

# CRYSTALLIZATION AND THERMAL EXPANSION CHARACTERISTICS OF LITHIUM BARIUM BOROSILICATE GLASSES

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*The contribution of BaO to the crystallization characteristics and crystalline phase assemblages developed from thermally treated glasses based on  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system were investigated by differential thermal analysis (DTA), X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Different barium-containing phases including barium silicates and lithium barium borate together with lithium diborate, lithium meta-, di-silicates and, in some cases, minor of  $\alpha$ -quartz were detected. SEM micrographs showed that BaO promoted volume crystallization of the studied glasses. The addition of  $\text{TiO}_2$  and  $\text{MgF}_2$  as nucleation catalysts to glass with high content of BaO led to the formation of fresnoite, and magnesium fluoride phases. The thermal expansion characteristics of the glasses and their crystalline solids were investigated. The data of the glasses were correlated to the local structure changes induced by BaO,  $\text{TiO}_2$  or  $\text{MgF}_2$  and their contributions to the thermal expansion property of the glasses. The results of the crystalline solids were explained in relation to the nature, composition and concentration of all phases formed including a residual glass matrix.*

## INTRODUCTION

Glass-ceramics are polycrystalline solids prepared by the controlled crystallization of suitable glass compositions. A key feature of glass-ceramics is the maintenance of shape of a previously formed glass article. This is most effectively achieved through internal nucleation and growth of crystals [1-3]. Their texture is characterized by uniform fine-grained randomly oriented crystals with some residual glassy matrix [1].

Lithium barium silicate glasses are phase separated over most of the glass-forming region. The study [4] demonstrated that phase separation strongly affected some properties of the glasses, e.g. glass transformation temperature and dilatometric softening temperature.

Borosilicate glasses are used in wide range of technological applications, from chemical containers and piping to fiber composites and radioactive waste storage.

The range of chemical compositions of the glass-forming region of the system  $\text{BaO}-\text{B}_2\text{O}_3-\text{SiO}_2$  and the properties of the glasses in the system are of fundamental importance to glass technologists. Glasses in this system may be considered to be the base glasses for the large family of barium crown optical glasses [5].

The coefficient of thermal expansion (CTE) of different types of glass and glass-ceramic materials is another important property and is often fundamental in determining their field of application [6-8].

Lithium borosilicate glasses containing various proportions of BaO replacing  $\text{B}_2\text{O}_3$  with addition of nucleating agents like  $\text{TiO}_2$  or  $\text{MgF}_2$  could be potential candidates to glass-ceramics. It was the objective of this work to provide an examination of the crystallization characteristics of  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  (BaO)- $\text{SiO}_2$  glass. Emphasis was placed on the study of the crystallization-temperature process, the temporal sequence and nature of the crystal phase formation, the microstructure developed in relation to the glass oxide constituents and heating conditions, as well as the thermal expansion behaviour of the glasses and the corresponding glass-ceramics.

## EXPERIMENTAL

### Glass composition and preparation

Glasses of compositions expressed by the formula:  $33.63 \text{ Li}_2\text{O} - (29.48 - X) \text{ B}_2\text{O}_3 - X \text{ BaO} - 36.89 \text{ SiO}_2$  mole %, were prepared, where  $X = 0, 4, 8, 12$  and  $16$  mole %.  $\text{TiO}_2$  (6.0 g) and  $\text{MgF}_2$  (6.0 g) were added as nucleating agents over 100 g of glass constituents (with 16 mole % BaO). The batches were prepared from acid-washed pulverized quartz sand and reagent grade powders of  $\text{Li}_2\text{CO}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{BaCO}_3$ ,  $\text{TiO}_2$  and  $\text{MgF}_2$  were used as starting materials. The weighed batches were thoroughly mixed and melted in Pt-2%Rh crucible in an

electric heated furnace, with SiC heating elements, at 1200-1250°C for 3 hours duration with occasional stirring to ensure homogeneity. The homogeneous bubble-free melts were cast into rectangular rods (0.5×0.5 cm cross section and 1.5 cm length), and as buttons, which were then well annealed in a muffle furnace for approximately 1 h at about 50°C below the glass transition temperature,  $T_g$ , then cooled at 1°C/min to room temperature to minimize the strain of the glasses.

