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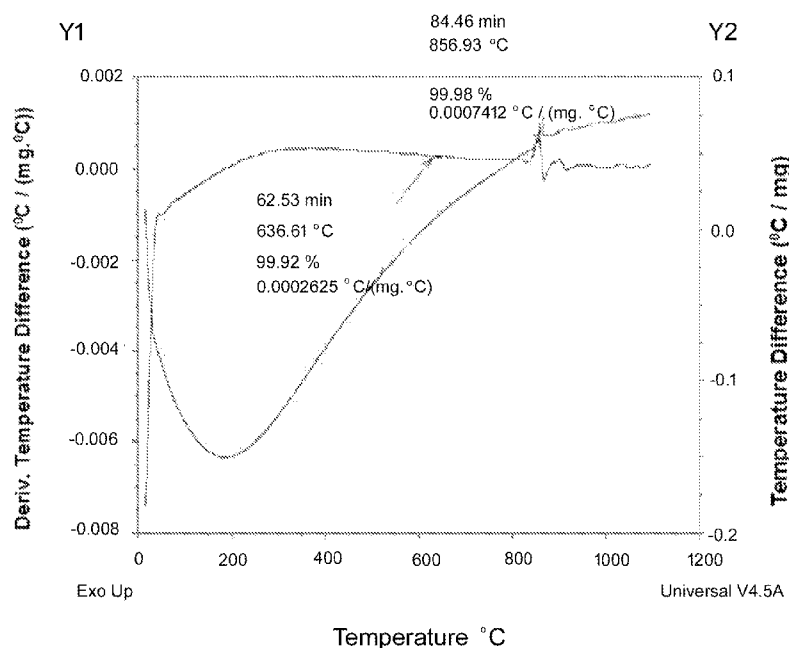


Figure 1

(57) Abstract: The present invention relates to a method developed for obtaining the highest crystalline amount of the related composition in glass ceramics in LAS system and a glass ceramic obtained by using this method.



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APPLICATION OF CONTROLLED CRYSTALLIZATION METHOD IN PRODUCTION OF GLASS CERAMIC WITH LOW THERMAL EXPANSION COEFFICIENT

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TECHNICAL FIELD

The present invention relates to application of controlled crystallization method in production of glass ceramic with low thermal expansion coefficient, in Lithium-Alumina-Silicate (hereafter, it will be called as LAS system).

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PRIOR ART

There are various different glass ceramic systems like $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$. The $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ (LAS) system is one of the most frequently used systems in production of glass ceramic material having low thermal expansion coefficient. In production of glass ceramic material, oxides like SiO_2 , Al_2O_3 and Li_2O_3 form lithium alumina silicate as main crystal phase. In LAS system, it is substantially difficult to determine the thermal process parameters since the endothermic peak, which shows the glass transition temperature, and the exothermic peak, which belongs to the crystallization temperature, are very close to each other.

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In glass ceramic production, the main aim is to obtain a material with the highest crystal phase amount. For this reason, one of the most important points in production is the determination of optimum nucleation and crystallization temperature and time. In the present art, since peak temperatures are very close to each other as mentioned above, the thermal process parameters cannot be exactly determined. Thus, the amount crystal phase in glass ceramic materials obtained at the end of production process cannot reach at desired level.

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As a result, because of all of the abovementioned problems, an improvement is required in the related technical field.

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BRIEF DESCRIPTION OF THE INVENTION

The present invention relates to glass ceramic material production method having high crystal phase amount to be able to eliminate the abovementioned disadvantages and to bring new advantages to the relevant technical field.

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The main object of the present invention is to provide a production method, which helps to obtain a glass ceramic material having high crystal phase amount.

- 5 Another object of the present invention is to provide a glass ceramic having a high crystal phase amount.

Another object of the present invention is to provide a glass ceramic material having low thermal expansion coefficient.

