added before the heat treatment to frits which were increased from micro-cracks by long and quantity and helps to decrease the homogeneity and made the Weibull modulus sharper slope.

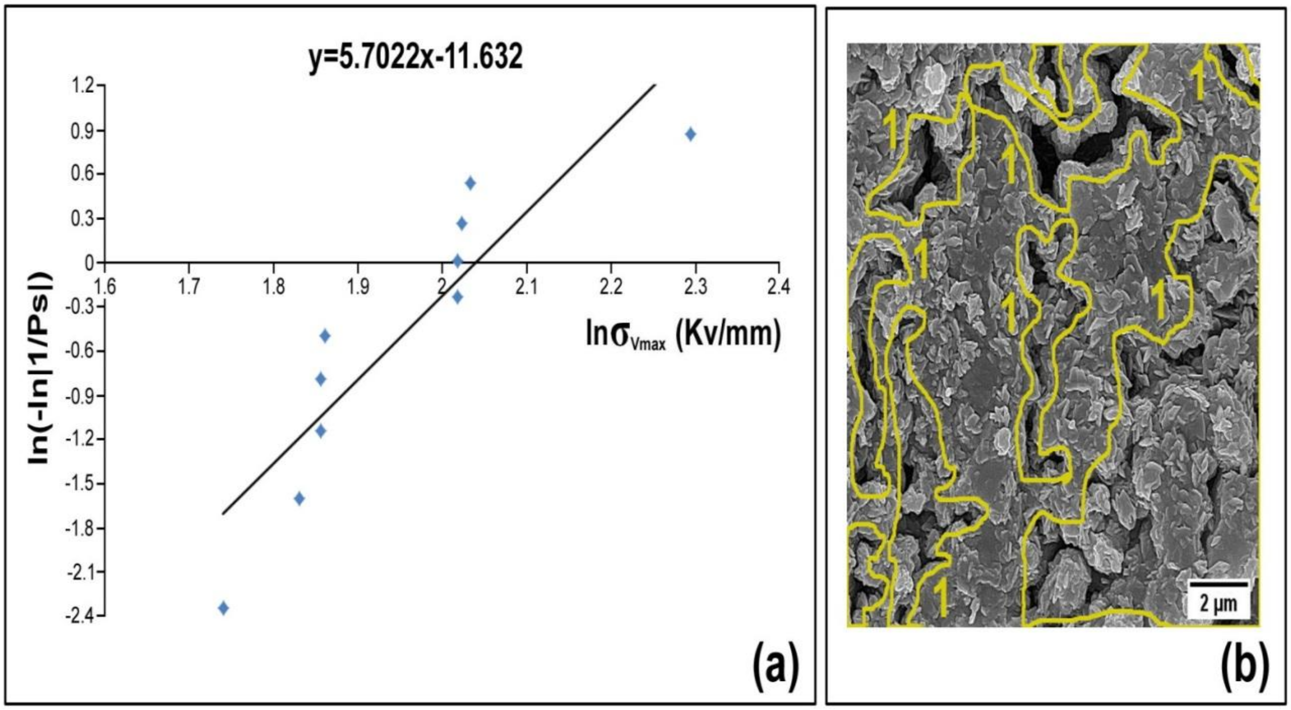

Figure 4: (a) Weibull modulus determination for LC3S as homogeneity indicator. (b) FESEM image for LC3S microstructure 2 µm.

The value of probability difference is equal to -0.49521 in all specimens as shown in figure (5). The relationship between average ln(-ln|1/Ps|) and average ln σ_{Vmax} is showing good indicators that guide the existence of the similar homogeneity in all specimens despite the difference in Weibull modulus among them and addition weight percentage of CuO to them. This backs to the existence of the same glass network in all specimens and they were prepared in the same conditions.

