

Mechanical properties Of Nepheline Syenite-Limestone Glass-Ceramic And Its Use In The Sidewalk Tiles And Curb Stones

Ass. Prof. Dr. Hanaa A. El Kazazz

Helwan University, Faculty of Applied Arts,
Glass Dep., P.C.12612,Cairo, Egypt

Prof. Dr. Esmat M. A. Hamzawy

National Research Center, Glass
Research Dep. Dokki P.C.12622, Cairo,
Egypt

1. Abstract:

Sidewalk is the most essential component of the street and it reflects how much the country is civilized and developed, the more the country is advanced the use of the sidewalk is easier and there is an inverse relationship between the height of the sidewalk and the development of the country. The higher the sidewalk the undeveloped and uncivilized the country. For a long time Egypt has been suffering from the absence of sidewalks which can be used by passers-by from the elderly, children and the handicapped, or even utilize it by going up and down comfortably; because of its high height which sometimes exceeds 60 cm, the pedestrians suffered during the ups and downs, even in affluent areas which characterized by a large number of foreign embassies such as El Maadi, critical areas such as Ramses, as we can see in the research's pictures.

Crystallization of glasses based on processed nepheline syenite -limestone raw materials and doped with TiO₂ were experimented. wollastonite, nepheline, melilite, prevoakite and hematite were formed in these heat -treated glasses. The coefficients of thermal expansion CTE, microhardness and densities are reported for such glasses and the corresponding glass-ceramics. Variation of glass compositions and the glass-ceramic phases modify the CTE and microhardness too. Nine batches were designed; the best mechanical properties one was chosen to make the curb stones and the sidewalk tiles. Several designs for the proposed sidewalk were inspired from motifs of ancient Egyptian civilization, one of the most prestigious civilizations all over the world.

Key words: Glass-ceramic, sidewalk tiles-curb, design

1- Introduction:

Since the dawn of history, the known of human civilization and progress, and more than seven thousands years; Egypt was a beacon of science and knowledge, so Egypt deserves to be on a par with the developed world in the existence of well designed sidewalk which passers-by can use and utilize it by going up and down on it comfortably. However, there is an international standard measurement to design the sidewalk; the height of the sidewalk should not be high so the children, old people and handicapped (يدي ماغلا، 1420) can go ups and downs easily. For a long time Egypt has been suffering from the lack of proper sidewalks in most streets, because of the sidewalk's height and the disqualification of the sidewalk's floor. **So the research problem clears as:** The lack of proper sidewalks in the Egyptian streets, which passers-by can use comfortably. Therefore, **the research's goal is:** to produce a glass-ceramic batch suitable for using in sidewalks tiles and curb stones and using it in designing the sidewalk taking into account the international standards (height- width), in order to achieve both functional and aesthetic requirements.

The importance of the search coming from: the fact that the sidewalk is an essential component in the street and the attention must be paid in order to

achieve a passers -by comfort in using the sidewalks, and to highlight the proper image and prestige of Egypt. Generally, devitrification must be avoided in glasses that are used in several applications, but in producing glass-ceramic controlled devitrification is essential, crystallized glass is desired in many fields of applications. Glass-ceramic materials formed at least in two steps; glass melting and forming process followed by careful controlled crystallization. Therefore, not only the glass-ceramic process is more expansive than that of glasses, but also needs reliable mind in mineral-chemical bases. Physical and chemical properties of glass-ceramics depend primarily on composition. Such properties play an important role in direct the article to different purposes of applications. Nepheline syenite was evaluated according to the chemical composition and grain size for ceramic industry (Firat Burat et al, 2006) . The fluxing contents in nepheline syenite mean that it is desirable for preparation porcelain stone ware body mix (Esposito, 2005). Crystallization of nepheline syenite -dolomite glasses was difficult in absence nucleation, however, LiF has maximum effect on the crystal growth whereas, Cr₂O₃ in its small quantity (0.5%), gives high dense nucleant and good quality glass-ceramic (El-Shennawi et al, 2001). Glass-ceramic based on the processed nepheline syenite-limestone glasses show the crystallization of wollastonite and nepheline in

the lowest $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio, where as melilite and hematite were appears in the glasses containing high $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio, however, perovskite appears in the glasses doped by TiO_2 (Hamzawy, 2005). Crystallization of glasses based on nepheline syenite-magnesite gives aluminum diopside $[\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6]$, nepheline, forsterite, magnesium titanate MgTi_2O_5 and hematite of uniform fine microstructures (Hamzawy and Khater, 2005).

