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THE POTENTIAL OF USING LOCALLY AVAILABLE RAW MATERIALS FOR THE PRODUCTION OF ALKALINE EARTH ALUMINOSILICATE BASE GLASS SYSTEM

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ABSTRACT
The study placed emphasis on utilizing locally available raw materials to produce a calcium-magnesium-alumino-silicate (CaO-MgO-Al_2O_3-SiO_2) base glass system. Major sources of oxides for preparation of glass batch were feldspar, limestone and magnesite. The chemical composition of the base glass system consists of 52 wt% SiO_2, 16 wt% Al_2O_3, 16 wt% CaO, 8wt% MgO, 2 wt% K_2O, 3.7 wt% trace oxides, and 0.3 wt% NaCl. After production, the glass transition temperature (T_g) of the sample was 273℃. SEM analysis displayed the presence of amorphous phase due to lack of long range order.XRF analysis was used to determine the chemical compositions of the three samples and the results revealed that they are suitable for making CaO-MgO-Al_2O_3-SiO_2 base glass system. 280 HV was the micro hardness average value of glass sample produced, 2.2 g/cm^{3}was average value of apparent density, and 0.5g/cm^3 and 0.7g/cm^3 were the average results of the chemical durability of produced samples in 1M HCl and 1M NaOH solutions respectively. Determination of various properties suggests that superior properties depended on composition, melting condition, temperature and annealing of the glassy material. The properties of the glass samples highlighted the potential of local raw materials for making calcium-magnesium-alumino-silicate base glass system.

Keywords: Local Raw Materials, Characterization, CaO-MgO-Al_2O_3-SiO_2 Base Glass System

1.0 INTRODUCTION

Glassy materials are amorphous non crystalline ceramics which exhibit transformation behaviour and do not have long range periodic order (Shelby, 2005). Glasses were used for centuries for a wide range of applications such as packing like bottles and jars, ware like drinking glasses among others. However, in the twentieth century, the inventions of radio, television and advanced electronics created a wide spectrum of new applications for glass, and resulted in a great deal of new compositions with superior mechanical, physical and thermal properties (Celia et al, 1991). Oxide-based glasses are classified as silicates, germinates, phosphates or borates depending on which of the glass forming oxides (SiO_2, GeO_2, P_2O_5 or B_2O_3) make up the network forming structure. More than 90% of glass in use is silica-based. However, a wide range of specialized glasses are not based on silica, for example, phosphate and fluro-phosphate glasses are used as hosts for lasers (Rao, 2002). Today, industrial glass globally is a vital component of national economies. In 1995, USA and Japan produced roughly 10 million metric tons of glass each (Rao, 2002).

To bring down the viscosity and softening range of oxide glasses, alkali and alkaline earth oxides are incorporated to the melt. Properties of oxides glass are altered considerably by making appropriate incorporation such as alumina to enhance strength and hardness and boron oxide to improve resistance to thermal shock (Shelby, 2005).

Numerous inorganic glasses are readily obtainable for commercial purposes notable among which include alkaline-earth alumino silicate, soda-lime silica glasses, alumino silicate glasses among others (Salama et al, 2002). Alkaline-earth alumino silicate glasses are intermediate between the soda-lime and vitreous silica for thermal expansion and chemical durability (Varshneya, 1994).

The emerging of glass industry has a significant role to play in the economy of Nigeria particularly employment opportunity for the teeming population. Aliyuet'al, (2013), Aliyuet'al, (2014), Aliyuet'al, (2015) carried out studies on the suitability of some local raw materials for glass making from various sources across Nigeria and the findings revealed that the raw materials are suitable for making various types of glasses, although the concentration of iron oxide in each case was above the tolerable level of 0.1-0.2 wt% for making quality colourless glass. However, according to Alex and David, (1979) each case can be upgraded through beneficiation to get rid of the undesirable colouration imparted by the impurities.

The aim of this study was to develop calcium-magnesium-alumino-silicate ($CaO-MgO-Al_2O_3-SiO_2$) baseglass system using local raw materials such as feldspar, limestone and magnesite and subject the resultant glass samples to characterization as well as determination of some properties so as to suggest areas of usage.

2.0 METHODOLOGY

Materials Sourcing

Feldspar was collected from Matari in Kaduna State; limestone was sourced from Kalambaina in Sokoto State and magnesite came from Tsakesimptah in Adamawa State and about 200kg of each sample was collected randomly from various spots.

