EFFECT OF THE COMPOSITION OF RAW MATERIALS AND NUCLEATING AGENTS
Crystallization behavior of nepheline-pyroxenic glass

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Abstract

Different combination of raw materials and nucleating agents were incorporated in the batch of nepheline-pyroxene glass to demonstrate their effect on the crystallization process. The effect of TiO_2, Cr_2O_3 and LiF with respect to crystallization of base glass was studied by differential thermal analysis (DTA). These materials improved the crystallization of glass between 50 to 150°C of heat treatment. When $LiF+TiO_2$ and $TiO_2+Cr_2O_3$ were put together in the glass batches, the rate of crystallization of glass was increased in the same manner. The presence of $TiO_2+LiF+Cr_2O_3$ improved the crystallization of the glass by decreasing the heat temperature by about 60°C. CaO/MgO and CaO/Na_2O ratios played an important role in the rate of crystal growth. The increase in the CaO/MgO ratio lowers the crystallization temperature by values ranging between 37 and 46°C.

Keywords: base glass, crystallization, DTA, nepheline-pyroxene glass

Introduction

The glass-ceramic technology is considered to be revolutionary among the existing glass industries. Recently, its technological importance has also been recognized in the fast growing nations like the Kingdom of Saudi Arabia with its ultimate objective of further improvement in the light of modern technology and industries. Limited work has been carried out in the Kingdom of Saudi Arabia regarding the study of glass crystallization using batches, which are formulated from minerals and rocks. There is an urgent need to locate suitable industrial mineral deposits for the glass ceramic industry. For this purpose, the best quality of raw materials such as dolomite and feldspar, available in the Kingdom were used in the present study.

Glass-ceramics covers a wide range of materials made by heat treatment of glass to convert it in a controlled manner to a dense micro-crystalline body. The chemical composition of raw materials and nucleant additions, are the important factors affecting the microstructure properties of the glass. Efficient nucleation of crystals from numerous centers results in fine-grained micro-structures and provide high-strength materials. The earlier works [1–9] have described several ways in which TiO_2, LiF

and Cr_2O_3 react with glassy raw materials in different manners such as lowering the melting point and raising the crystallizability of the glass.

Many workers such as [11–13] have carried out research on the properties of the glass and the composition of raw materials. The value of the maximum rate of crystal growth changed markedly even with a small change in glass composition [10]. The batch composition of the glass is directly related to the chemical stability of the glass-ceramics. Several workers [11–13] found that the variation of viscosity with composition is completely different in different combinations of the glass batches. The evolution or absorption of energy in the form of heat accompanies chemical reactions within a crystalline glassy substance. When a substance crystallizes, an exothermic effect occurs while on melting of a crystal, it gives rise to an endothermic effect. Differential thermal analysis (DTA) was used to elucidate the temperature difference, peak height, and the amount of the heat liberated or consumed during the thermal process peak area. The objective of the present study was to study the effect of different nucleating agents and composition of raw materials on the thermal behavior of the nepheline-pyroxenic glass with the help of DTA.

Experimental

Batch composition and preparation

The batch composition (in relative ratios and in percentages) for the experimental work is given in Table 1.

Table 1 Batch composition of the base nepheline-pyroxenic glass-ceramics

Batch	Feldspar	Dolomite	Clay	Na_2CO_3
N1	1.3 (56.96)	1.0 (43.03)	– (–)	– (–)
N2	1.5 (57.48)	1.0 (38.46)	0.05 (2.02)	0.05 (1.92)
N3	1.0 (36.69)	1.1 (38.44)	0.55 (2.01)	0.13 (4.71)

Addition of nucleating agent per 100 g of glass oxides is shown in Table 2.

Table 2 Nucleating agent added in batch composition

Nucleating agent	Additions/g
TiO_2	6
Cr_2O_3	0.5
LiF	1.5
$LiF+TiO_2$	1.5+6
$TiO_2+Cr_2O_3$	6+0.5
$TiO_2+LiF+Cr_2O_3$	6+1.5+0.5

For the glass-ceramics preparation, locally available inexpensive raw materials such as feldspar, dolomite and clay with pure Na_2CO_3 for the nepheline-pyroxene group, were used as the starting batch materials. 90% contents of the raw materials of the batch were collected from different parts of the Kingdom. An adjustment of the chemical composition of the raw materials was performed by addition of a calculated amount of feldspar, dolomite clay and Na_2CO_3 to give nepheline-pyroxenic mineral molecules upon crystallization. In addition to the raw materials, pure chemical reagents such as TiO_2, LiF and Cr_2O_3 were also used in small amounts as nucleating catalysts separately or in combination as shown in Table 2. It may be mentioned that the role of the nucleating agents is to promote controlled crystallization of glasses.

