Commun. Fac. Sci. Univ. Ank. Series B
V.51 (1). pp. 1- 12 (2005)

PREPARATION AND DIELECTRIC PROPERTIES OF PYROXENIC BASALT BASED-GLASS/MULLITE COMPOSITES

SALWA A .M. ABDEL-HAMEED AND A. A. EL-KHESHEN

National Research Centre, Glass Tech. Dept. Dokki, Cairo- EGYPT

(Received Feb. 07, 2005; Accepted March 17, 2005)

ABSTRACT

Pyroxenic basalt-based glass /mullite composites were prepared. The effect of sintering temperatures on crystallized phases were studied by X-ray diffraction patterns; also the details of microstructure and mineralogical constituents were examined by using SEM. The crystallization of augite ss and mullite at low temperature and plagioclase and spinel at higher temperature were observed. Apparent porosity and relative density of the sintered samples were also measured. Measurements of dielectric constants showed preparation of good insulators of samples containing plagioclase and spinel phases.

INTRODUCTION

Basalt is a dark gray to black, dense fine-grained igneous rock composed basically of silica, alumina, iron oxide, calcia, magnesia and of lesser importance sodia, potassia and titania. Its essential mineral constituents are plagioclase, monoclinic pyroxene and magnetite.

Glass-ceramics obtained from basalt are very useful as wear resistant materials for industrial applications (e.g., piping, tiles, etc.) and in various hostile thermal and chemical environments [1-6]. The Egyptian basaltic rocks from Abu-Zaabl are excellent candidates to produce this type of material [7-10]. Furthermore, plagioclase feldspar based glass-ceramics exhibit high refractoriness and moderate coefficients of thermal expansion (~ 35×10^{-7} /°C, 20-300°C). Such bodies, wherein the predominant crystal phase is anorthite ss have low dielectric constants and dc volume resistivities coupled with low ac dielectric losses, and consequently would be competitive with commercial electrically insulating materials[11].

From a technological standpoint, pyroxenes have been widely used as a basis for useful glass-ceramics of high wear and chemical resistance.

Uniform ultrafine hard glass-ceramics materials composed of mono-mineralic pyroxene ss were successfully synthesized by El-Shennawi et al, [12] from Abu Zaabl basalt rock without adding nucleation catalysts but through rectifying the $FeO:Fe_2O_3$, $CaO:Na_2O$ and $CaO:MgO$ ratios in basalt by adding small amount of limestone, soda ash and ammonium nitrates to the basalt rock.

To enable high-speed switching of large-scale integrators (LSIs) in a system, the circuit boards should have a low dielectric constant, thus following the high-speed signal to propagate with a shorter delay [13,14].

In the present work an attempt is done to study the changes in physical properties when adding mullite ($3Al_2O_3.2SiO_2$) , which is high refractory , to pyroxenic basalt glasses. Also the effect of heat-treatment parameters on the type and nature of the developed phases and microcrystalline structure of the glass /ceramic composites developed, is investigated.

MATERIALS AND METHODS

The glass compositions (Table 1) were formulated to yield single pyroxene ss from basalt rock, by heat-treatments. Egyptian basalt rock (Abu-Zaabl), limestone, soda ash and NH_4NO_3 as oxidizing agents served as starting materials (Table2 summarizes the analysis of raw materials used) . 150 g of the requisite finely powdered batch materials were thoroughly mixed in a mechanical agate mortar for 1 h and melted in Pt crucibles in an electrically heated globar furnace at 1350°C for 2.5 h with occasional swirling every 20 min. to ensure complete homogenization and oxidation; the homogeneous blackish glasses were annealed at 650°C.

It is worth mentioning that lower viscosities and good workability were noticed; according to the qualitative viscosity test[12].

Mullite was prepared by firing 3:2 mole ratio of pure alumina and fumed silica (which is produced as a by-product from ferrosilicon alloy industries) at 1550°C for 1h. The obtained mullite ceramic contains a small amount of cristobalite as unreacted silica.