Materials Characterization

The lump samples of (feldspar, limestone and magnesite) were crushed, milled and sieved with Tyler mesh No.140 to desirable particle size distribution of 105 µm and then stored in small polythene bags. About 2 Kg was drawn and utilized to conduct this study. Each of the samples was characterized using XRF to determine chemical composition. The result of the chemical composition was presented in Table 1.

Batch Formulation

A batch composition for the quaternary alkaline earth alumino silicate base glass system was prepared and composed of 54wt% SiO_2, 16wt%Al_2O_3, 16wt% CaO, 8wt% MgO, 2wt% K_2O, 0.3wt%NaCl, trace 3.7wt%.

Melting of Glass

Six (6) batch compositions for the quaternary alkaline earth alumino silicate base glass system ($CaO.MgO.Al_2O_3.SiO_2$) were formulated. Each sample was thoroughly mixed and put into crucible and then transferred into an electric muffle furnace. The batches were melted at 1600℃ for 3 hours. The homogeneity of the melt was achieved by frequent swirling the crucible containing the melt severally at 20 minutes interval. Melting the batches was carried out at normal laboratory condition without controlling the atmosphere. After melting, the samples were cooled to annealing temperature and then annealed at 600^{o}C for 1 hour to remove residual stress. The samples were further cooled to room temperature and the physical appearances of the produced glass samples were observed.

Characterization of produced Glasses

Differential Scanning Calorimetry (DSC) thermo gram was carried out using Mettler Toledo DSC model with 4.8 mg of the glass powders against Al_2O_3 as reference material at a heating rate of 10℃/min. The analysis was carried out in a crucible using nitrogen atmosphere at temperature of 500℃ and then cooled to room temperature at the same heating rate and the glass transition temperature (T_g) was determined. Furthermore, another sample was subjected to Scanning Electron Microscope (SEM) to study surface morphology. Also, XRD patterns of the sample were studied. In addition, hardness was determined using Vickers micro hardness indenter, Apparent density was measured using Archimedes Principles and chemical durability was carried out by immersing the sample in 1M HCl and 1M NaOH solutions.

Heat Treatment of Glass Samples

Four (4) glass samples (Sample 1, Sample 2, Sample 3 and Sample 4) were subjected to heat treatment for a period of 1,2,3, and 4 hours duration respectively. Thereafter, some properties were determined such as hardness, chemical durability and apparent density to ascertain their suitability for making calcium-magnesium-alumino-silicate (CaO-MgO-Al_2O_3-SiO_2) glasses.

3.0 RESULTS AND DISCUSSION

Table 1 shows chemical compositions of feldspar, limestone and magnesite and their respective loss on ignitions (LOI). Table 2 depicts the micro hardness of glass samples, Table 3 displays the weight loss of glass samples in 1 M HCl acid, Table 4 shows the weight loss of glass samples in 1 M NaOH solution and Table 5 displays the apparent densities of the glass samples under study. In addition, Figure 1 shows glass transition temperature of the sample, Plate 1 displays SEM micrograph of glassy phase and Figure 2 shows the diffraction pattern of the glassy material.

The result in Table 1 shows that Matari feldspar is rich in SiO_2 (67.32wt %), Al_2O_3 (17.54 wt %) and K_2O (11.33 wt %) with 0.1 wt% Fe_2O_3 and other oxides such as MnO_2, NiO_2, Cr_2O_3 were used as colouring agent in glass making(Shelby, 2005). The result revealed that Matari feldspar deposit is potash feldspar because it is composed of 11.33 wt% potash (K_2O) which falls within the range of 10-15 wt% for potash feldspar needed in the glass industry (Gulsory et al.,2005). In addition, Matari feldspar being rich in potash, suggests that it is suitable as fluxing agent for fast melting and energy saving in glass making (El-Meliegy and Richard, 2012). Therefore, Matarifeldspar deposit is a good source of potash, alumina and silica as the oxides are suitable for making alumino silicate and soda lime-silica glasses (Alexis and David, 1979 and Shelby, 2005).

Table 1: Results of XRF Analysis of the Raw Materials.