#### Differential thermal analysis (DTA)

The thermal behaviour of the finely powdered (45-75 m) glass samples was examined using a NETZSCH Geratebau GmbH Sleb Bestell-Nr. 348, 472°C. The powdered sample was heated in Pt-holder against another Pt-holder containing  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a reference material. A uniform heating rate of 10°C/min. was adopted. The results obtained were used as a guide for determining the heat-treatment temperatures applied to induce crystallization.

#### Thermal-treatment

The progress of crystallization in the glasses was followed using single and double stages heat-treatment regimes depending on the DTA results. Crystallization is generally viewed as a two-step process. The first step (nucleation) involves the formation of a stable nucleus at the endothermic peak temperature for 5 h and the second is the growth of the nucleus to form crystal growth at the exothermic peak temperature for 30 h.

#### Material investigation

Identification of crystal phases precipitating in the course of crystallization was conducted by the X-ray diffraction (XRD) analysis using a Philips type diffractometer (P.W. 1730) with Ni-filtered Cu-K $\alpha$  radiation. The crystal characteristics and internal microstructures of the resultant materials were examined by scanning electron microscopy (SEM), where representative electron micrographs were obtained using Jeol, JXA-840 A Electron Probe Microanalyzer.

#### Thermal expansion measurements

The coefficients of thermal expansion of the investigated glasses and glass-ceramics were carried out on (0.5×0.5 cm cross-section and 1.5 cm length) rods using a Linseis L76/1250 automatic recording multiplier

dilatometer at a heating rate of 5°C/min. The coefficients of thermal expansion of the investigated glasses were measured from room temperature up to 300°C while the glass-ceramics were measured up to 600°C. The linear thermal expansion coefficient ( $\alpha$ ) was automatically calculated using the general equation:

$$\alpha = (\Delta L / L) \cdot (1/\Delta T)$$

where: ( $\Delta L$ ) is the increase in length, ( $\Delta T$ ) is the temperature interval over which the sample is heated and ( $L$ ) is the original length of the specimen.

## RESULTS

#### Differential thermal analysis

The DTA data of the glasses (G<sub>1</sub>-G<sub>5</sub>, G<sub>5</sub>T and G<sub>5</sub>F, figure 1) showed endothermic effects in the 408 - 506°C temperature range. These endothermic effects are to be attributed to the glass transition, at which the atoms begin to arrange themselves in preliminary structural elements preceding the nucleation. Various exothermic effects in the 532-660°C range, indicating crystallization in the glasses, are also recorded.

#### Crystallization characteristics

The progress of crystallization in the glasses, the type and proportions of the crystalline phases formed were markedly dependent on the variation of the glass oxide constituents, the extent of BaO/B<sub>2</sub>O<sub>3</sub> replacements, the effect of thermal treatment as well as the role of the nucleating agents added.

The DTA data (figure 1) of the glasses (G<sub>1</sub>-G<sub>5</sub>) revealed that the addition of BaO at the expense of B<sub>2</sub>O<sub>3</sub> led to a shift, both of the endothermic dips and the onset of crystallization exotherms to lower temperatures.

However, the TiO<sub>2</sub> addition (as a nucleating agent) to the BaO-containing glass G<sub>5</sub>T, led to the shift of both the endothermic dips and the onset of crystallization exotherms to higher temperatures as compared with the TiO<sub>2</sub>-free (G<sub>5</sub>), while the presence of MgF<sub>2</sub> in glass G<sub>5</sub>F led to the decrease of the endothermic dips and exothermic peaks to lower values.

SEM micrographs of fractured surfaces of crystalline samples G<sub>1</sub> and G<sub>5</sub> showed the effect of adding BaO at the expense of B<sub>2</sub>O<sub>3</sub> on the microstructure formed. BaO promoted volume crystallization of interlocked-like growths in the studied glasses. For example SEM micrograph of G<sub>1</sub> (BaO-Free) clearly showed well-developed spherulite-like growths (figure 2). However with addition of BaO (up to 16 %, G<sub>5</sub>), volume crystallization interlocked-like growths were developed (figure 3).