2. Experimental work:

The investigated glasses were prepared from processed nepheline syenite, i.e. Non-magnetic, middling and tailing

fractions, and limestone with some little commercial TiO_2 Table (1). The weighed

batches were thoroughly mixed and were melted in Pt crucibles in electrically heated globar furnace at 1400-1450°C for 3 hours with occasional stirring. Fig. 1 (a, b) shows base glass samples and glass ceramic samples (NLF0, NLFT1,NLFT2, NLM0, NLMT1 and NLMT2 respectively).

Measurements of coefficient of thermal expansion CTE (α) were made on a Linseis dilatometer (model L76/1250) at heating rate 5°C/min. Microhardness of glass and glass-ceramic was measured using a Shimadzu (model type-M, Japan). The densities of glass and glass-ceramic were determined at room temperature by Archimedes method using xylene as fluid.

Table (1) Chemical composition of base glass batches oxides wt. %.

Sample Code	Chemical composition of the glass batches Oxides in wt %										
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂ 1
NLF0	43.42	0.01	16.73	0.33	0.01	0.06	27.79	6.99	4.56	0.09	----
NLFT1	43.42	0.01	16.73	0.33	0.01	0.06	27.79	6.99	4.56	0.09	4.00
NLFT2	43.42	0.01	16.73	0.33	0.01	0.06	27.79	6.99	4.56	0.09	8.00
NLM0	43.92	0.14	10.56	3.31	0.01	0.06	29.85	7.37	4.46	0.14	----
NLMT 1	43.92	0.14	10.56	3.31	0.01	0.06	29.85	7.37	4.46	0.14	4.00
NLMT2	43.92	0.14	10.56	3.31	0.01	0.06	29.85	7.37	4.46	0.14	8.00
NLT0	38.86	0.65	7.30	15.26	0.35	0.76	27.58	5.54	3.60	0.09	----
NLTT2	38.86	0.65	7.30	15.26	0.35	0.76	27.58	5.54	3.60	0.09	4.00
NLTT2	38.86	0.65	7.30	15.26	0.35	0.76	27.58	5.54	3.60	0.09	8.00

TiO₂ added gram per 100% glass batch oxide gram, TiO₂ added over 100% glass oxides

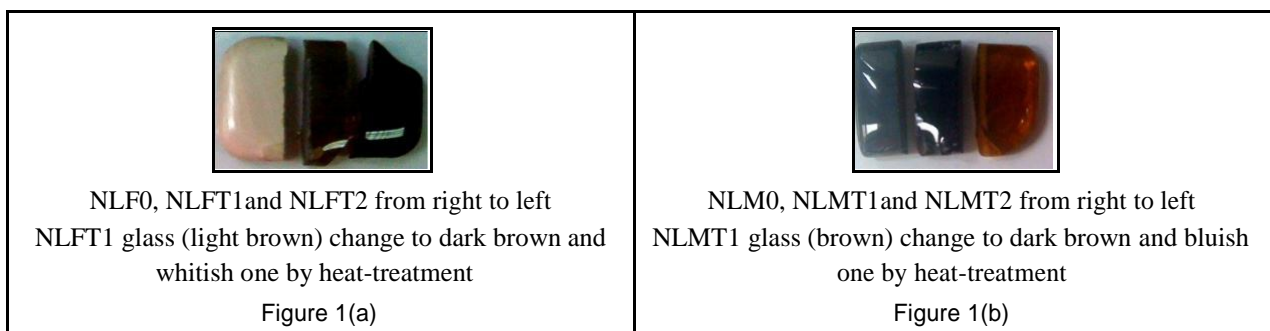


Fig. 1 (a, b) samples (NLF0, NLFT1,NLFT2, NLM0, NLMT1 and NLMT2 respectively)

3. Results and Discussions:

3.1.1. CTE of the base glasses:

The coefficient of thermal expansion CTE, the dilatometric transformation T_g and softening T_s temperatures , The CTE values were in the 8.8 to 10.5 and 9.6 to 11.4x 10⁻⁶°C⁻¹ in the 20-300°C and

20-500 °C range respectively are given in Table (2). On the other hand, the T_g °C and T_s °C range 553 - 620 and 589 – 668 °C respectively. In figure (2), the T_g°C and T_s°C as well as CTE (α) values are reported as a function of the composition, expressed with respect to Al/Fe ratios.