Constituent Oxides	Matari Feldspar (Wt. %)	Kalambaina Limestone (Wt. %)	Tsakesimptah Magnesite (Wt.%)
SiO_2	67.32	3.38	17.7
TiO_2	0.00	0.04	0.352
Al_2O_3	17.54	0.75	4.86
Fe_2O_3	0.10	0.55	2.86
MnO_2	0.02	0.03	0.08
MgO	< 0.01	0.73	63.03
CaO	0.12	53.08	9.77
Na_2O	2.75	< 0.01	0.09
K_2O	11.33	< 0.01	0.74
P_2O_5	0.35	0.11	0.05
Cr_2O_3	< 0.01	< 0.01	-
NiO_2	< 0.01	< 0.01	-
V_2O_5	< 0.01	< 0.01	-
ZrO_2	0.01	< 0.01	0.0128
CuO	< 0.01	< 0.01	-
SrO	-	-	0.0453
Rb_2O	-	-	0.0083
LOI	0.14	42.00	0.11

Similarly, Kalambaina limestone contains 53.08 w% CaO which is close to 54-56 wt% required as standard for making plate and window glasses (Alexis and David, 1979). Apart from high lime (CaO) content, it contains little or no magnesia (0.73 wt %). Usually, CaO rich limestone is almost free from magnesia when compared with standard of less than 3.0 wt %. Iron oxide in glass making is undesirable due to its colouring effect, but the concentration of iron oxide(0.55 wt%) in Kalambaina limestone is far above the permissible level for making quality colourless glasses(0.1-0.3 wt%) (Alexis and David, 1979).

In a similar vein, Tsakesimptah magnesite has 63.3 wt% magnesia (MgO). The high concentration of magnesia (MgO) in the sample has made it suitable as one of the starting materials for making soda -lime glasses. However, Tsakesimptah magnesite deposit has high iron oxide (2.86 wt %) content above the tolerable level of 0.1 wt%. However, the iron oxide concentration can be lowered through beneficiation, as iron oxide inclusion tends to undesirably colour resultant glasses. Also, Tsakesimptah magnesite deposit contains traces of oxides such as titanium oxide, manganese oxides among others which act as opallizing agent and colourant respectively in glass manufacture (Alexis and David, 1979). Generally, the XRF analyses of the three samples (Matari feldspar, Kalambaina limestone and Tsakesimptah magnesite) have shown their suitability in making alkaline alumino silicate and soda-lime silica glasses. Matari feldspar is a potential source of silica (SiO_2), potash (K_2O) and alumina (Al_2O_3) for glass making. The Kalambaina limestone and Tsakesimptah magnesite can serve as sources for lime (CaO) and magnesia (MgO) respectively.

The role of Alumina (Al_2O_3) and silica (SiO_2) in glass making include; effectiveness in increasing the viscosity and transition temperature of calcium-magnesium-alumino silicate base glass system due to the formation of building block units like the SiO_4 tetrahedron and AlO_4 group which have an effect on the strength of glass network connectivity of structure.(Salama et al., 2002). But, CaO and MgO are very effective in decreasing glass viscosity and transition temperature (T_g) through the introduction of non-bridging oxygen (Aliyu et al, 2013).Therefore, the presence of Al_2O_3 in base glass system is an added advantage for it eliminates the non-bridging oxygen present in the melt (Aliyu et al, 2015).

The produced glass yielded undesirably brownish glasses; this was due to the presence of huge amounts of impurities present in the starting materials (feldspar, limestone & magnesite). The impurities include iron oxide (Fe_2O_3), Chromium oxide (Cr_2O_3), Manganese oxide (MnO_2) copper oxide (CuO) and vanadium pentoxide (V_2O_5) among others, which are often used as colourants in glass making (Doyle, 1979 and Shelby, 2005).

Table 2: Micro hardness Values of the Glass Samples

Glass Sample	Length of Heating Time	Micro Hardness Value (HV)
Sample 1	1 (hr)	192
Sample 2	2 (hrs)	221
Sample 3	3 (hrs)	288
Sample 4	4 (hrs)	418

The micro hardness is a bond sensitive property which provides an insight on the nature of the chemical bonding present in the glass sample (Rezvani, 2011). The Vickers hardness value of calcium magnesium aluminate silicate base glass system is generally regulated by the glass composition. According to Omar et al, (2009), high concentration of SiO_2 in the melt increases hardness value of a glass sample. However, the presence of modifier ions such as Ca^{+2} and Mg^{+2} in the melt reduces hardness value simply because they introduce non bridging oxygen that disrupts network connectivity (Salah, 2016 and Harper, 2001). But the presence of Al_2O_3 in the melt eliminates the modifier ions hence restoring the network connectivity of structure, transition temperature, elastic modulus as well as mechanical properties like hardness. Also, the presence of Al2O3 in the glass melt inhibited the formation of cords and crystals (Khater et al, 1999). According to Bourne (1994), high concentration of iron oxide and other impurities increase the melting point of molten glass and impart colouring effect.