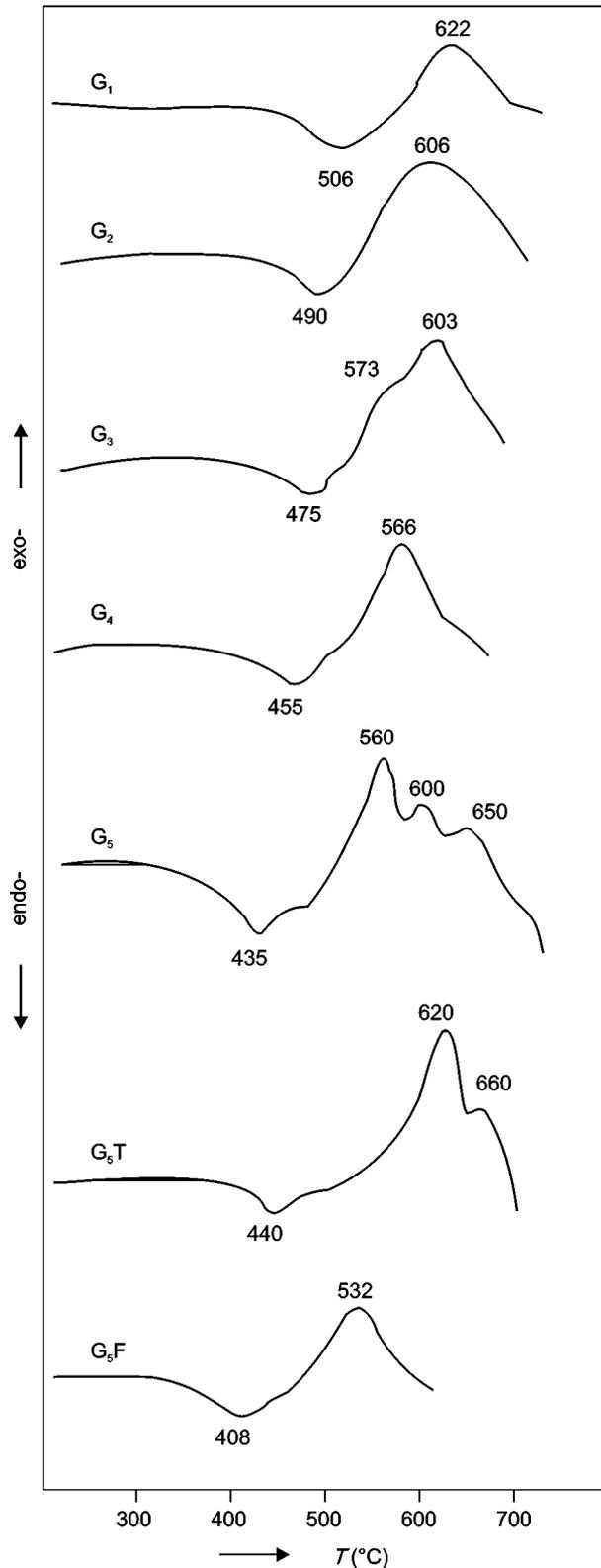


Figure 1. DTA thermograms of the studied glasses.

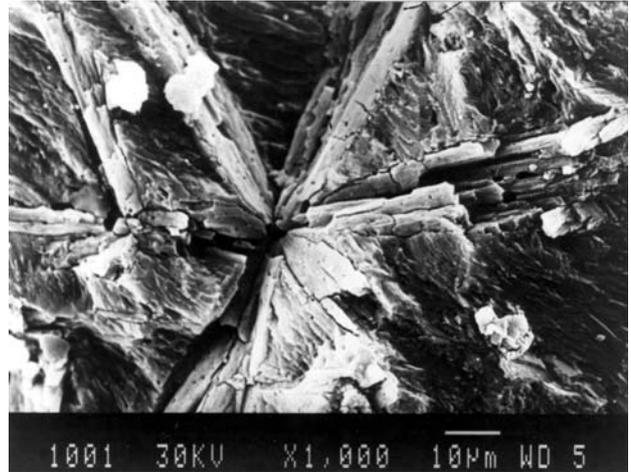


Figure 2. SEM micrograph of fracture surface of  $C_1$  crystallized at 505°C/5h-622°C/30h showing spherulite crystals.