Table (2) Thermal expansion properties of the NLF0, NLM0 and NLT0 base glasses

Glass Code	Transition (T _g) °C	Softening (T _s) °C	CTE(α) $\times 10^{-6} \text{ } ^\circ\text{C}^{-1}$	
			20-300 °C	20-500 °C
NLF0	620	668	8.8	9.6
NLM0	605	657	9.6	10.3
NLT0	553	589	10.5	11.4

From table (2) we deduce that gradual decrease in both the transition T_g and softening T_s temperatures with gradual increase in the CTE from NLF0 to NLT0 sample that is accompanied by decrease in the Al₂O₃ / Fe₂O₃ ratio of the glass (Table 1). Thermal expansion of glass is a complex property depends mainly on the internal network structure, the arrangement of the individual building unit and their bonding to each other. In silicate glasses, the CTE values increases with the decrease of the electrostatic bond strength (= ionic valency of the cation divided by its coordination number) of the cations in the glass structure (Takashi, 1953). For this response, the value of electrostatic bond strength of Al and Fe are similar (3/4). Depending on the bond strength of Al—O (= 511±3 D₂₉₈/KJ mol⁻¹) and Fe—O moles (= 390.4 ±17.2 D₂₉₈/KJ mol⁻¹) respectively, (Cocke et al 1973) the high value the stronger bond the low value the weaker bond.

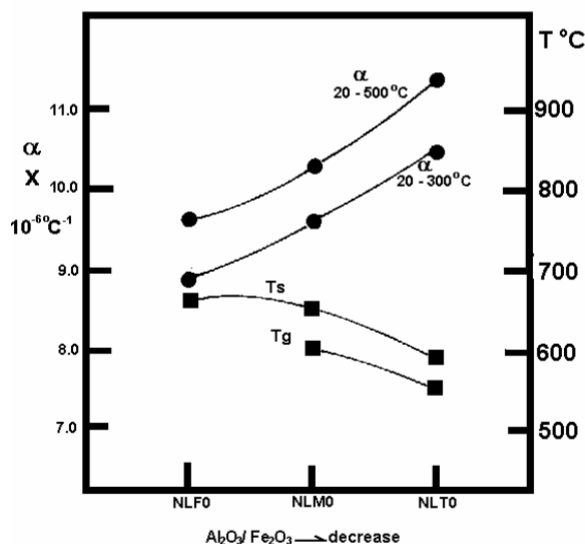


Fig.(2) CTE curves and thermal effect of the NLF0, NLM0 and NLT0 base glasses.

In addition to the bond strength the electropositivity of Al is higher than of Fe (electronegativity of Al and Fe is 1.61 and 1.8 respectively, Pauling, 1960). In glasses, aluminum may act as a glass-former and it has high facility for formation the covalent bond than iron, which is stronger than the ionic bond.

Therefore, the effect of the Fe contents on the increasing the thermal expansion values and decreasing the T_g and T_s temperatures may be explained on the basis of later two factors ; the bond strength and the electropositivity. The successive increase of Fe₂O₃ will introduce weaker Fe-O bond which results in a much less rigid, loosely compact nature of glass structure, leading to higher expansion coefficient values and lower T_g and T_s temperatures.

Fig.2. shows CTE curves and thermal effect of the NLF0, NLM0 and NLT0 base glasses.

3.1.2. CTE of crystalline base glasses:

The CTE of NLF0, NLM0 and NLT0 glasses after heat-treatment at 1000 °C for 3 hours and the corresponding crystalline phases are listed in Table (3). The thermal expansion of glass-ceramic materials is influenced by the dominated phases, the minor phases and the residual glass in between.

The CTE of NLF0 sample, containing wollastonite as a major phase with subordinate nepheline, was 8.6 to 10.0 $\times 10^{-6}$ in the 20 to 700 °C ranges. However, crystallization of nepheline, as a main phase with some wollastonite and little melilite in the NLM0 sample, increase the expansion coefficient from 10.5 to 11.6 $\times 10^{-6}$ in the 20 to 700 °C ranges. Crystallization of melilite as a major phase in the NLT0 sample decrease the expansivity to 8.9 - 9.6 $\times 10^{-6}$ in the 20 to 700 °C ranges too. The later results show that, domination of nepheline increase the CTE in NLM0 sample but relative decrease occurs when wollastonite or melilite become dominant in NLF0 and NLT0 samples. The demonstrated curves drawn in Figure 3, which roughly interpolate the measured data of α , show that the increase of nepheline percent in NLM0 glass-ceramic sample increase the value of α at all temperature range. The recorded CTE of wollastonite is 9.4 $\times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (McMillan, 1979) and is 9.1 - 16.6 $\times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ for nepheline NaAlSiO₄ (Duke et al, 1967).