The fine glass powder was well mixed with different amounts of mullite to form 3 different glass/ceramic composites ratios, i.e. 7/3M, 6/4M and 5 /5M glass/ mullite, respectively, the mixed batches were uniaxially pressed at 60MPa in a disc

shape of about ½ inch diameter and ½ inch height, then heated at 900 to 1300°C for 2 h.

Apparent porosity and bulk density of the sintered samples were measured by the Archimedes method. X-ray diffraction patterns were obtained by using a Philips Powder Camera (Type CPM 9920/02) with CuKα radiation and Ni filter. The instrument settings were maintained for all the analysis by using an external standard Si disc. The details of the microcrystalline structure and mineralogical constituents were examined by SEM using (JEOL JSM-T20) .

The dielectric constant (ε') of the fired composites discs of 10mm in diameter and 1-2.4 mm thick was measured at 100KHz, by using a Philips R.L.C bridge type PM 6304 programmable automatic RLC meter.

Results and Discussion

X-ray diffraction patterns of the sample 7/3M heat treated at 900°C/2h (Fig.1), shows crystallization of augite ss as major phase in addition to minor amounts of mullite and cristobalite. This last being residue from unreacted silica during mullite formation. At 1300°C/2h, the X-ray diffraction pattern (XRD) (Fig.2) shows, for all samples, crystallization of plagioclase feldspar as major phase with spinel and cristobalite as minor phases. It seems that mullite were dissociated into its oxides, Al_2O_3 and SiO_2. SiO_2 from mullite and excess cristobalite were reacted with augite ss to form plagioclase feldspars ss. While part of the Al_2O_3 (from dissociation of mullite) replaced MgO in augite ss to form plagioclase feldspar, the other part were reacted with this free MgO to form spinel. Simply , the following reaction is occurred:

Mullite + augite $\longrightarrow$ plagioclase + spinel + cristobalite

Increasing the percentage of mullite from 30% in 7/3M to 50% in 5/5M sample, leads to increasing the crystallization propensity of the above mineral phases.

SEM of samples heat-treated at 1300°C for 2h (Fig. 3a) reveals the maturity of plagioclase microlites progressed giving rise to prismatic lath shaped (in bundles) which embedded in rounded shape crystals of spinel. Figure 3b shows another zone at higher magnification.

From the relation between the change in composition and the relative density (Fig.4) as well as apparent porosity of glass /ceramic composites fired at 1300°C/2h, it appeared that the relative density is increased from 62.60 in 5/5M to 74.72 in 7/3M, while the apparent porosity is decreased from 40.6 in 5/5M to 30.86 in 7/3M, by increasing the percentage of glass added. It may be explained by considering that when the sample of composite is sintered, the glass is melted and fill its pores and consequently leads to increased density and decreased porosity.

It was noticed that the dielectric constant was decreased as the glass content increased, when the sample was sintered at 1300°C/2h. By comparing the dielectric constant for all sintered composites at 10kHz (Table3), it was noticed that

increasing the heat-treatment parameter from 900°C/2h to 1300°C/2h leads to a large decrease in the dielectric constant from 65.5 to 4.75 for 7/3M (as example).

It can be revealed that, the dependence of the dielectric constant on the composition is obtained by way of the polarizability and the potential of movement of the ions. In glasses, the oxygen ion is the most easily polarizable ion. The introduction of network modifiers, through the formation of more easily polarizable nonbridging oxygen, will raise the dielectric constant. With the decreasing field strengths of the network modifiers, the nonbridging oxygens are less strongly bound; thus with equal alkali content, the dielectric constants increase in the sequence Li-Na-K. With the alkali earths, it increases as the field strength of the cations falls. In the case of transition elements[15]. So by replacing the Mg in augite with Al, and creating bridging oxygens, they reduce the polarizability and thereby reduce the dielectric constant.

So, adding mullite at the expense of the oxides as Na, K, Mg which exist in basalt glass leads to an increase in dielectric constant. Also, the formation of low dielectric constant plagioclase leads to a lower dielectric constant than augite which crystallized at low temperature.