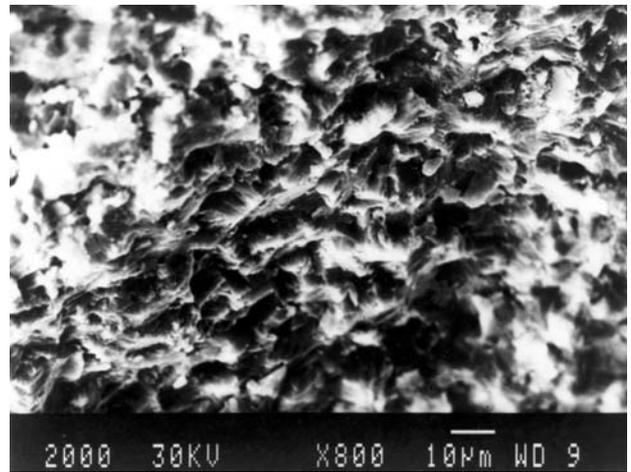


Figure 3. SEM micrograph of fracture surface of  $C_5$  crystallized at 435°C/5h-650°C/30h showing volume crystallization of interlocked-like growths.

### Crystal phases formed

#### Effect of BaO/B<sub>2</sub>O<sub>3</sub> replacements

The X-ray diffraction analysis (figure 4, pattern I) revealed that lithium disilicate-Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (lines 5.46, 3.76, 3.67, 3.58, PDF File 17-447) [9], lithium diborate-Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (4.09, 3.50, 2.62, PDF File 22-1140) [9], lithium metasilicate-Li<sub>2</sub>SiO<sub>3</sub> (lines 4.7, 3.32, 2.70, PDF File. 29-828) and traces of  $\alpha$ -quartz (lines 4.26 and 3.36, PDF File 5-0490) were formed in the crystalline base glass  $G_1$  (BaO-free). However, the addition of BaO instead of B<sub>2</sub>O<sub>3</sub> (i.e.,  $G_2$ - $G_5$ ) revealed that different barium-containing phases such as barium silicates, e.g. Ba<sub>5</sub>(Si<sub>8</sub>O<sub>21</sub>), BaSiO<sub>3</sub> and lithium barium borate- LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>) were developed, (table 1).