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In order to realize the abovementioned object and the objects, which are deducted from the detailed description below, the present invention has been developed to obtain the highest crystalline structure percent of the related composition in LAS system glass ceramics and essentially comprises the steps of:

- 15 a) Melting the composition from which is suitable for the production of LAS system glass ceramic and obtaining the glass sample,
b) Determining the crystallization temperature by means of optimum nucleation temperature and time,
c) Obtaining glass ceramic by applying thermal process to the glasses in step (a) at
20 the temperatures and time determined in step (b)

Accordingly, said invention is characterized by in step (b) which comprises the following sub-steps:

- (i) Applying DTA analysis to the glasses obtained in step (a) at the temperatures which are over the glass transition temperature and times which increase at
25 predetermined periods,
(ii) In step i), determining the optimum nucleation temperature of glass from the endothermic peak temperature, which corresponds to the lowest crystallization temperature obtained as a result of DTA analysis,
(iii) In step (ii), applying DTA analysis to the glasses obtained in step (a) at the
30 temperature determined in step (ii) and times which increase at predetermined periods,
(iv) In step (iii), determining the optimum nucleation time of glass from the holding time, which corresponds to the lowest crystallization temperature obtained as a result of DTA analysis,
35 (v) In step (iv), determining the crystallization temperature from the DTA graph, where the obtained optimum nucleation temperature and time are detected

In order to realize the abovementioned object and the objects which are to be deducted from the detailed description below, the present invention is a LAS system glass ceramic obtained by means of the mentioned method and comprising SiO_2 between 64-66%; Al_2O_3 between 21-23%; Li_2O_3 between 3.5-4.5%, MgO between 0.4-0.5%, ZnO between 1-1.5%, TiO_2 between 3.5-4%; BaO between 0.5-0.8%, ZrO_2 between 1.2-1.5%; 0.6% Na_2O and 0.8% SnO_2 . Accordingly, the present invention is characterized by comprising Fe_2O_3 in range of 0.03-0.05% and V_2O_5 in range of 0.03-0.04% as coloring agents.

In a preferred embodiment of the present invention, the crystalline percent is between 93-95%.

In another preferred embodiment of the present invention, $\text{Tir}\%$ value for 3 mm thickness is at least 71%.

In another preferred embodiment of the present invention, $\text{Tir}\%$ value for 3 mm thickness is at least 76%.

In another preferred embodiment of the present invention, $\text{Tv}\%$ value for 3 mm thickness is at most 4.5%.

In another preferred embodiment of the present invention, $\text{Tv}\%$ value for 3 mm thickness is at most 1.3%.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is the DTA graph of the glass sample.

DETAILED DESCRIPTION OF THE INVENTION

In this detailed description, the subject matter glass ceramic material production having high crystal phase amount and the production method are explained with examples without forming any restrictive effect only in order to make the subject more understandable.

In said invention, by using controlled crystallization method, it is aimed to produce transparent LAS system glass ceramic material with low thermal expansion coefficient and having β -quartz phase, which is suitable especially for the cooktops.

DTA is a method applied for detecting optimum nucleation temperature and time. In DTA method, it is accepted that the crystallization peak temperature (T_p) of the glass material obtained in the constant heating rate is a function of the nucleation temperature (T_n). For the glasses having the same composition, the crystallization peak temperature is inversely proportional with the nucleation number formed in unit volume. In other words, a decrease in the crystallization peak temperature shows that the nucleation number formed in unit volume increases.

The present invention essentially relates to a controlled crystallization method developed by means of optimum nucleation temperature and time obtained as a result of DTA analyses in glass ceramics in LAS system. In more details, the present invention relates to detection of thermal process parameters applied to the glass by means of determined optimum nucleation temperature and time.

The subject matter method essentially comprises three steps:

a) Glass material production: Before production of a glass ceramic material of the LAS system, the batch prepared with the suitable composition is melted at high temperature and glass production is realized.

b) Determination of the optimum thermal process parameters (optimum nucleation temperature and time): In order to provide high crystal phase amount of the glass ceramic material, the final product, first of all, the glass transition temperature and the crystallization temperature of the glass obtained in step (a) have been determined by DTA. Afterwards, crystallization peak temperatures are detected by applying thermal process separately to each of the glass samples obtained in step (a) at temperatures above the glass transition temperature for a determined time detected by DTA. The nucleation temperature, which corresponds to the lowest crystallization peak temperature, is determined as the optimum nucleation temperature.

In order to determine the optimum nucleation time, thermal process is applied to the glasses in step (a) at different times with predetermined increases at the determined optimum nucleation temperature, and the crystallization peak temperatures are detected. The holding time, which corresponds to the lowest crystallization peak temperature, is determined as the optimum nucleation time.