So, sintering pyroxenic basalt-based glasses/mullite composites at 900°C/2h shows the crystallization of augite ss and mullite as designed, but increasing the heat-treatment temperature to 1300°C/2h leads to crystallization of plagioclase + spinel which has a much lower dielectric constant than augite ss + mullite composite.

CONCLUSION

Pyroxenic basalt based-glass/mullite composite were prepared. The effect of heat-treatments show the crystallization of augite ss as major phase and minor mullite and cristobalite at 900°C/2h which indicate that no reaction occurred between glass and mullite. Heat treatment at 1300°C/2h revealed the crystallization of plagioclase and spinel, which indicate reaction between glass and mullite at high temperature .Dielectric constant show very low values when plagioclase and spinel were crystallized and these values decreased by increasing the ratio of glass to mullite.

ÖZET: Pirosenik basalt esaslı – cam/mullite kompoziteleri hazırlandı. Kristalleşmiş fazlarda sinterlenme sıcaklıklarının etkisi X-ışınları dağılım izlerinde ayrıca mikro yapı ayrıntıları ve mineralojik bileşimi SEM kullanılarak incelenmiştir. Augitess ve mullite'in düşük sıcaklıkta ve "plagioclase" ile "spinel"in yüksek sıcaklıkta kristaleştiği gözlenmiştir. Sinterlenmiş örneklerin bağıl yoğunluğu ve görünür gözenekliliği de ölçülmüştür. Dielektrik sabitleri ölçümlerinden plagioclase ve spinel fazlarını içeren numunelerden iyi yalıtkanlar hazırlandığı görülmüştür.

REFERENCES

1.Kopeky L. and J., Voldan, 1964 "The cast basalt industry", Ann. N. Y. Acad.Sci.,1088-1105.

2.Berezhnoi,A.I., 1970 "Glass-ceramics and photositalls" ; Plenum Press, N.Y.

3.Beall, G.H. and H. L., Rittler, 1971 "Process for forming a basaltic glass ceramic product"; U.S.Patent 3.557,579, Jan26.

4. Beall, G.H. and H. ., Rittler, 1976 "Basalt glass-ceramics"; Am. Ceram. Soc. Bull. 55: 579-82.

5.McCollister, H.L.1977, "Method of making glass-ceramics from modified basalt"; U.S. Patent (19)4009015.Feb.

6.Yilmaz, S.; O. T. Ozkan, and V. Gumay , 1996 "Crystallization kinetics of basalt glass" Ceramics International 22: 477-481.

7.El-Shennawi, A.W.A.,1970 "Crystallization in some molten Egyptian basalts"; M.Sc. Thesis, Cairo Univ./Egypt.

8. Omar, A. A. and A. W. A., El-Shennawi 1971 " Glass ceramic material based on Abu-Zaabal basaltic rocks"; Nature, Phys. Science,231, May 10:44.

9. Abdel-Hameed, S. A. M. 1995 " Controlled crystallization of some Egyptian basalt based glasses"; M.Sc. Thesis, Zagazig Univ./Egypt.

10. Abdel-Hameed,S. A. M.2000 " Effect of some nucleation catalysts on crystallization of different modified basaltic glass-ceramic compositions" Ph.D Thesis, Ain-Shams Univ./Egypt.

11. Read, R.F. 1980 U. S. Patent 4187115 " Anorthite glass ceramics" February 5.

12. El-Shennawi, A.W.A., M. M. Mandour, and S. A.M. Abdel-Hameed, 1999,"Basalt-basalt monopyroxenic glass-ceramics" J.Am.Ceram.Soc.,82:1181-86.

13. Schwartz, B. 1984 "Review of multilayer ceramics for microelectronic packaging", J. Phys. Chem. Solids, 45:1051-68 .

14. Bodgett, A.J., Jr., 1980,"Multi-chip module" 283-85 in Proceedings of the 30Th Electronic Components Conference, IEEE, New York, vol.30.