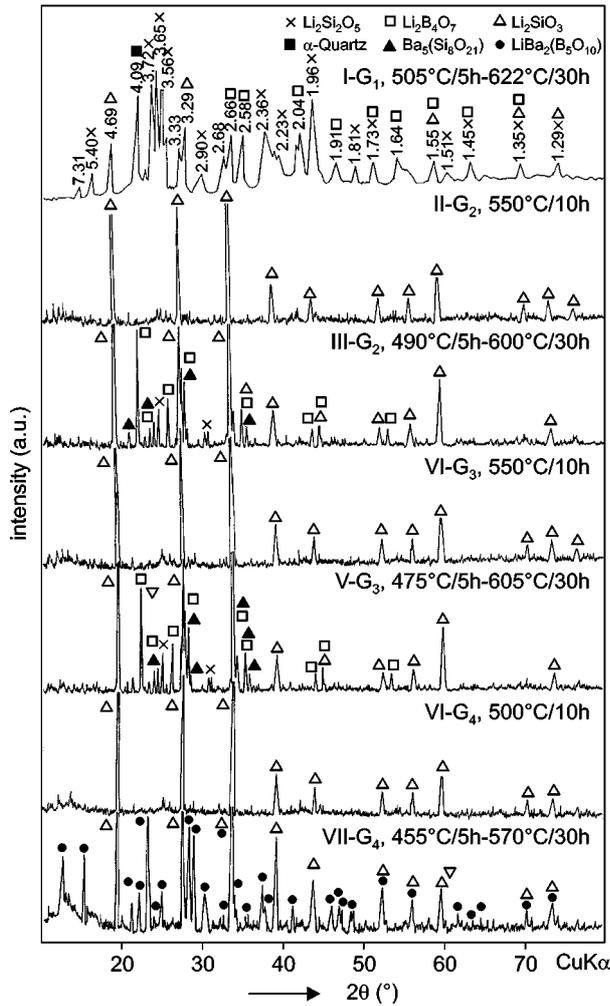


Figure 4. XRD patterns of crystallized glasses (G<sub>1</sub>-G<sub>4</sub>).

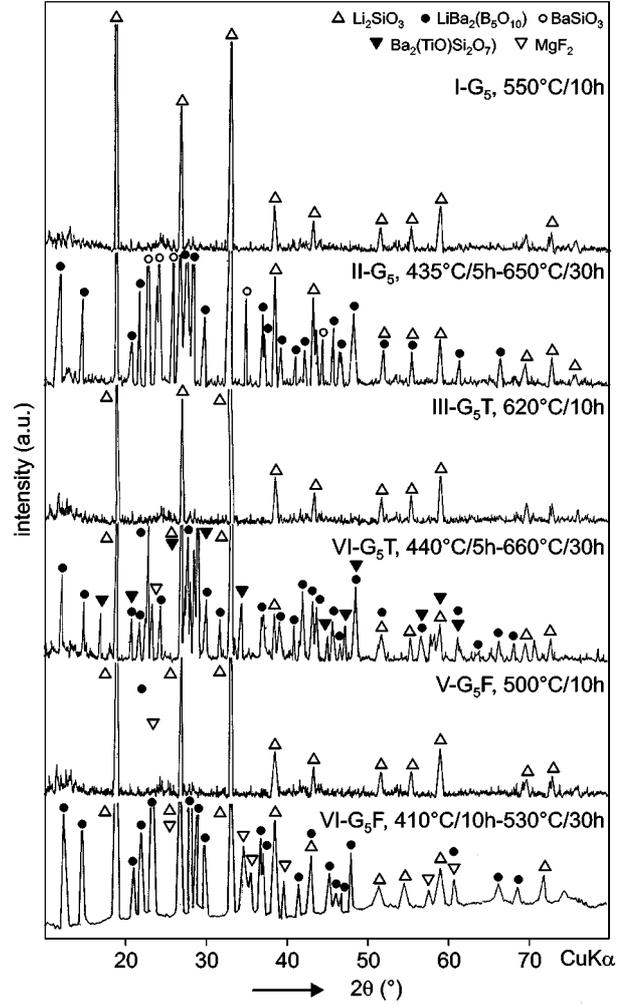


Figure 5. XRD patterns of crystallized glasses (G<sub>5</sub>, G<sub>5T</sub> and G<sub>5F</sub>).

Table 1. The crystalline phases developed in the studied glasses.