Twenty-one glass compositions were formulated. Mixing of the batch was performed by pestle and agate mortar. The batch was thoroughly mixed by simple hand operation for 1 h. Different quantities of prepared batch materials were taken for the formation of 100 g oxide glasses. This batch was then poured in a platinum crucible where it was electrically heated in a furnace (Nethertherm 213L-1801 and HT 04/17) at a temperature of 1500–1650°C for five hours with an interval of half an hour swirling to ensure complete homogenization to get a bubble free melt.

Differential thermal analysis (DTA)

DTA was carried out using the computerized Perkin Elmer differential thermal analyzer (DTA) 7 series in a dynamic N_2 purging gas atmosphere (at a constant rate of 50 cm^3 min^{-1}). 70–80 mg of the powdered sample (0.09–0.25 mm), a heating rate of 10°C min^{-1} and Al_2O_3 as the reference material was applied in all DTA runs.

Results and discussion

Base glass without nucleating agents (N1, N2 and N3)

Differential thermal analysis traces of the glasses show that minor variations in peak positions and intensities in relation to the composition. It shows a small variation in glass transition (T_g) temperature between the three ranging from 685–715°C. They are batches followed by a wide range of low intensity exothermic effect with a maximum range between 811 and 889°C.

The broad nature of the exothermic peaks indicates the wide temperature span, over which crystallization may take place. The low peak height indicates that relatively long soaking times are needed to achieve a reasonable degree of crystallization.

Role of nucleating agents

TiO_2

The general assumption about TiO_2 as a nucleating agent in the glass batches is that it facilitates the melting point and homogenization of the melt. It also decreases the melting temperature by nearly 50–100°C [9].

The results of DTA analysis (1T, 2T and 3T) have supported the general assumption of TiO_2 being a nucleating agent in glass. This was evident by the increased crystallization of the glass. The exothermic crystallization peak was increased in intensity and shifted, at the same time towards lower temperature. The exothermic crystallization peak-temperature of specimen 1T, 2T and 3T decreased by 81, 124 and 78°C respectively compared with nucleating free glass. Titanium dioxide is regarded as having an intermediate effect in glass structures implying that some of Ti^{4+} ions occupy tetrahedral network-forming sites. Due to limited ability of Ti^{4+} ion to participate in tetrahedral networks, these ions tend to attract non-bridging oxygen ions, which leads to the lowering of crystallization on temperature [3].

This is in agreement with the earlier works [1–3, 6, 7], which have described several ways as to how TiO_2 reacted with glassy raw materials and how it decreased the melting point and raised the crystalizability of the glass. Also some workers, [8–9] came to the same conclusions when they used TiO_2 as the nucleating agent with several local Egyptian raw materials during the study of glasses. The study of Hillig [3] revealed that the mechanism of the action of TiO_2 crystals as a melting agent leads to speeding up the liquid–liquid phase separation in the glass and its subsequent crystallization.

LiF

A general effect of the introduction of fluorides to crystallize the glass can be attributed to the weakening effect on the glass network. Generally, the fluoride nuclei are formed at a temperature where the growth rate of the fluoride crystal is low so the fluoride is precipitated as a large number of very fine crystals rather then as few large crystals. The use of metallic fluorides in the crystallization of the glass has also been described. It also decreased the viscosity of the glass melt as fluoride may act like network breakers in the glassy anionic structure [14].

The effect of LiF on the crystallization of the nepheline-pyroxene (1L, 2L and 3L) can be seen in Tables 3a, b and c. It was found that the addition of LiF decreased the melting of 1L, 2L and 3L by 46, 94 and 60°C respectively. The bridging oxygens can be replaced by fluoride ions due to their similarity in radius without causing great disturbance in the arrangement of other ions. The result of this replacement of strong Si–O–Si linkage by a pair of the weak = Si–F can result in the weakening of the glass network structure. It was found that the addition of LiF to nepheline-pyroxene glass reduced the temperature of the crystallization by nearly 50–100°C. The difference in value of melting point was the compositional difference between 1L, 2L and 3L.