3.1.3. CTE of the crystalline TiO₂-containing glasses:

The coefficient of thermal expansion CTE of the former base glasses containing TiO₂ ; NLFT2, NLMT2 and NLTT2, were listed in Table (3) and represented by drawn curves in Fig (4).

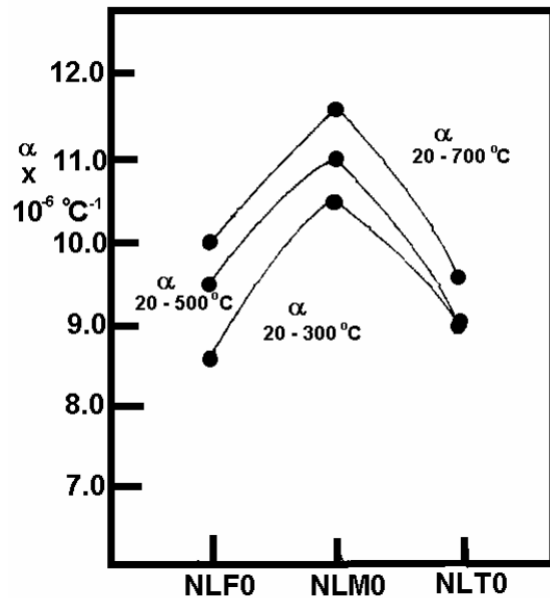


Figure (3)

Fig (3) CTE curves of the NLFO, NLM0 and NLTO base glasses heat-treated at 1000 °C / 3h .

Table (3) Coefficient of thermal expansion of TiO₂-containing base glasses heat- treated at 1000 °C for 3 hours

Glass code	CTE (α) x 10 ⁻⁶ °C ⁻¹			Developed Phases
	20-300 °C	20-500 °C	20-700°C	
NLFO	8.6	9.5	10.0	Wo-Ne
NLFT2	9.7	10.4	11.1	Wo-Ne-P
NLM0	10.5	11.0	11.6	Ne- Wo-Me
NLMT2	9.8	10.1	10.5	Ne-Wo-P-He(I)
NLTO	8.9	8.9	9.6	Me-Ne-Wo-He
NLTT2	9.6	10.1	10.6	P-He-Ne-Me-Wo

Table (4) Microhardness and densities of the present glasses and glass-ceramics(after heat-treatment at 1000 °C for 3 hours) VH= Vicker's microhardness D= Density

Sample code	(VH kg/mm ²)		D (g/cm ³)		Developed Phases
	Glass	Glass-Ceramic	Glass	Glass-Ceramic	
NLFO	724	780	2.720	2.702	Wo-Ne
NLFT1	724	724	2.760	2.747	Wo-Ne-P
NLFT	702	618	2.782	2.764	Wo-Ne-P
NLM0	748	824	2.774	2.778	Ne-Wo-Me
NLMT1	724	862	2.781	2.754	Ne-Wo-P-Me
NLMT	714	852	2.803	2.774	Ne-Wo-P-He
NLTO		583	2.928	2.923	Me-Ne-Wo-He
NLTT1		641	2.934	2.904	Me-P-He-Ne-Wo
NLTT2		606	2.950	2.951	P-He-Ne-Me-Wo

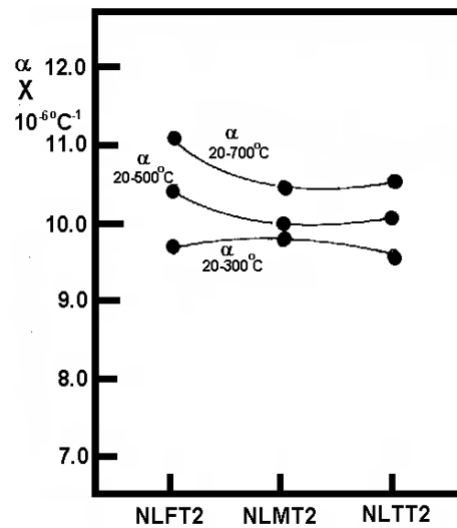


Figure (4)

Fig. (4) CTE of TiO₂ containing-glasses heat-treated at 1000 °C / 3h.