Glass No.	Heat-treatment (°C/h)	Phases developed
G <sub>1</sub>	505/5 - 622/30	Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , Li <sub>2</sub> SiO <sub>3</sub> , α-Quartz (traces)
G <sub>2</sub>	550/10	Li <sub>2</sub> SiO <sub>3</sub>
G <sub>2</sub>	490/5 - 600/30	Li <sub>2</sub> SiO <sub>3</sub> , Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , Ba <sub>5</sub> (Si <sub>8</sub> O <sub>21</sub> ), Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (traces)
G <sub>3</sub>	550/10	Li <sub>2</sub> SiO <sub>3</sub>
G <sub>3</sub>	475/5 - 605/30	Li <sub>2</sub> SiO <sub>3</sub> , Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , Ba <sub>5</sub> (Si <sub>8</sub> O <sub>21</sub> ), Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (traces)
G <sub>4</sub>	500/10	Li <sub>2</sub> SiO <sub>3</sub>
G <sub>4</sub>	455/5 - 570/30	Li <sub>2</sub> SiO <sub>3</sub> , LiBa <sub>2</sub> (B <sub>5</sub> O <sub>10</sub> ), α-Quartz
G <sub>5</sub>	550/10	Li <sub>2</sub> SiO <sub>3</sub>
G <sub>5</sub>	435/5 - 650/30	Li <sub>2</sub> SiO <sub>3</sub> , LiBa <sub>2</sub> (B <sub>5</sub> O <sub>10</sub> ), BaSiO <sub>3</sub>
G <sub>5T</sub>	620/10	Li <sub>2</sub> SiO <sub>3</sub>
G <sub>5T</sub>	440/5 - 660/30	Li <sub>2</sub> SiO <sub>3</sub> , LiBa <sub>2</sub> (B <sub>5</sub> O <sub>10</sub> ), Ba <sub>2</sub> (TiO)Si <sub>2</sub> O <sub>7</sub>
G <sub>5F</sub>	500/10	Li <sub>2</sub> SiO <sub>3</sub>
G <sub>5F</sub>	410/5 - 530/30	Li <sub>2</sub> SiO <sub>3</sub> , LiBa <sub>2</sub> (B <sub>5</sub> O <sub>10</sub> ), MgF <sub>2</sub>

Detailed study by X-ray diffraction analysis (figures 4 and 5) of the glasses crystallized through both single and double stage regimes (table 1) revealed that the crystallization process was also dependent on the heating and /or duration effects. The glasses G<sub>2</sub> and G<sub>3</sub> (with 4 and 8 mole % BaO, respectively) crystallized at 550°C for 10 h (figure 4, patterns II-V), yielding the lithium metasilicate phase. At higher temperature for long duration (table 1), the crystallinity of samples increased and lithium diborate, barium silicate-Ba<sub>5</sub>(Si<sub>8</sub>O<sub>21</sub>) (lines 4.27, 3.91, 3.81, 3.65, 2.66, PDF File 83-1443) and traces of lithium disilicate were crystallized as well. The crystallization of glass G<sub>4</sub> (with 12 mole % BaO) at 500°C/10 h led to the formation of lithium metasilicate (pattern VI). Prolonged heating at higher temperature led to the formation of lithium barium borate [LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>)] (lines 7.33, 5.94, 3.89, 3.20, 3.11, PDF File 81-521) and  $\alpha$ -quartz (pattern VII). Glass G<sub>5</sub> (with 16 mole % BaO) crystallized at 550°C for 10 h gave lithium metasilicate (figure 5, pattern I). However, heating the glass G<sub>5</sub> at higher temperature (table 1), the crystallinity increased and lithium barium borate together with barium silicate-BaSiO<sub>3</sub> (lines 3.40, 3.64, 2.03, PDF File 70-2112) phases were formed (pattern II).

#### Effect of TiO<sub>2</sub> and MgF<sub>2</sub> as nucleating agents

X-ray diffraction analysis (figure 5) revealed that the crystallization of glass G<sub>5</sub>T (with 16 mole % BaO + 6.0 g TiO<sub>2</sub>) at 620°C for 10 hours led to the formation of lithium metasilicate (pattern III). At higher temperature for long duration, i.e. 440°C/5 h - 660°C/30 h, the crystallinity of the sample increased and fresnoite-Ba<sub>2</sub>

(TiO)Si<sub>2</sub>O<sub>7</sub> (lines 5.02, 3.29, 3.07, 2.60, PDF File 70-1920) together with lithium barium borate-LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>) developed (pattern IV). However, no BaSiO<sub>3</sub> phase could be detected.

Thermal-treatment of glass G<sub>5</sub>F (with 16 mole % BaO + 6.0 g MgF<sub>2</sub>) at lower temperature, i.e. 500°C for 10 hours led to the formation of lithium metasilicate (pattern V). However thermal treatment through double stage regimes, i.e. at 410°C/5 h - 530°C/30 h, lithium barium borate-LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>) and MgF<sub>2</sub> (lines 3.31, 2.59, 2.25, 2.08, 1.47, PDF File 16-0160) phases crystallized as well (pattern VI).