Cr_2O_3

In the present study, when Cr_2O_3 was added in batch glass the viscosity of the resultant melts was increased. The differential thermal analysis results showed that low percentage of Cr_2O_3 changed the crystallization kinetics of the glass, peak temperature and span of the DTA effects. The peak temperature of specimen 1C, 2C and 3C was found to be 692, 677 and 884°C respectively (Tables 3a, b and c). The value of variations between these peaks was due to the composition variation of raw materials.

Table 3a DTA results of nepheline-pyroxene glass

Sample No.	Raw materials	Nucleating agents	Onset/ °C	Glass transition temp. T_g/°C	Peak (1)/ °C	Peak (2)/ °C	Observation
N1	Feldspar, Dolomite	–	664	715	857	1048	Low-intensity exothermic effects
1T	Do	TiO_2 – 6 g	685	703	776	905	Increased the crystallizability
1L	Do	LiF – 1.5 g	601	638	806	970	Decreased the melting
1C	Do	Cr_2O_3 – 0.5 g	542	591	692	917	Highly intensified peak at low temperature
1TL	Do	TiO_2 – 6 g LiF – 1.5 g	624	652	806	979	Decreased the melting point
1TC	Do	TiO_2 – 6 g Cr_2O_3 – 0.5 g	658	705	827	897	Increased the crystallizability
1TLC	Do	TiO_2 – 6 g LiF – 1.5 g Cr_2O_3 – 0.5 g	595	629	853	977	Low intensity exothermic

Table 3b DTA results of nepheline-pyroxene glass

Sample No.	Raw materials	Nucleating agents	Onset/ °C	Glass transition temp. T_g/°C	Peak (1)/ °C	Peak (2)/ °C	Observation
N2	Feldspar, Dolomite, Clay, Na_2CO_3	–	650	685	811	1044	Very broad low-intensity exothermic effects
2T	Do	TiO_2 – 6 g	543	570	687	892	Increased the crystallizability
2L	Do	LiF – 1.5 g	574	594	704	839	Decreased the melting point
2C	Do	Cr_2O_3 – 0.5 g	536	559	677	900	Highly intensified peak at low temperature
2TL	Do	TiO_2 – 6 g LiF – 1.5 g	587	611	732	979	Low-intensity exothermic effects
2TC	Do	TiO_2 – 6 g Cr_2O_3 – 0.5 g	559	571	684	891	Decreased the melting point

Table 3c DTA results of nepheline-pyroxene glass

Sample No.	Raw materials	Nucleating agents	Onset/ °C	Glass transition temp. T_g/°C	Peak (1)/ °C	Peak (2)/ °C	Observation
N3	Feldspar Dolomite, Clay Na_2CO_3	–	647	685	889	1039	Low-intensity exothermic effects
3T	Do	TiO_2 – 6 g	625	677	811	911	Increased the crystallizability
3L	Do	LiF – 1.5 g	584	699	833	963	Decreased the melting point
3C	Do	Cr_2O_3 – 0.5 g	636	653	884	1035	Decreased the melting point
3TL	Do	TiO_2 – 6 g	619	642	841	980	Decreased the melting point
3TC	Do	Cr_2O_3 – 0.5 g TiO_2 – 6 g	626	661	839	979	Increased the crystallizability
3TLC	Do	TiO_2 – 6 g LiF – 1.5 g Cr_2O_3 – 0.5 g	594	633	837	979	Low-intensity exothermic

