

Glass-ceramic enamels derived from the $\text{Li}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ system

DRAGICA S. GAVRILOVSKI¹, NIKOLA S. BLAGOJEVIĆ^{2#}, MILORAD P. GAVRILOVSKI¹
and SNEŽANA R. GRUJIĆ^{2#}

¹SARTID – Institute for Metallurgy, Goranska 12, YU–11300 Smederevo and ²Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, YU–11001 Belgrade, Yugoslavia

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The results of research on the conditions for obtaining model glass-ceramic enamels, derived from the basic $\text{Li}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ system, by varying the initial composition and thermal treatment conditions, are presented in this paper. Segregation of the crystal phases in the glassy-matrix was carried out during subsequent thermal treatment. The formation of different crystal phases was evidenced through the results of differential-thermal analysis and X-ray powder diffraction analysis.

Keywords: glass-ceramic enamels, thermal treatment, silicate coatings, crystallization.

INTRODUCTION

Technical glass-ceramic enamels represent crystallized silicate coatings, which, after suitable thermal treatment, contain a significant concentration of finely dispersed and uniformly distributed crystalline phases.^{1,2} These special enamels possess much better thermo-mechanical properties relative to conventional enamel coatings.

Glass-ceramic enamels are characterized by high thermal stability, working ability at considerable higher temperatures, depending on their composition and structure.^{3,4}

The technology of producing glass-ceramic enamels by the induced crystallization method is based on principles similar to producing other types of glass-ceramics. The processes of directed crystallization occur during coat formation, *i.e.*, during the process of enamel adhesion to the base or on additional heat treatment, whereby the phase composition of the crystallization products depends on both the heating and cooling rate.^{3–10}

The possibilities of obtaining model glass-ceramic coat enamels, derived from the basic $\text{Li}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ system, were examined in this paper. The formation of different crystalline phases depends on the initial composition, increasing the SiO_2 concentration and decreasing the Li_2O concentration, and also on the thermal treatment conditions.

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According to the composition and structure, these crystallized materials should correspond to typical glass-ceramic enamels.¹

EXPERIMENTAL

Enamel series within the $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2$ system were synthesized, whereby the composition of the initial melt was varied by increasing the SiO_2 content and decreasing the Li_2O concentration, while maintaining a constant Al_2O_3 concentration. The compositions of the synthesized glasses are shown in Table I.

TABLE I. Composition of the synthesized glasses (mol. %)

Oxides	Enamels				
	E1	E2	E3	E4	E5
SiO_2	58	64	64	70	76
Al_2O_3	3	3	3	3	3
Li_2O	31	25	3	19	13
TiO_2	4	4	16	4	4
Na_2O	4	4	14	4	4

Based on the raw material mixture calculation, the synthesis of model enamels systems of projected chemical composition have been derived. The following has been used as starting components for glass granules: quartz sand, feldspar, calcined soda, titanium dioxide, lithium carbonate. The prepared mixture was homogenized and melted in a Pt crucible at 1200 °C for $\tau = 3.5$ h. The formed melt was poured into water. Bright, transparent granules were obtained.

The initial pulverized glass was subjected to differential-thermal analysis, which was carried out at a heating rate of 10 °C/min, with Al_2O_3 as the reference substance.

The thermal treatment of the synthesized glasses with the view of obtaining glass-ceramic enamels was performed by thermally cycling the pulverized samples within the temperature interval 650–850 °C. The heating rate was approximately 10 °C/min, and cooling rate about 7 °C/min. The last cooling was continued in the furnace down to room temperature–inertion cooling (designated as mode I).

Some samples were subjected to another thermal treatment mode which consisted of heating the sample up to a temperature of 900 °C, at a heating rate of approx. 10 °C/min, maintaining that temperature for 3 h, and then continuous cooling in the furnace down to room temperature–inertion cooling (designated as mode II).

The thermal treatment modes of the synthesized glasses are presented in Table II.