15. Scholze, H.N.Y.,1991 "Glass: Nature, Structure, and Properties" Springer-Verlag Inc.,New York.

Table (1) Chemical Composition of The Rectified Basaltic Pyroxene Glass; in wt.%.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2
Wt.%	44.06	12.88	10.65	19.13	5.48	4.14	0.63	3.03

Table (2) Chemical analysis of raw materials.

Raw Oxide wt%	Ab Zaabal Basalts	Samalout Limestone
SiO_2	50.26	0.27
TiO_2	3.46	-
Al_2O_3	14.73	0.39
Fe_2O_3	3.96	-
FeO	7.37	-
MgO	6.25	0.18
CaO	10.79	99.16
Na_2O	2.46	-
K_2O	0.72	-

Table (3) Dielectric Constant and Phases Developed of Different Composites at Different Heat-Treatment Parameter.

Sample	Heat-treatment parameter °C/h	Dielectric constant at 10kHz	Phases developed
7/3M	900/2	65.503	au +M +Cr
7/3M	1300/2	4.756	Pl +M +Cr
6/4M	1300/2	5.088	Pl +M +Cr
5/5M	1300/2	5.279	Pl +M +Cr

au= Augite, M=Mullite, Pl=Plagioclase, and Cr=Cristobalite.

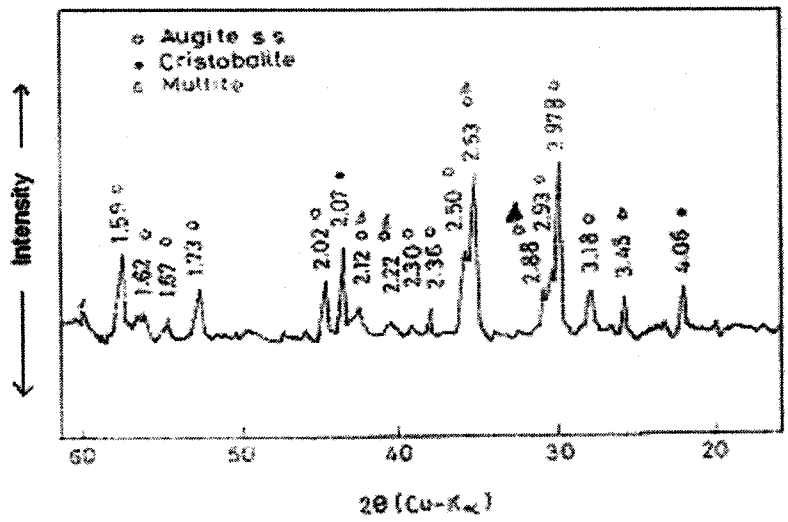

Fig.(1) X-ray diffraction pattern of 7/3 M sample heat-treated at 900°C/2h.