The micro hardness of calcium-magnesium-alumino-silicate glasses in Table 2 ranges from 192-418 HV, with an average value of 280 HV.The increase in hardness was due to the presence of Al_2O_3 in the melt which eliminates the modifier ions hence restoring the network connectivity of structure as well as viscous flow formation induced by prolonged heat treatment (Aliyu, 2018).

Table 3: Chemical Durability of the Glass Samples in 1 M HCl Solution

Glass Sample	Length of Heating Time	Wt. Loss (g/cm^3)
Sample 1	1 (hr)	0.6831
Sample 2	2 (hrs)	0.5825
Sample 3	3 (hrs)	0.4653
Sample 4	4 (hrs)	0.4253

Table 3 shows that the effect of 1M HCl on glass samples is weight loss ranging from 0.6 – 0.4 g/cm^3 with an average weight loss value of 0.5 g/cm^3. This is expected because mineral acid attacks alkali through dissolution of alkali in glass composition which left porous surface that is composed of silica network (Naruporn et al, 2013).

Table 4: Chemical Durability of the Glass Samples in 1M NaOH Solution

Glass Sample	Length of Heating Time	Wt. Loss (g/cm^3)
Sample 1	1 (hr)	0.8432
Sample 2	2 (hrs)	0.6876
Sample 3	3 (hrs)	0.6524
Sample 4	4 (hrs)	0.5458

Similarly, Table 4 revealed that the weight loss in 1M NaOH ranged from 0.8-0.5 g/ cm^3 with an average weight loss of 0.7 g/cm^3. The alkali simply attacked the silica network causing dissolution of silica network structure. The results show high chemical resistance to both acid and alkali attack. This might result from the presence of high concentration of alumina. This was in agreement with the finding of (Sinton et al, 2001 and Naruporn, et al, 2013), who showed that high alumina content reduces alkali attack on glass samples.

Table 5: Apparent Density Values of the Glass Samples

Glass Sample	Length of Heating Time	(g/cm^3)
Sample 1	Sample 1 (hr)	2.1233
Sample 2	Sample 2 (hrs)	2.1399
Sample 3	Sample 3 (hrs)	2.1700
Sample 4	Sample 4 (hrs)	2.1849

Table 5 displays apparent density of the samples ranging from 2.1 – 2.2 g/cm^3 with an average value of 2.2 g/cm^3 which is relatively low as opposed to the density of soda-lime-silica glasses which ranged from 2.40 – 2.42 g/ cm^3.

The DSC result in Figure 1 reveals that the produced glass sample exhibited 273^{o}C as its glass transition temperature (T_g).

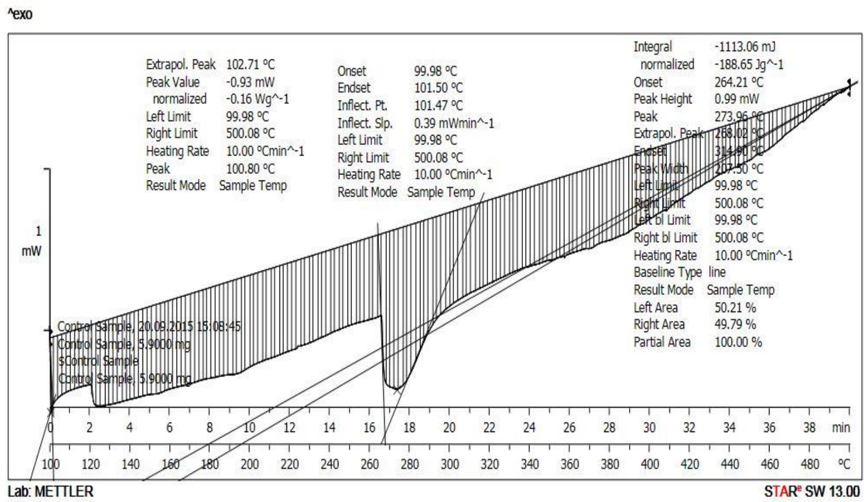

Figure I: DSC Thermo gram of glass sample showing glass transition temperature at 273°C