TABLE II. Thermal treatment modes of the synthesized glasses

Systems	Mode I		Systems	Mode II		Time/h			
	Temp./°C	Heating (cooling) rate/(°C/min)		Temp./°C	Heating (cooling) rate/(°C/min)				
E1	650 – 850	≈ 10	E3	20 – 900	≈ 10	–			
E2			E4				900	–	3
E3			E5						
E5	850 – 650	≈ 7							
	850 – 20	Inertion cooling							

The crystallized phases of the heat treated samples were identified by the X-ray powder diffraction method using a Philips PW-1710 diffractometer.

RESULTS

Thermal analysis

Differential-thermal analysis (DTA) was performed with the view of monitoring the phase transformation processes.

The DTA and TG curves of the basic glass powders E1 and E2 are presented in Fig. 1. The DTA curves of other glass powders are presented in Fig. 2.

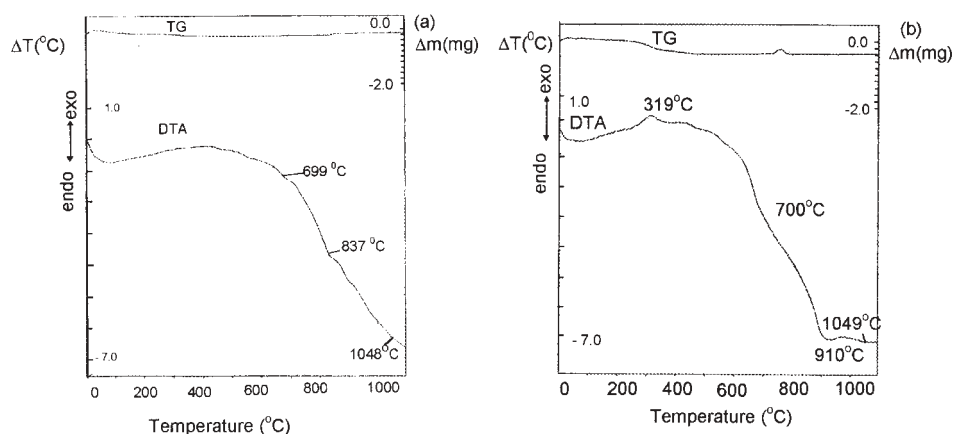


Fig. 1. TG and DTA curves of the glasses E1 (a) and E2 (b).

Weak endothermic effects can be noticed on the DTA curve of the glass E1, at temperatures of 699 °C and 837 °C, followed by a mass change, as well as a further endothermic effect at 1048 °C (Fig. 1a).

The DTA curve of glass E2 shows an expressed exothermic effect at 319 °C, which is followed by a mass loss, and a weak endothermic effect at 700 °C, which is accompanied with a mass change, as well as endothermic effects at 910 °C and 1049 °C, with no mass change (Fig. 1b).

The glass E3 has an exothermic peak at 567 °C, and an endothermic peak at 878 °C (Fig. 2a).

The glass E4 has an exothermic effect at 630 °C, and an endothermic effect at 861 °C (Fig. 2b).

The glass E5 exhibit no expressed effects (Fig. 2c).

The results of differential-thermal analysis were the basis for the selection of the thermal treatment modes.

X-Ray diffraction

The amorphous nature of the synthesized enamel systems was established by X-ray diffraction analysis of the basic glasses, namely, crystallization did not occur during cooling after melting.