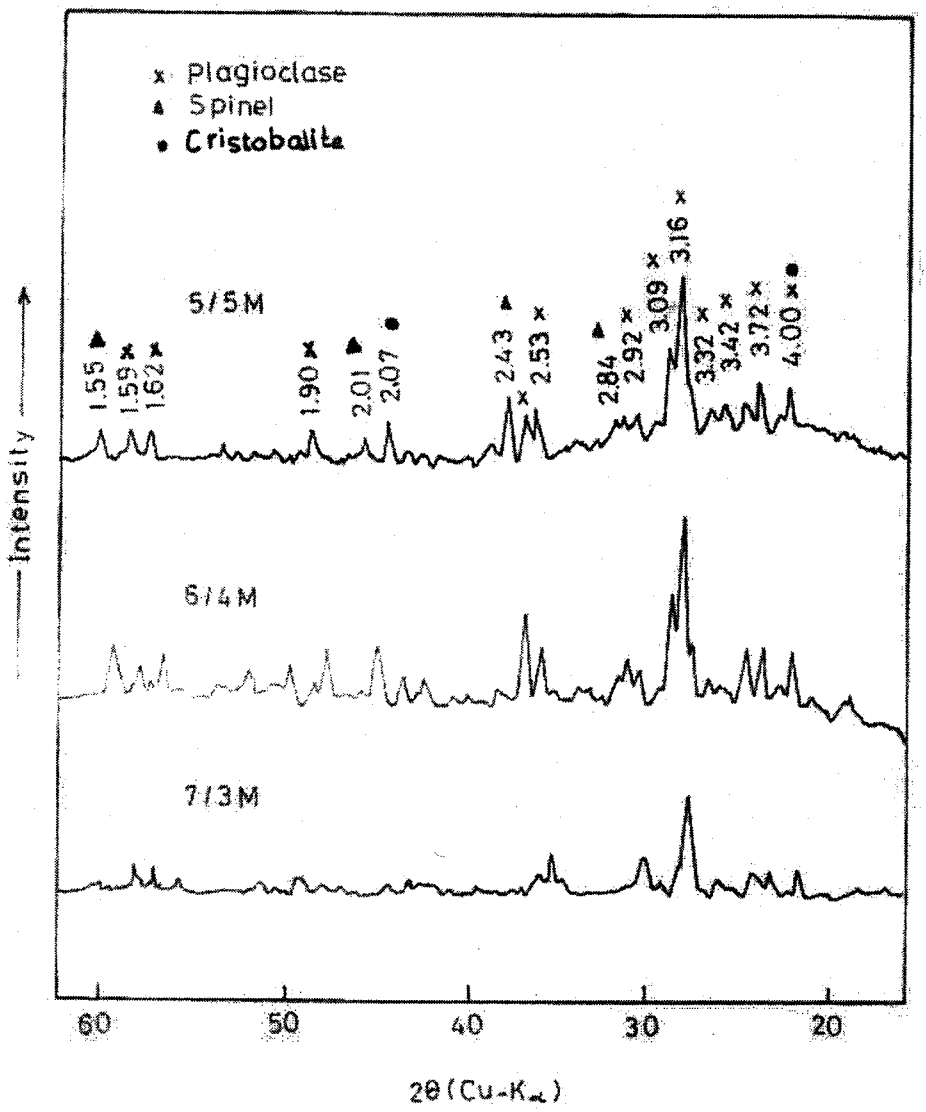

Fig.(2) X-ray diffraction pattern of 7/3 M, 6/4M and 5/5M samples heat-treated at 1300°C/2h.

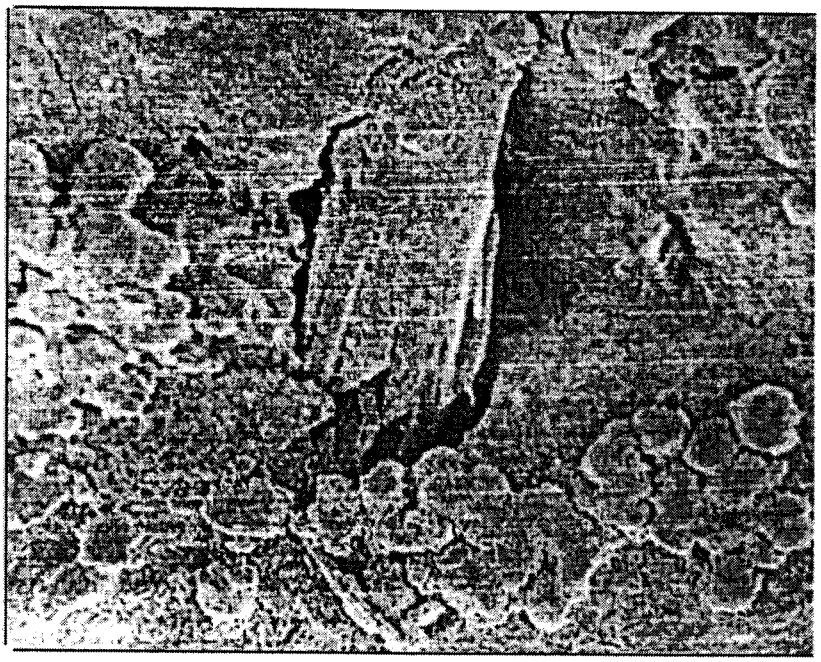

Fig.(3a) SEM of 5/5M sample heat-treated at 1300°C/2h (X750).