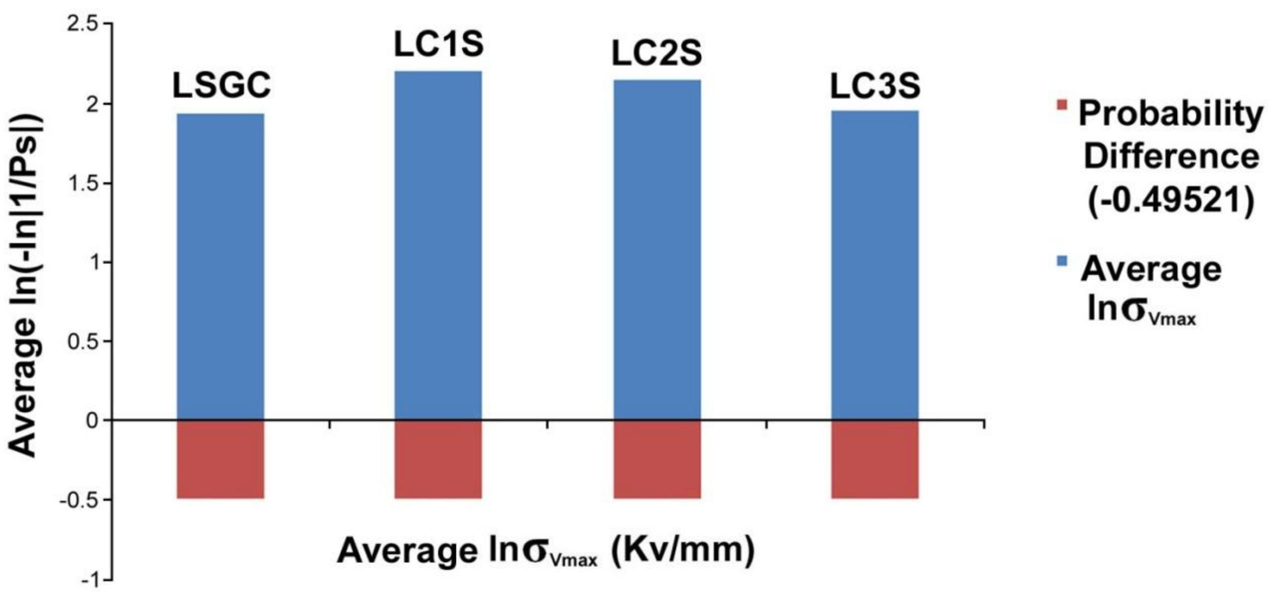

Figure 5: The probability difference value for all specimens.

When the addition increasing of CuO weight percentage, the average dielectric strength is increasing until 1% wt of CuO and starting to decrease gradually as shown in figure (6). This back to CuO was helped to decreasing the melting point of the glass batch and made the glass structure more order and homogeneous with fewer micro-cracks, pores and defects in LC1S than LSGC. So that, the average dielectric strength of LC1S specimen equal to 9.116 kV/mm larger than 7.101 kV/mm of LSGC specimen. The addition increasing of CuO weight percentage than 1wt%, the values of average dielectric strength were 8.585 and 7.133 kV/mm for LC2S and LC3S specimens respectively. This back to increase in the amount of Cu^{+} in interstitial sites which were active as charge carriers (ions) and approaching the lithium metasilicate glass-ceramic properties from semiconduction properties, plus increase from microcracks, pores, and grooves in LC2S and LC3S leading to lower from the values of average dielectric strength. This what the Weibull modulus results referred to it.

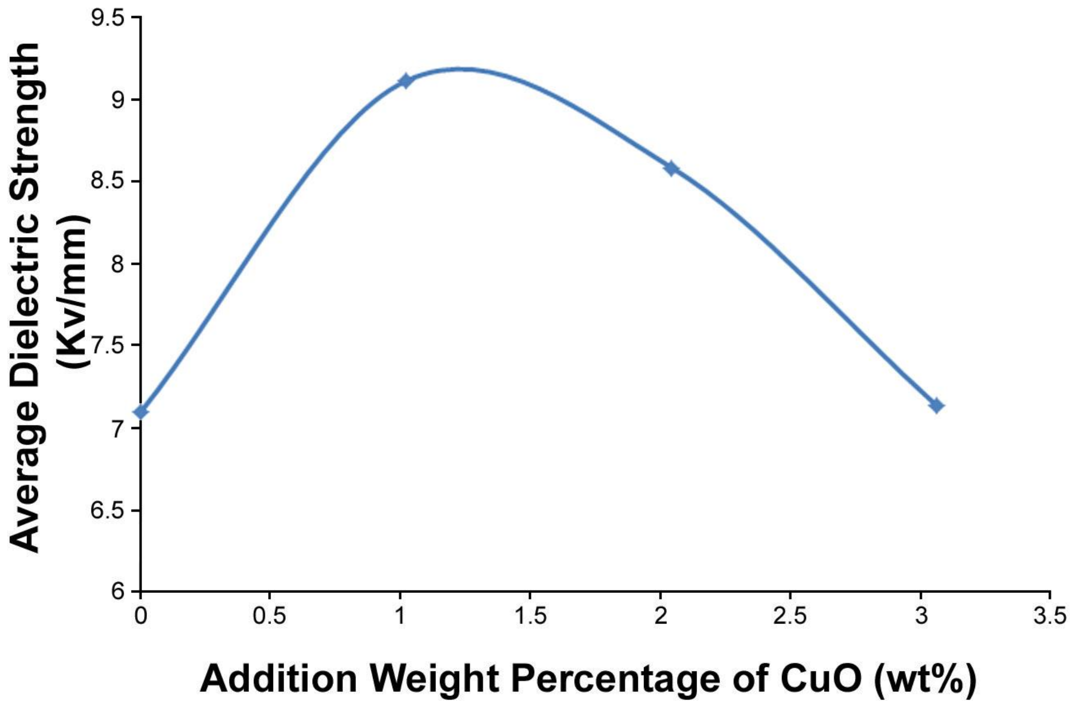

Figure 6: The relationship between average dielectric strength and addition weight percentage of CuO.