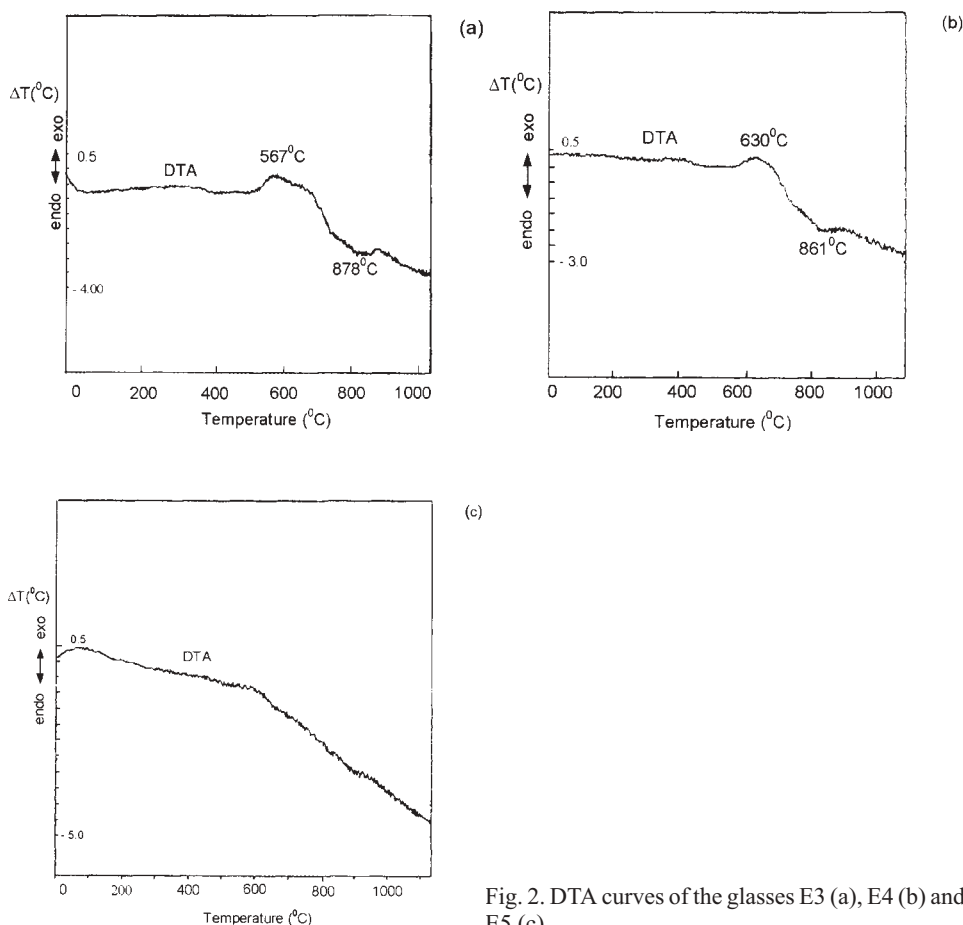


Fig. 2. DTA curves of the glasses E3 (a), E4 (b) and E5 (c).

The X-ray diffractograms of the examined samples, subjected to the stated thermal treatment modes, are presented in Fig. 3 to Fig. 7.

Good crystallization was achieved in the system E1 by alternate heating and cooling, with segregation of crystal phases of lithium metasilicate Li_2SiO_3 and lithium titanium silicate $\text{Li}_2\text{TiSiO}_5$.

Good crystallization was also achieved in the system E2, and the presence of crystal phases of lithium metasilicate and lithium titanium silicate was confirmed.

In the system E3, segregation of one crystal phase, TiO_2 (rutile), was identified in the glassy-matrix, after both heat treatment modes.

The degree of crystallization in system E4 was reduced by subsequent thermal treatment, according to mode II, and two crystal phases segregated: lithium metasilicate and traces of lithium titanium silicate.

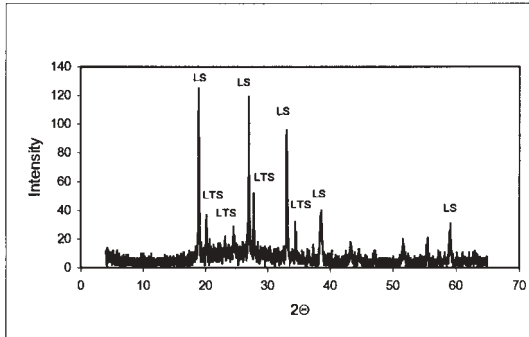


Fig. 3. X-Ray diffraction pattern of a crystallized sample E1-mode I (LS-Li₂SiO₃, LTS-Li₂TiSiO₅).