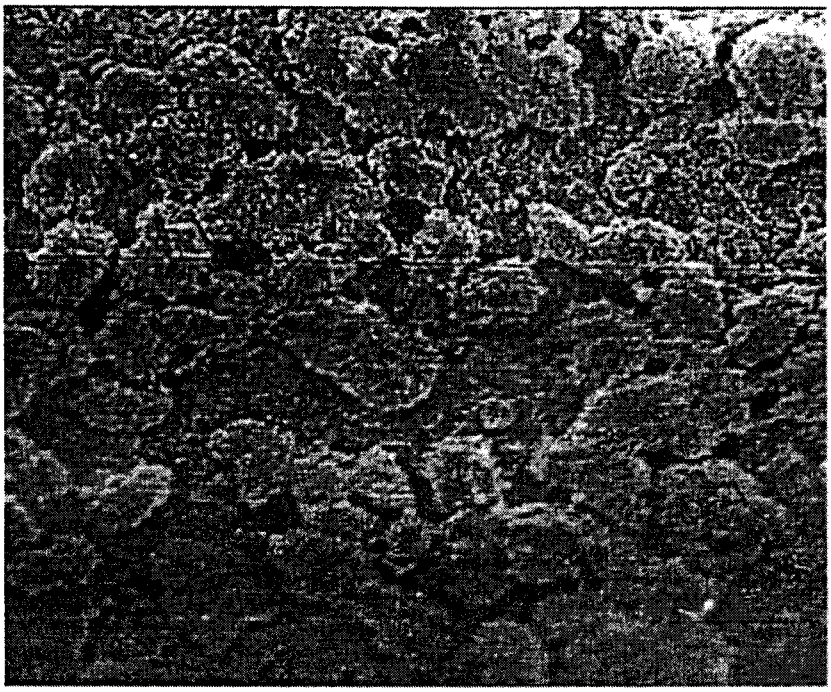

Fig.(3b) Another zone from the above sample at higher magnification (X1000).

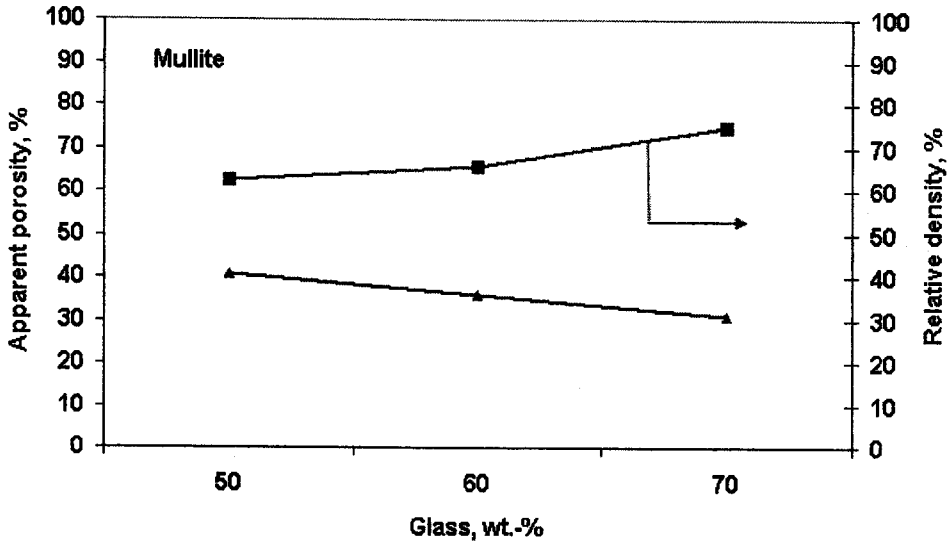

Fig.(4) Relative Density and apparent porosity of glass/mullite composites sintered at 1300°C/2h. with different glass wt.%.