Cr_2O_3 may increase the extent of isomorphous substitution of the Ca containing Tschermark's molecule, $CaAlO_2SiO_6$, into the pyroxene structures, leading to enhancement of aluminous-pyroxene formation, at the expense of the basic ingredients of plagioclase. Sawai [5] has reported that 1–3 percent of chromic oxide could be successfully used to catalyze the crystallization of an aluminosilicate glass containing lithia potash and calcium oxide.
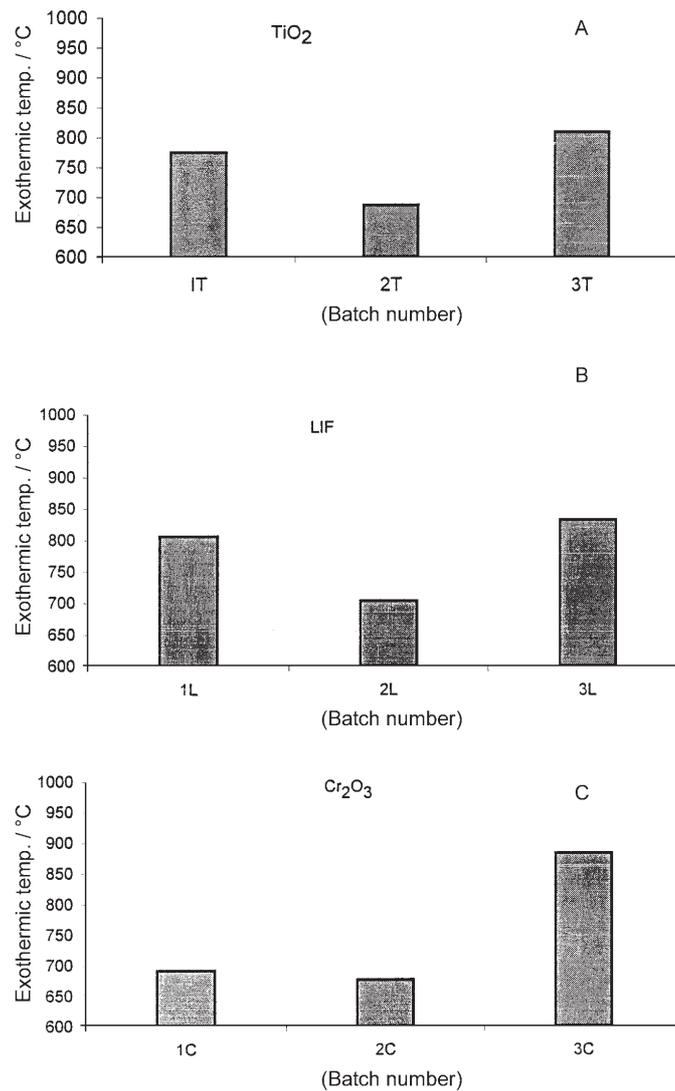

Fig. 1 Effects of nucleating agents on different batch composition of nepheline-pyroxene glass

The thermal effects of Cr_2O_3 containing glass were highly intensified and emerged at a low temperature in comparison with the very broad low intensity exothermic effects of the glass. The glass with the nucleating agent Cr_2O_3 has its crystallization temperature reduced by 165, 134 and 5°C receptively for 1C, 2C and 3C as compared to the nucleating free glass. Similar trends were found by Hamzawy [9] using DTA analysis.

Figures 1 (A, B, C) show the decrease in exothermic temperature when TiO_2, LiF and Cr_2O_3 were used as nucleating agents. Figures A, B and C show a maximum decrease in exothermic temperature in 2T, 2L and 2C followed by 1T, 1L and 1C and then 3T, 3L and 3C.

LiF+TiO_2

The endothermic and exothermic effects of glass were changed when LiF and TiO_2 were used as the nucleating agents. The nucleated glass endothermic value were 544, 627 and 625°C for ITL, 2TL and 3TL respectively. The exothermic crystallization points were 806, 732 and 841°C, respectively for which are lower than those of nucleating free glass. But very little variation occurred when it was compared with batch nucleated by LiF and TiO_2 separately. It was found that the melting point decreased and crystallizability increased, with the addition of both LiF and TiO_2 as the nucleating agent.

TiO_2+Cr_2O_3

When TiO_2 and Cr_2O_3 were added as nucleating agents, the endothermic temperature changed to 705, 571 and 661°C, for 1TL, 2TL and 3TL respectively. The exothermic crystallization temperature was also decreased to 827, 684 and 839°C respectively. These values are different from those obtained for the batch composition nucleated by TiO_2 and Cr_2O_3 separately. It is concluded, therefore, that the addition of the nucleating agent such as TiO_2 and LiF decrease the endothermic and exothermic values as shown in Tables 3a, b and c.