Comparing between TiO₂-containing samples, TiO₂ catalyze the crystallization of nepheline, the coefficient of thermal expansion α increase in the NLFT2 sample due to the increasing of nepheline content. On the other hand, formation of TiO₂ containing phases like perovskite and hematite (titanhemaite contains TiO₂) led to relative decreases of α in NLMT2 and NLTT2 samples.

3.2. Density of glasses and glass-ceramics:

The measured density of glasses and glass-ceramics are given in Table (4). Fig.5. shows the densities of glass and the corresponding glass-ceramic. In the present glasses, the density increases with an increase of iron content. Density of the corresponding glass-ceramics increases in a way similar to glass but with relatively little decrease in its values Fig (5).

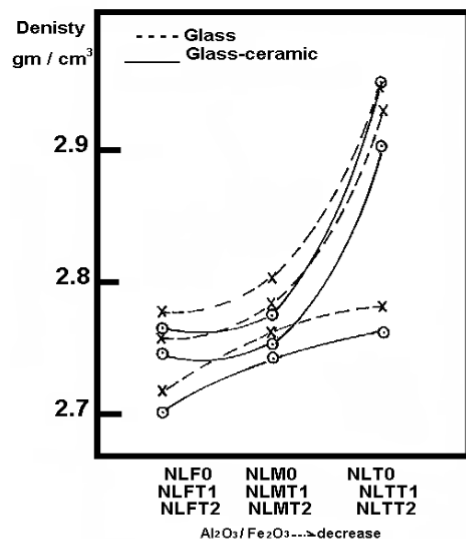


Figure (5)

Fig. (5) Densities of base and TiO₂ containing - glasses before and after heat-treatment at 1000 °C /3h.

The recorded densities of the formed phases (hematite: 4.9-5.3 g/cm³; perovskite: 4.00 g/cm³; melilite: 2.9 -3.0 g/cm³; wollastonite: 2.8-2.9 g/cm³; nepheline : 2.6 g/cm³, Deer et al, 1992) are of different values. However, whereas nepheline has the lowest value and hematite has the highest value, The present results show that crystallization of nepheline and wollastonite alone has the lowest value 2.702 g/cm³, whereas in case of domination the perovskite and hematite the maximum value attain 2.951 g/cm³.

3. 3. Microhardness of glasses and glass-ceramics:

The microhardness of the present glasses are between 702-748 kg/mm² and 862 -618 kg/mm² for the corresponding glass-ceramics Table (4), in comparison with the compositions, the Vickers's values may be depending on the Al/Fe ratio. The high values are these containing highest aluminum contents and the lowest values are these containing the highest iron contents, in corresponding glass-ceramics, the values depend on the dominant phases. Samples containing nepheline as a dominant phase gives highest values, where as domination of melilite, hematite and perovskite has lower values. As mentioned in table (4).

Nine glass and glass - ceramic samples were produced to choose the best of them for the applied work, samples were chosen to produce sidewalk tiles and curb¹ (ITE, 1997) glass ceramic stones were (NLF0, NLFT1,NLFT2, NLM0, NLMT1 and NLMT2).

4- Comparing sidewalks in Egypt, Finland,

¹ curb stones is a line of stones or concrete forming an edge between a pavement and a roadway, so that the pavement is some 15 cm above the level of the road

Australia and Turkey:



Figure (6)

Fig. (6) shows that the advertisement board takes almost half of the sidewalk's width and the electric wires took the other half, so pedestrians do not have any room to walk or pass through (Maadi Egypt).



Figure (7)

Fig. (7) shows that the curb sidewalk is broken, the sidewalk floor's level is not homogenous and there are missing floor tiles (Maadi Egypt).



Figure (8)

Fig. (8) shows how the sidewalk is damaged and is not designed correctly and we can see that the street lights located very close to the trees, it's that tight that nobody could pass through it.



Figure (9)

Fig. (9) shows that the width of the sidewalk is not

consistent with the standard measurements. The sidewalk's width is less than 1 meter and it should not be less than 1.5 meters (AASHTO, 2001).