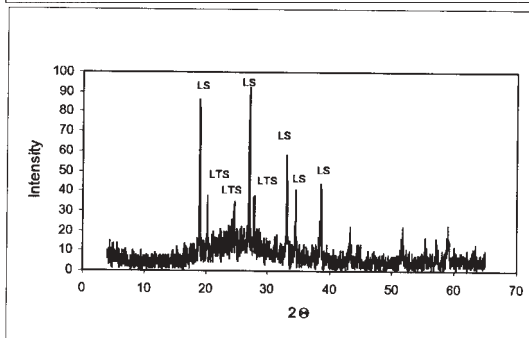


Fig. 4. X-Ray diffraction pattern of a crystallized sample E2-mode I (LS-Li₂SiO₃, LTS-Li₂TiSiO₅).

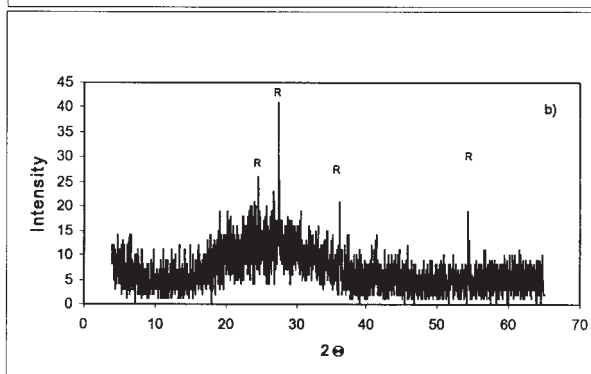
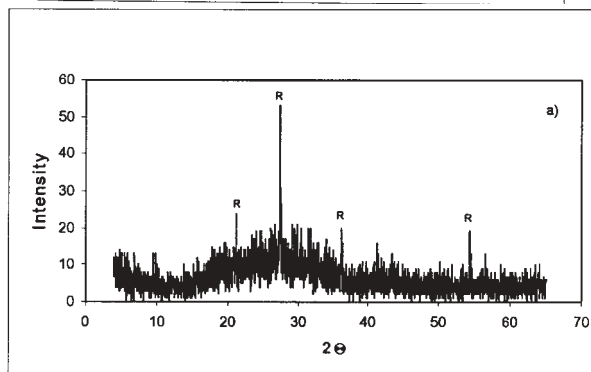


Fig. 5. X-Ray diffraction pattern of a crystallized sample E3-mode I (a) and mode II (b) (R-rutile).

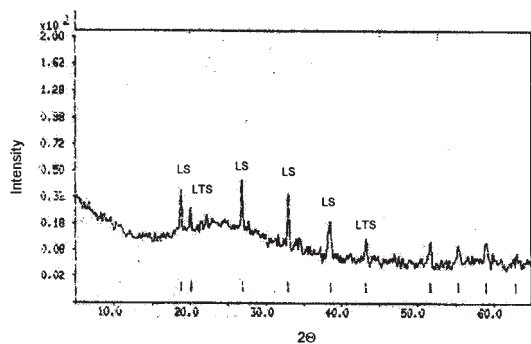


Fig. 6. X-Ray diffraction pattern of a crystallized sample E4–mode II (LS- Li_2SiO_3 , LTS- $\text{Li}_2\text{TiSiO}_5$).