TiO_2+LiF+Cr_2O_3

When three nucleating agents (TiO_2+LiF+Cr_2O_3) were used, the endothermic temperature were recorded as 629, 627 and 621°C for 1TLC, 2TLC and 3TLC and the exothermic values which were 853, 793 and 837°C respectively corresponding to the 1TLC, 2TLC and 3TLC, as compared with the base glass (Tables 3a, b and c).

Figures 2 (A, B, C) show some values of exothermic temperature when a combination (TiO_2+LiF, TiO_2+Cr_2O_2+LiF) of nucleating agents is added in nucleating free batch instead of adding individual nucleating agents.

Figures 3A shows the maximum exothermic temperature for different batches when Cr_2O_3, TiO_2 and LiF are used as nucleating agents. Figure 3B shows almost the same values of exothermic temperature as Fig. 3A. Figure 3C shows the maximum exothermic temperature for different batch when TiO_2, LiF and Cr_2O_3 were used as nucleating agents.
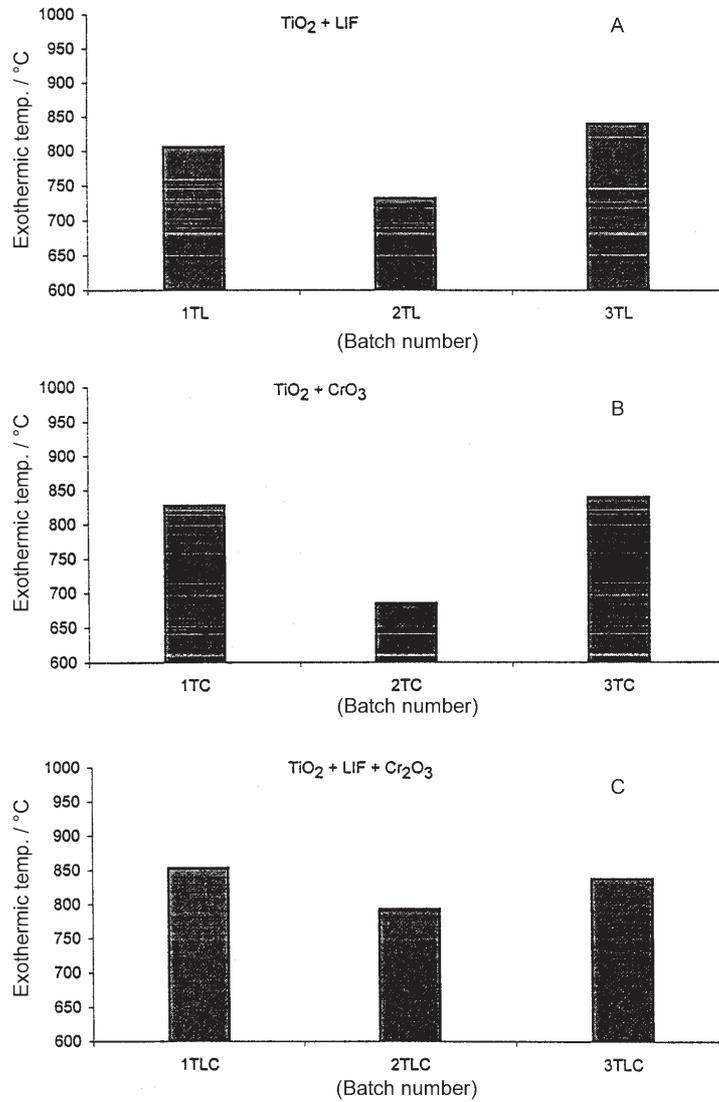
Fig. 2 A, B, C show the effects of nucleating agent on different batches

Figure 4A shows the maximum lowering exothermic temperature values for different batches as when TiO_2+LiF, $TiO_2+Cr_2O_3$ and $TiO_2+LiF+Cr_2O_3$ were used as nucleating agents. Figure 4B shows the maximum exothermic temperature for different batches as when $TiO_2+Cr_2O_3$, TiO_2+LiF and $TiO_2+LiF+Cr_2O_3$ were used as nucleating agents. Figure 4C shows almost the same values of exothermic temperature for