Figure (10)

Fig. (10) shows that the sidewalk has a ramp, however by assessing the distance between the street lights and the curb sidewalk. The outcome clearly shows the width of the sidewalk is too narrow to be utilized by pedestrians. (Lalani, N, 2001).



Figure (11)



Figure (11 -1)

Figs (11, 11-1) show how much do the Egyptian pedestrians suffer from the height of the sidewalk and show also that the pavement of the sidewalk has a winding surface, from all the previous pictures we can see that the edge of the curb is too sharp and does not have a ramp (Ramses Egypt), (www.un.org).



Figure (12)

Fig. (12) shows a sidewalk in Tampere Finland in front of the main conference hall, the sidewalk's width is 3 meters and its height does not exceed 10 cm.

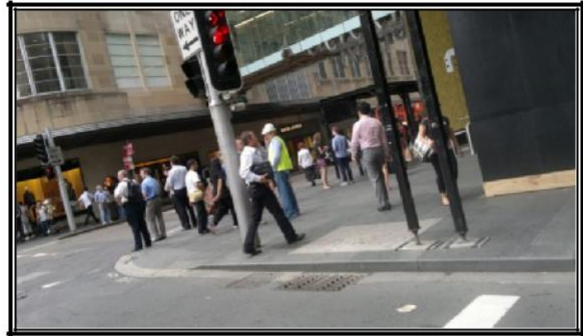


Figure (13)

Figs. (13, 14) shows the large width of the sidewalk, its short height less than 15 cm and shows also the good ramp it has (Australia).

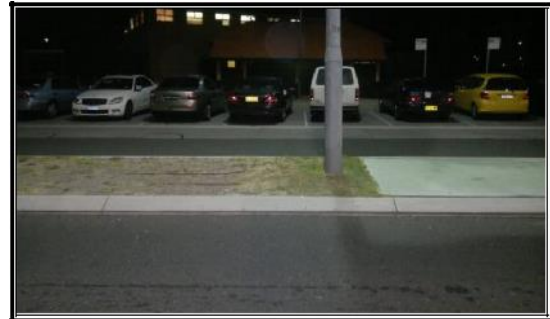


Figure (14)



Figure (15)

Fig. (15) shows a sidewalk in Anadolu University Turkey, its width is 2 meters, its height does not exceed 15 cm, every sidewalk has 2 ramps one at the beginning and one at its end.

By comparing between figs (6, 7, ..., 11) which showed some sidewalks in Egypt and (12,13, 14, 15) which showed sidewalks in Finland, Australia and Turkey we can feel how much do the Egyptian pedestrians suffer.

5. Applied glass ceramic samples:

According to the chemical compositions of the batches in table (1) we have prepared 500 gm from samples NLFT2 and NLM0. The weighed batches were thoroughly mixed and were melted in refractory crucibles using an electric furnace at 1400-1450°C for 3 hours with occasional stirring.



Figure (16)

Fig. (16) shows Applied glass ceramic samples 10X10 cm (NLFT2 sample).

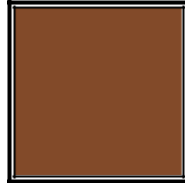


Figure (17)

Fig. (17) shows Applied glass ceramic samples 10X10 cm (NLM0 sample).

6- Proposed sidewalk curbs and tiles designs:

6-1 Proposed sidewalk curbs design:

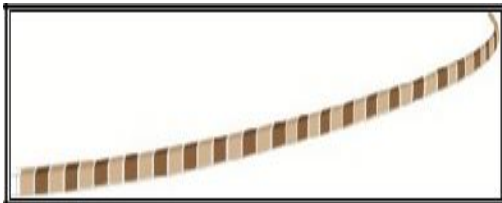


Figure (18)

Figure (18) a proposed curb sidewalk designed by using Auto Cad and Photoshop programs



Figure (19)

Figure (19) a sketch for the curb sidewalk using Lotus Egyptian flower



Figure (19-1)

Fig (19 -1) a proposed sketch for the curb sidewalk using Lotus Egyptian flower.