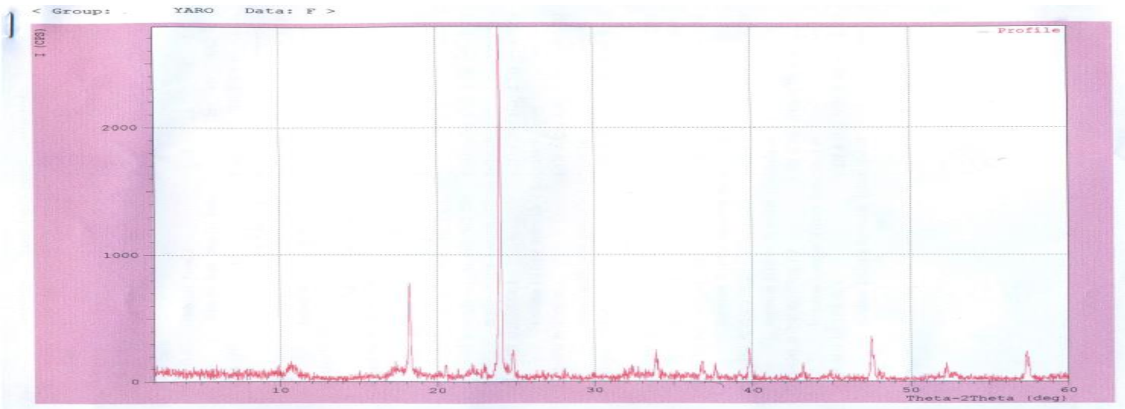

Figure 2: XRD patterns of Glass Sample

The X-Ray Diffraction patterns in Figure 2 lack crystalline features such as sharp diffraction peaks and hump at low diffraction angle two theta (2θ) value which are indication of short range-order in glassy phase (Shelby, 2005 and Park, 2008).

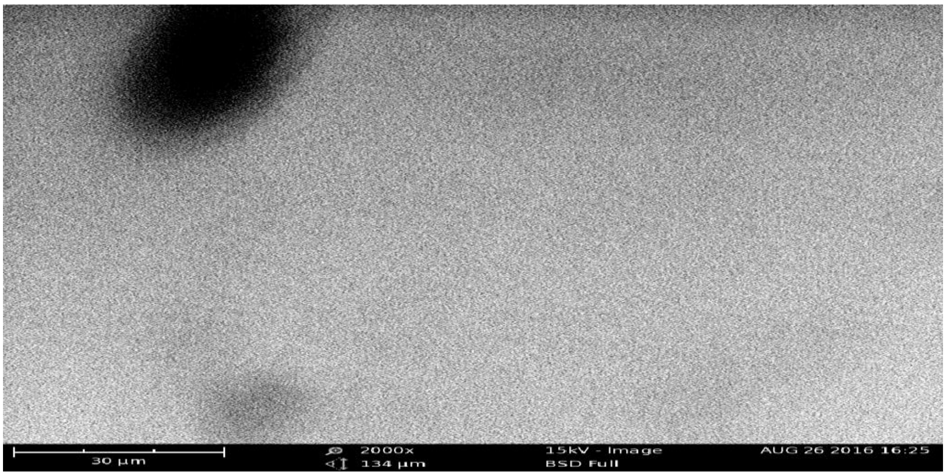

Plate I : SEM micrograph of a glassy phase without crystals at X 2000 Magnification

Plate I shows the SEM image of the glassy phase displaying absence of crystals on SEM micrograph. SEM image of the glassy phase displaying absence of crystals on SEM micrograph.

4.0 CONCLUSION

Calcium-magnesium-alumino-silicate base glass system was prepared from local raw materials such as feldspar, limestone and magnesite. The glasses produced were brownish due to the presence of high concentration of impurities. The findings revealed that the produced glass samples exhibited 273^{o}C as glass transition temperature (T_g) and X-Ray Diffraction patterns of the glass samples lack crystalline features such as sharp diffraction peaks and hump at low diffraction angle two theta (2θ) value which are indication of short range-order in glassy phase. The results of the Microhardness, apparent density and chemical durability of the glass samples demonstrated positive correlation with the batch composition. The glass samples produced seem to be viable for the production of calcium-magnesium-alumino-silicate glasses based on their determined properties (hardness, chemical durability and apparent density). It is recommended that the starting materials could serve as sources for making calcium-magnesium-alumino-silicate glasses. However, due to high concentration of impurities present in the samples, there is need for beneficiation to upgrade the samples so as to achieve quality products. Contrary to this, due to high cost implication of beneficiation, the samples can be used as starting materials for the production of other products such as fertilizer, paint, ceramic kiln, refractory bricks, among others.

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