different batches when $TiO_2+LiF+TiO_2+Cr_2O_3$ and $TiO_2+LiF+Cr_2O_3$ are used as nucleating agents.
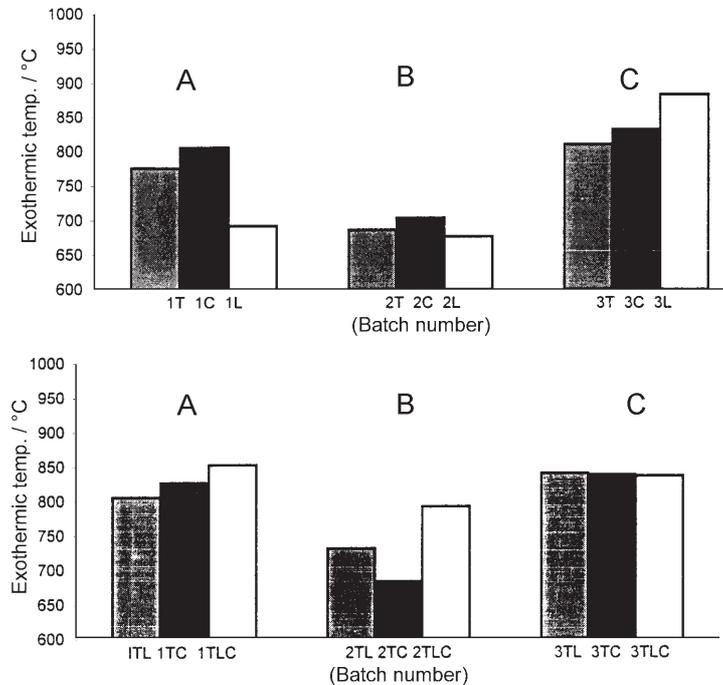

Fig. 3 A, B, C show the effects of nucleating agent on different batches

In this study no single nucleating agent or combination was found to be exceptionally good in lowering exothermic temperature, therefore, it can be concluded that any of the nucleating could be used at commercial level depending upon its availability and ease in its usage.

Role of batch composition

The effect of batch composition on the crystallization of glass showed that even a small change in batch composition changed the rate of crystallization. In the present study, glass batches consisted of feldspar, dolomite, clay and Na_2CO_3. Batch numbers N1, N2 and N3 had a different composition by mass and ingredients presented in Tables 1a and 1b. The results of DTA analysis showed that glass transition (T_g) values were 715, 685 and 685°C corresponding to N1, N2 and N3 respectively and the peaks of crystallization were at 857, 811 and 889°C respectively.

For the batch N1 the batch composition of the glass was feldspar and dolomite, which consisted mainly of oxides of SiO_2, CaO, MgO, Na_2O and Al_2O_3 (Table 4). The ratio between CaO and MgO (Table 3) played an important role in decreasing the

viscosity of glass. As a result, the mobilities and diffusion rates of different ions and ionic complex-forming glass were increased during the crystallization process. Earlier El-Shennawi *et al.*, [15] studied the effect of CaO and MgO ratio on the crystallization behavior of glass. They found that different molar ratios of CaO and MgO affect the crystallization of glass in a different manner thus decreasing the crystallization point by 40–65°C,

The main ingredients of N2 batches were feldspar, dolomite, clay and Na_2CO_3 (Tables 1a and 1b). The results of DTA analysis showed that the values of T_g and crystallization peak were 685 and 811°C, respectively. These values are lower than those of N1 by 30 and 40°C for T_g and crystallization peak respectively. This is due to the effect of CaO/ Na_2O ratio as shown in Table 4. Na_2O reacted with lime and probably
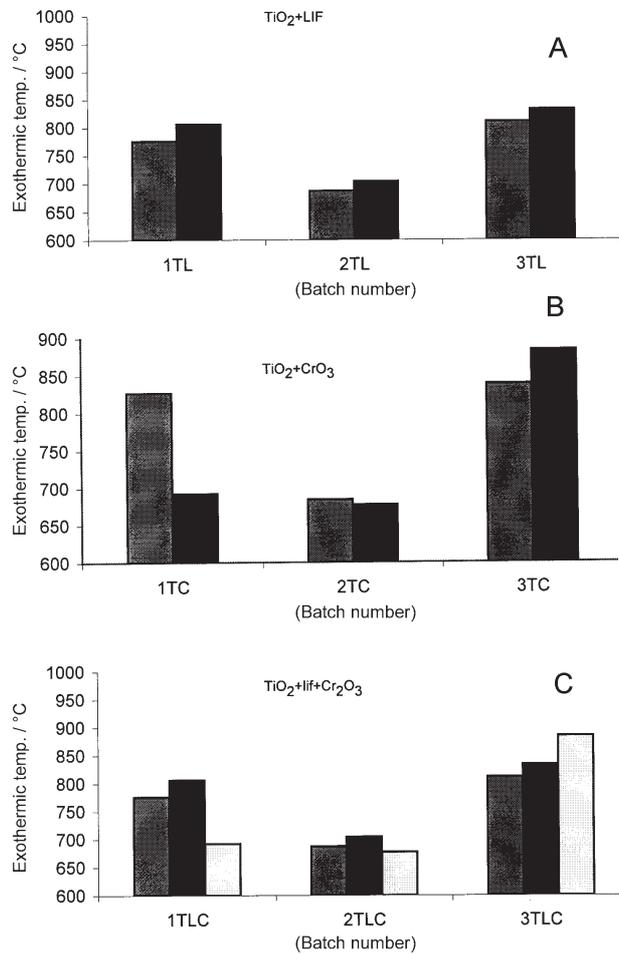