Upon the addition weight percentage of CuO within glass batch ingredients is increasing, the value of Weibull modulus is increasing until 2 wt% CuO and starting to decrease as shown in figure (7). The dissolved CuO within the glass batch helps the glass structure be more homogeneous by occupied octahedral sites in the glass network with Cu^{2+} ions while Li^{+} ions are the most occupied interstitial sites. During the heat treatment, the movement of the ions be more with high content of CuO but facing the high viscosity of the glass ingredients which causing micro-cracks and pores. P_2O_5 and TiO_2 as nucleating agents help to increase the size and amount of the micro-cracks, pores despite the high value of the Weibull modulus 9.0792 at 2 wt% CuO that indicated more homogeneity but different and spacing between the values of dielectric strength in figure (3) a. The homogeneity is improved with addition CuO but little amounts and proofs it by Weibull modulus and FESEM and figure (7) represents the basic relation and idea in the work.

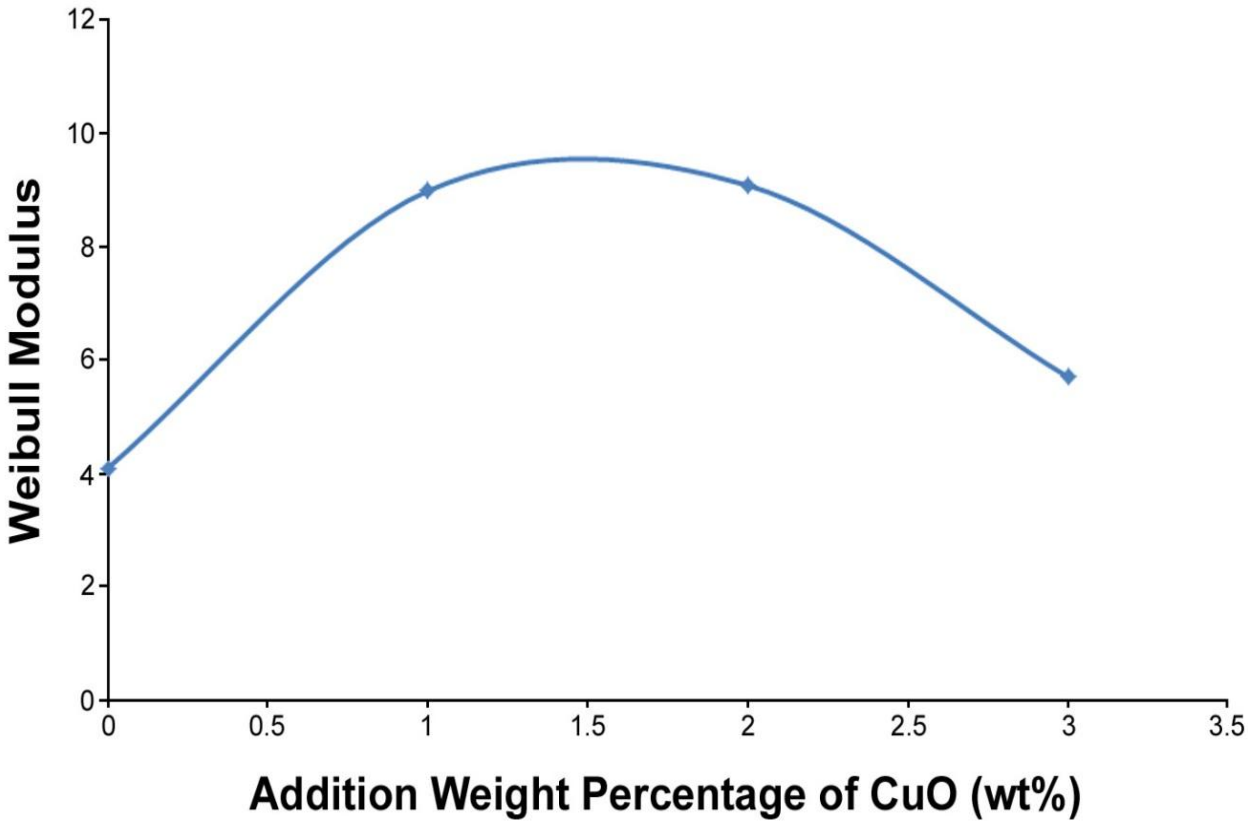

Figure 7: The relationship between Weibull modulus and addition weight percentage of CuO.

5. Conclusions

The manufacturing conditions have a significant effect on the properties homogeneity of glass-ceramic, such as the dielectric strength, as it avoids the occurrence of microstructure defects during manufacturing that reduces the properties homogeneity of the glass-ceramic. The good agreement of the result explanations between the Weibull modulus and FESEM images for dielectric strength. The Weibull modulus is a good active tool that can be used to know the symmetry of any property in any spot and direction in the same specimen. It should add P_2O_5 and TiO_2 as nucleating agents with glass batch ingredients during the melting process to avoid the micro-cracks, pores, and other defects that can be created during the heat treatment when added the nucleating agents before the heat treatment. It can get on conduction or semiconduction properties for glass-ceramic generally and lithium metasilicate glass-ceramic, especially by addition conductive or semiconductive materials like CuO but lower weight percentage, do not pass 1.5wt%. Copper oxide helps to improve the homogeneity at weight percentage 2% in LC2S specimen significance the Weibull modulus and FESEM image. It can use other conductive or semiconductive materials like Ag, Au, MoO_2, WO_3, etc.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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