Thus, before the glass obtained in step (a) is turned into glass ceramic, the optimum nucleation temperature and time of the glass of that composition are determined. Afterwards, this temperature and time are applied to all glasses of the related composition. Thus, in the related composition, glass ceramics having the highest crystal phase amount can be obtained.

- c) The method applied in step (b) can be applied to other glasses provided in LAS system and the glasses obtained in step (a), are transformed glass ceramics having high crystal phase amount.

An exemplary application obtained by means of the subject matter method is described below.

The glass ceramic material, which will be obtained by means of the subject matter method and which will be particularly used in cooktops, comprises the main components added to the mixture and which can be turned into the final product by means of thermal process and whose weight percent are given in Table 1.

Table 1: Glass component

Components	Oxides %
SiO ₂	64 - 66
Al ₂ O ₃	21 - 23
Li ₂ O ₃	3.5 - 4.5
MgO	0.4 - 0.5
ZnO	1 - 1.5
TiO ₂	3.5 - 4
BaO	0.5 - 0.8
ZrO ₂	1.1 - 1.5
Na ₂ O	0-0.6

SnO₂	0-0.8
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The subject matter glass ceramic material is amber-colored and has low visible region transmittance and high infrared region transmittance. In order to obtain the glass ceramic material with the desired color and optical properties, different colorant oxide compositions are added into the batch and experimental studies have been performed. In the table 2 given below, the experimental studies related to coloring of the glass and the Tv% and Tir% values of the obtained glass ceramic materials have been given.

Table 2: Experiments for coloring oxide compositions

	1	2*	3	4*	5	6	7	8
Fe₂O₃ %		0.230	0.100			0.1	0.05	0.05
NiO %	0.060			0.100	0.100			
MnO %		0.650			0.650			
CoO %	0.370		0.005					
Cr₂O₃ %			0.005	0.500				
V₂O₅ %						0.03	0.03	0.04
Tv % (3 mm std.)	0.7	-	28.6	-	12.9	1.3	4.5	1.2
Tir % (3 mm std.)	45.3	-	66.5	-	61.0	66.2	76.1	71.1

*For the samples with numbers 2 and 4, spectrophotometric measurements cannot be obtained and therefore, Tv% and Tir% values cannot be calculated since the targeted amber color has not been observed.

As a result of the experimental studies, V₂O₅ colorant oxide has an effect of decrease in the visible region transmittance and it does not have an important effect on infrared transmittance. Since Fe₂O₃ has a wider absorption band in the spectrum, it decreases transmittance in the infrared region. Therefore, the optimum weight percentage values for Fe₂O₃ and V₂O₅ have been determined as 0.03-0.05% and 0.03-0.04%, respectively.

Figure 1 shows the DTA graph of the glass sample whose composition has been given above. Accordingly, the obtained glass transition temperature has been determined as 637°C and the crystallization temperature has been detected as 857°C.

- 5 In order to detect the nucleation temperature, the glass sample has been held for 60 minutes at temperatures above 637°C, which is the glass transition temperature, and afterwards, the temperature has been increased to the maximum working temperature (1100°C) of the DTA. The temperatures obtained as a result of DTA have been presented in Table 3. According to
- 10 Table 3, the lowest crystallization peak temperature has been obtained as 848°C, which corresponds to nucleation temperature of 662°C. After this temperature, it has been observed that the crystallization peak temperature increased. Therefore, the optimum nucleation temperature has been detected as 662°C, which corresponds to the lowest crystallization peak temperature.

15 **Table 3: DTA results of the glasses which are thermally processed at different temperatures**

Nucleation Temperature (°C)	Holding Time (minute)	Crystallization Temperature (°C)
642	60	860
647	60	894
652	60	894
657	60	849
662	60	848
667	60	855

- In order to determine the optimum nucleation time, the produced glass samples have been held at 662°C for 30, 60, 90, 120 and 180 minutes and afterwards, the temperature has been
- 20 increased to the maximum operation temperature of DTA. The crystallization temperatures obtained as a result of DTA have been presented in Table 4. According to Table 4, the crystallization peak temperature decreases as the holding time increases at the nucleation temperature and the crystallization peak temperature increases after 60 minutes of holding time. The duration of 60 minutes, which is the duration where the lowest crystallization peak
- 25 temperature is obtained, has been determined as the optimum nucleation time.