Fig. 4 A, B, C show the effects of $TiO_2+Cr_2O_3$, TiO_2+LiF and $TiO_2+LiFCr_2O_3$ nucleating agents on different batches

Table 4 Chemical analysis results of different raw materials and ratio of CaO/MgO and CaO/Na$_2$O in nepheline-pyroxenic batch glass-ceramics

Raw materials	Range and average	Oxides/%								Ratio	
		SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	CaO	MgO	K$_2$O	Na$_2$O	CaO/ MgO	CaO/ Na$_2$O
Feldspar	Range	63.5–78.29	17.67–21.45	0.11–0.33	0.05–0.09	0.32–2.89	0.05–0.24	0.78–10.73	2.69–10.31	16.57	0.22
(15)	Average	67.20	18.66	0.18	0.07	1.29	0.14	5.61	5.61		
Dolomite	Range	1.33–5.60	0.03–0.26	0.03–1.10	–	26.10–40.60	16.28–24.11	0.2–0.08	0.02–0.54	0.96	0.53
(41)	Average	2.76	0.12	0.15	–	30.55	22.08		0.11		
Clay	Range	45.0–68.2	16.27–38.22	0.46–5.30	0.14–2.02	0.14–3.28	0.05–2.02	0.11–1.48	0.8–1.80	1.36	296.8
(31)	Average	55.836	26.52	2.42	1.18	1.12	0.69	0.47	0.68		

( ) The number of samples analyzed.

consumed most of the CaO content and increased the MgO level. Na_2O and MgO are the main oxides responsible for decreasing the melting point and improving the crystallization of the glass as stated by Wilburn *et al.* [16], who showed that sodium carbonate reacts with CaO and forms the double carbonate $Na_2Ca(CO_3)_2$. Also Roth *et al.* [17] studied commercial glass, which had a higher molar content of soda than lime and showed that the reaction consumed most of the lime from the batch.

The batch composition of N3 included feldspar, dolomite, clay and Na_2CO_3 (Table 1). The DTA result of N3 showed that T_g value is to be equal to that of N2 but crystallization peak was higher than N2 by about 70°C. This is due to its high alumina content. It is known that, higher percentage of alumina decreases the number of non-bridging oxygen, resulting in the decrease of viscosity of the resultant melt [18]. This probably explains the reason for the higher value of the crystallization temperature.

Conclusions

- TiO_2 decreases the exothermic crystallization peak-temperature by about 9–15% as compared to glass without nucleating agent.
- It was found that the addition of LiF decreased the melting point by 40–94°C as compared to glass without nucleating agent glass.
- It was found that the addition of Cr_2O_3 decreased the crystallization temperature by 165, 134 and 5°C corresponding to 1C, 2C and 3C, respectively, compared to the nucleating agent free glass.
- Addition of LiF and TiO_2 together acted in the same manner as they did individually.
- Little variation in exothermic values occurred when $TiO_2+LiF+Cr_2O_3$ were added together.
- DTA revealed the CaO/Na_2O and CaO/MgO content effect on the crystallization of the glass.

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