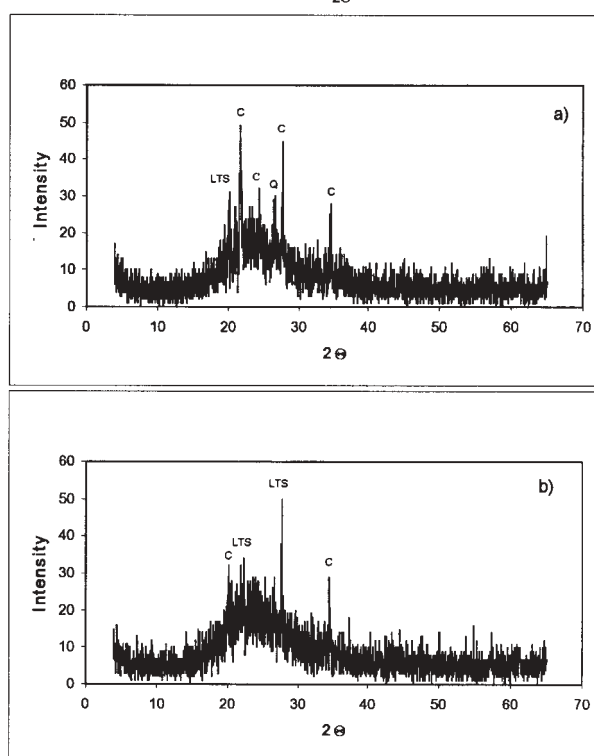


Fig. 7. X-Ray diffraction pattern of a crystallized sample E5–mode I (a) and mode II (b) (C-cristobalite, Q-quartz, LTS- $\text{Li}_2\text{TiSiO}_5$).

Crystallization was achieved in system E5, by alternate heating and cooling, with the most dominant crystal phase being cristobalite, followed by quartz and then lithium titanium silicate. The degree of crystallization was reduced by thermal treatment, according to mode II, so only slight segregation of lithium titanium silicate and cristobalite was identified in the amorphous base.

DISCUSSION

It is characteristic for the investigated systems that phase transformation processes are accompanied by very slight latent heat transformations,¹¹ so that only changes in the

DTA curves can be noticed, without distinct exothermic or endothermic effects, although the presence of crystalline phases was proved by X-ray diffraction analysis.

The exothermic peaks should mark the beginning of crystal phase segregation within the system, while the endothermic peaks can correspond to the beginning of melting in the glass-crystal system.^{1,3}

The endothermic peaks at 1049 °C should designate complete melting.¹

In all enamel systems, volume crystallization occurs in the investigated temperature interval.

Very good degrees of crystallization were achieved by thermal treatment, according to mode I, in systems E1 and E2, with segregation of the same crystal phases, lithium metasilicate and lithium titanium silicate, as well as in system E3, with segregation of rutile.

The degree of crystallization of the phases in the glassy-matrix was reduced with increasing SiO₂ content, with simultaneously decreasing Li₂O content, whereby system E5 had the poorest crystallization. Also, the degree of crystallization was reduced by thermal treatment, according to mode II, compared to thermal mode I, except in system E3. The segregation of a single crystalline phase – TiO₂ was confirmed in this system, a phase which was stable in thermal mode II as well.

CONCLUSION

Several model enamels, derived from the basic Li₂O-Na₂O-Al₂O₃-TiO₂-SiO₂ system, were synthesized, by changing the initial composition, *i.e.*, increasing the SiO₂ content and reducing the Li₂O content, by constant Al₂O₃ concentration.

The crystallization of all systems was achieved by subsequent thermal treatment, whereby glass-ceramic enamels were obtained. The principal crystal phases which segregate are Li₂SiO₃, Li₂TiSiO₅, TiO₂ and cristobalite. The degree of crystallization is reduced with increasing SiO₂ content.

ИЗВОД

СТАКЛО-КЕРАМИЧКИ ЕМАЈЛИ ИЗВЕДЕНИ ИЗ СИСТЕМА Li₂O-Na₂O-Al₂O₃-TiO₂-SiO₂

ДРАГИЦА С. ГАВРИЛОВСКИ¹, НИКОЛА С. БЛАГОЈЕВИЋ², МИЛОРАД П. ГАВРИЛОВСКИ¹ и
СНЕЖАНА Р. ГРУЛИЋ²

¹САРТИД – Институт за металургију, Горанска 12, 11300 Смедерево и ²Технолошко-металуршки факултет, Карнегијева 4, 11000 Београд

У раду је представљено истраживање услова добијања моделних стакло-керамичких емајла, изведених из основног система Li₂O-Na₂O-Al₂O₃-TiO₂-SiO₂, променом поласног састава и услова топлотне обраде. Издвајање кристалних фаза у стаклој матрици остварено је током накнадне топлотне обраде. Образовање различитих кристалних фаза утврђено је на основу резултата диференцијално-термијске анализе и методом рендгенске дифракције.

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