Table 4: DTA results of the glasses which are thermally processed at different time

Nucleation Temperature (°C)	Holding Time (minute)	Crystallization Temperature (°C)
662	30	867
662	60	848
662	90	861
662	120	860
662	180	870

In order to be able to show the efficiency of the controlled crystallization process, thermal heat treatment processes have been applied to the glass having the same composition at different temperatures and times. XRD analysis results of glass ceramic samples, which are obtained by means of applying different thermal process and controlled thermal process conditions, have been given in Table 5. In this table, the samples with numbers 1-9 show the samples obtained in different thermal process conditions selected randomly based on glass transition temperature (637°C) obtained as a result of raw DTA data; and the sample with number 10 shows the sample obtained as a result of applying controlled crystallization based on temperatures and times mentioned in Table 3 and Table 4.

Table 5: Different thermal process conditions and XRD analysis results

Sample	Thermal Process Conditions		XRD Analysis Results	
	Nucleation temperature (°C) / Time (minute)	Crystallization temperature (°C)/ Time (minute)	Crystal (%)	Amorphous (%)
1	647 / 30	867 / 15	91.8	8.2
2	647 / 60	867 / 15	90.4	9.6
3	647 / 120	867 / 15	91.2	8.8
4	657 / 30	867 / 15	92.4	7.6
5	657 / 60	867 / 15	-	100
6	657 / 120	867 / 15	-	100
7	667 / 30	867 / 15	90.7	9.3
8	667 / 60	867 / 15	-	100
9	667 / 120	867 / 15	91.0	9.0
10	662 / 60	848 / 15	94.0	6.0

In accordance with Table 5, by means of XRD analysis result, it has been determined that the percent crystal amount of the sample which is obtained by applying thermal process condition based on optimum nucleation temperature and time (662 °C / 60 minutes) determined by means of detailed DTA study, is the highest among all samples given in Table 5.

It is known that the properties of glass ceramic materials having high crystal amount are more superior. The crystal phase amount of the glass ceramic samples in the exemplary composition obtained by means of said method change between 93-95%. Thus, by means of said method, products with higher crystallization amount are obtained when compared with the present art.

The protection scope of the present invention is set forth in the annexed claims and cannot be restricted to the illustrative disclosures given above, under the detailed description. It is because a person skilled in the relevant art can obviously produce similar embodiments under the light of the foregoing disclosures, without departing from the main principles of the present invention.

CLAIMS

1. The present invention has been developed for obtaining the highest crystalline amount of the related composition in glass ceramics in LAS system and essentially comprises the steps of:

a) Melting the composition from which is suitable for the production of LAS system glass ceramic and obtaining the glass sample,

b) Determining the crystallization temperature by means of optimum nucleation temperature and time,

c) Obtaining glass ceramic by applying thermal process to the glasses in step (a) at determined temperatures and time determined in step (b)

wherein the step (b) is characterized by comprising the following sub-steps:

2. Applying DTA analysis to the glasses obtained in step (a) at the temperatures which are above the glass transition temperature and times which increase at predetermined periods,

3. In step i), determining the optimum nucleation temperature of glass from the endothermic peak temperature, which corresponds to the lowest crystallization temperature obtained as a result of DTA analysis,

4. In step (ii), applying DTA analysis to the glasses obtained in step (a) at the temperature determined in step (ii) and times which increase at predetermined periods,

5. In step (iii), determining the optimum nucleation time of glass from the holding time, which corresponds to the lowest crystallization temperature obtained as a result of DTA analysis,

6. In step (iv), determining the crystallization temperature from the DTA graph, where the obtained optimum nucleation temperature and time are detected,

7. A glass ceramic in LAS system obtained by means of the mentioned method and comprising SiO_2 between 64-66%; Al_2O_3 between 21-23%; Li_2O_3 between 3.5-4.5%, MgO between 0.4-0.5%, ZnO between 1-1.5%, TiO_2 between 3.5-4%; BaO between 0.5-0.8%, ZrO_2 between 1.2-1.5%; 0.6% Na_2O and 0.8% SnO_2 , **wherein** the glass ceramic comprises Fe_2O_3 in range of 0.03-0.05% as colorant and comprising V_2O_5 in range of 0.03-0.04%.
8. A glass ceramic according to claim 3, **wherein** the crystalline percent is between 93.5-94.5%.
9. A glass ceramic according to claim 3, **wherein** $T_{\text{ir}}\%$ value for 3 mm thickness is at least 71%.
10. A glass ceramic according to claim 3, **wherein** $T_{\text{ir}}\%$ value for 3 mm thickness is at least 76%.
11. A glass ceramic according to claim 3, **wherein** $T_{\text{v}}\%$ value for 3 mm thickness is at most 4.5%.
12. A glass ceramic according to claim 3, **wherein** $T_{\text{v}}\%$ value for 3 mm thickness is at most 1.3%.