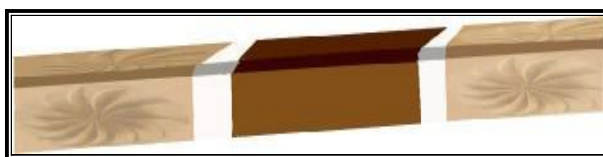


Figure (20)

Figure (20) a sketch for the curb sidewalk taking a part from the Lotus Egyptian flower and repeat it in a circular way



Figure (20 -1)

Fig (20 -1) a sketch for the curb sidewalk taking a part from the Lotus Egyptian flower and repeat it in a circular way

6- 2 Proposed sidewalk tiles designs:



Figure (21)

Fig (21) shows a plan to the proposed sidewalk, using some Pharaonic ornaments which depend on Lotus Egyptian flower.



Figure (22)

Fig (22) shows another plan sketch to the proposed sidewalk using some Pharaonic ornaments.

7- Conclusions and future perspectives:

Glasses and glass ceramics based on processed nepheline syenite-limestone raw materials and doped with TiO₂ were produced. wollastonite, nepheline, melilite, prevoskite and hematite were formed in these heat-treated glasses. The coefficients of thermal expansion CTE, microhardness and densities were reported for such glasses and the corresponding glass-ceramics. Variation of glass compositions and the glass-ceramic phases modify the CTE and microhardness too. Nine batches were designed; the

best mechanical properties one was chosen to make the curb stones and the sidewalk tiles. Some designs for the proposed sidewalk were inspired from the ancient Egyptian motifs (Lotus flower and other geometric ornaments). The sidewalk should be four feet wide, four inches thick except through driveway sections; it should be six inches thick. We hope that every sidewalk in Egypt follow the international standards so the Egyptian people will not suffer again from the sidewalks.

8. References

1. .يدماغلا يء ديعسد (1420 هـ) : ئداود رورملا في فءة كلمملا
تغيرملا تيدوعسلا: بابسلأا راتلاؤ لولحلاو. تئيدم كلمملا
زيزعلا دبع مولعلا تئيقنلاو، ضايرلا،
2. AASHTO(2001): A Policy on Geometric Design of Highways and Streets. American Association of State Highway and Transportation Officials, 4th ed., Washington, D.C.
3. Cocke, D.L.; Gingerich, K.A.; Kordis, J., (1973): Determination of the high bond dissociation energy of the molecule LaRh, High Temp. Sci., 5, 474.
4. D. A. DUKE, J. F. MacDowell, B. R. KARSTETTER, (1967) : Crystallization and Chemical Strengthening of Nepheline Glass-Ceramics Journal of the American Ceramic Society Volume 50, Issue 2, pages 67–74, February.
5. EL-Shinnawi A. W. A. ; Omar A. A. ; E. M. A. Hamzawy. (2001) : Effect of Cr₂O₃, ZrO₂ and LiF on nucleation and crystallization of nepheline syenite-dolomite glass-ceramic compositions. Glast. Berich., vol. 74, no11-12, pp. 317-323 .
6. Esposito L., Salemb A., Tuccia A., Gualtieric A., Jazayerid S.H. (2005): The use of nepheline-syenite in a body mix for porcelain stoneware tiles. Ceramics International 31(2005), 233-240.
7. Firat Burat , Olgac Kangal and Guven Onal, (2006) : An alternative mineral in the glass and ceramic industry: Nepheline syenite. Minerals Engineering 19, 370-371.
8. Hamzawy E. M. A. and Khater G.A. (2005) : Crystallization of Processed Nepheline Syenite-Magnesite Glasses” Advances in Applied Ceramics, V 104 (6) , p 177-181.
9. Hamzawy E. M. A. (2005): Crystallization of Processed Nepheline Syenite - Limestone Glasses. Ceramurgia and Ceramica Acta , C+CA , XXXV 3, p169-177.
10. ITE,(1997): Traditional Neighborhood Development: street design Guidelines. Institute of Transportation Engineers, Washington, D.C.,.
11. Lalani, N . (2001): Alternative Treatments for At-Grade Pedestrian Crossings. The ITE Pedestrian and Bicycle Task Force. Institute of Transportation Engineers, Washington, D.C.,.
12. McMillan, M.W (1979): "Glass-ceramic", Academic Press, London 2nd edition.
13. Pauling L.(1960): The Nature of the Chemical Bond 3rd ed., Cornell University Press.
14. W.A. Deer, R.A Howie and Zussman (1992): An introduction to the rock forming minerals. Prentice Hall N.Y.
15. www.un.org. (2003): A Design Manual for Barrier Free Environment