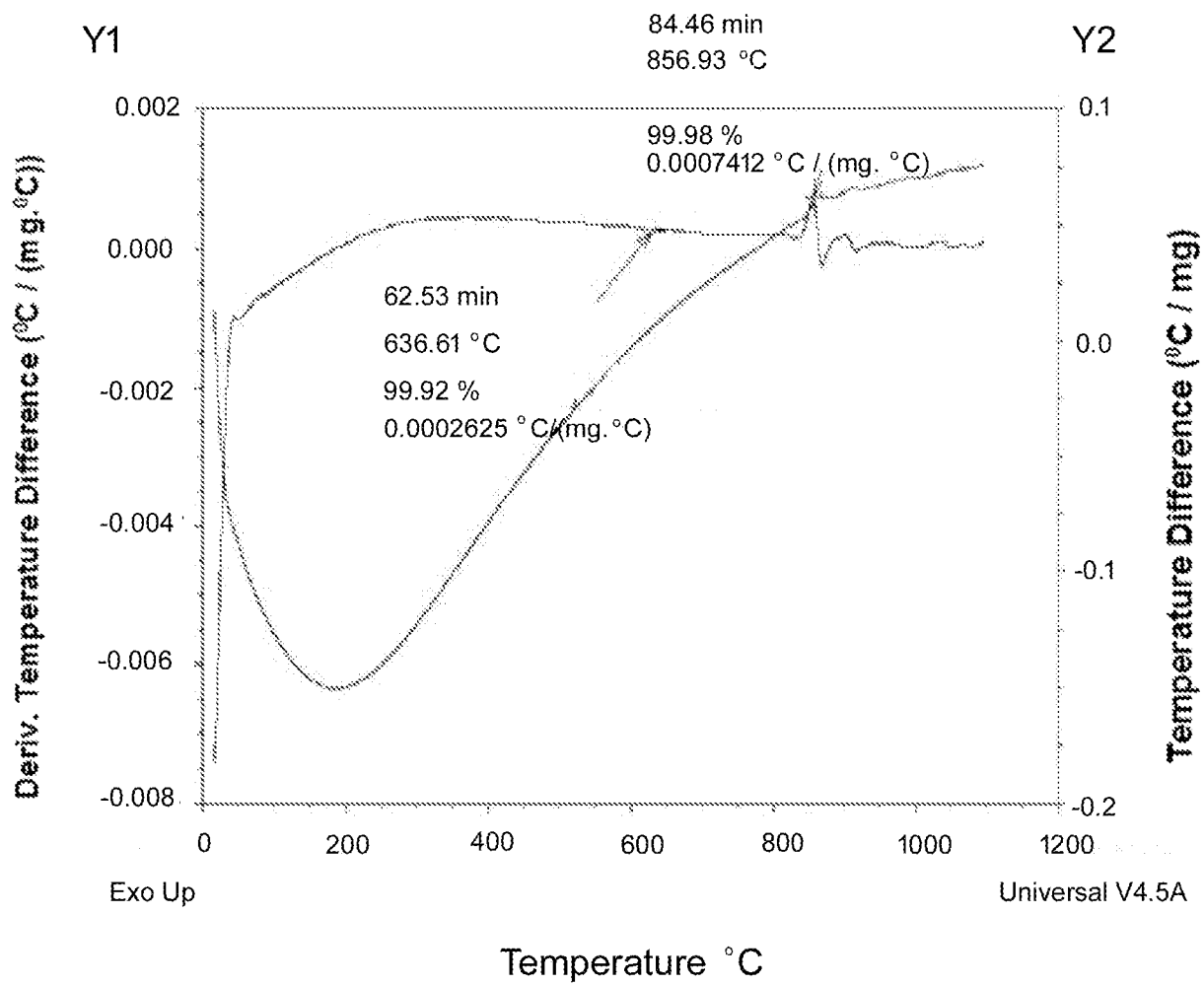


Figure 1