#### Thermal expansion

Table 2 lists the thermal expansion coefficients over different ranges of temperatures of the glasses and glass-ceramics, as well as the dilatometric transition (T<sub>g</sub>) and softening (T<sub>s</sub>) temperatures of the investigated glasses. Figures 6 and 7 show the changes in expansion coefficients of glasses and glass-ceramics as a function of BaO/B<sub>2</sub>O<sub>3</sub> replacements as well as the nucleating agents added.

#### Thermal expansion data of the glasses

Table 2 revealed that the thermal expansion coefficient of the glasses as well as their T<sub>g</sub> and T<sub>s</sub> values depend on the original composition of the base glass. With the increase of BaO at the expense of B<sub>2</sub>O<sub>3</sub>, the expansion coefficients increased (figure 6) with corresponding decrease in both glass transition (T<sub>g</sub>) and dilatometric softening (T<sub>s</sub>) temperatures.

Table 2. Dilatometric properties of the investigated glasses and glass-ceramics.

Glass No	T <sub>g</sub> (°C)	T <sub>s</sub> (°C)	Expansion coefficient ( $\alpha$ ) $\times 10^{-7}/^{\circ}\text{C}$					
			25-100°C	25-200°C	25-300°C	25-400°C	25-500°C	25-600°C
G <sub>1</sub>	460	480	75	79	84	-	-	-
C <sub>1</sub>	-	-	70	73	80	92	101	113
G <sub>2</sub>	442	463	89	97	105	-	-	-
C <sub>2</sub>	-	-	84	90	97	103	114	119
G <sub>3</sub>	429	443	97	109	116	-	-	-
C <sub>3</sub>	-	-	95	99	100	111	118	122
G <sub>4</sub>	414	432	98	113	122	-	-	-
C <sub>4</sub>	-	-	96	103	117	124	127	139
G <sub>5</sub>	383	406	109	122	131	-	-	-
C <sub>5</sub>	-	-	100	109	120	129	133	148
G <sub>5</sub> T	392	409	100	117	127	-	-	-
C <sub>5</sub> T	-	-	95	101	116	124	129	133
G <sub>5</sub> F	365	384	144	149	183	-	-	-
C <sub>5</sub> F	-	-	136	138	157	164	172	185

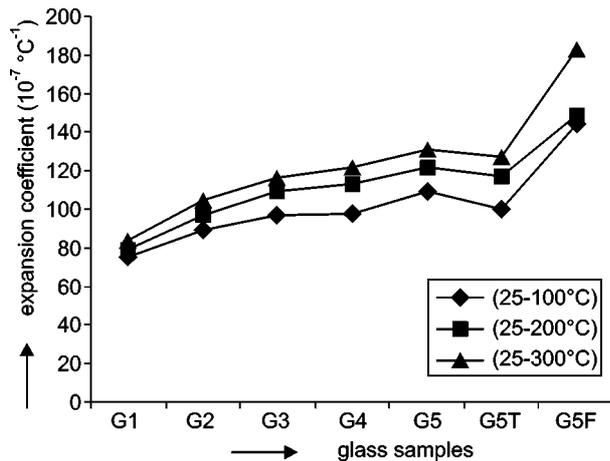


Figure 6. Changes in expansion coefficients of glasses as a function of composition.

On the other hand, the dilatometric properties of glass G<sub>5</sub>T (nucleated with TiO<sub>2</sub>) as well as those of G<sub>5</sub>F (nucleated with MgF<sub>2</sub>) are given in table 2 and graphically represented in figure 6. It can be seen that the incorporation of such nucleants of either TiO<sub>2</sub> or MgF<sub>2</sub> considerably influences the thermal properties of the glass. The presence of TiO<sub>2</sub> has a slight effect on decreasing the thermal expansion of G<sub>5</sub>T as compared with that of G<sub>5</sub> (TiO<sub>2</sub>-free). While the presence of MgF<sub>2</sub> in glass G<sub>5</sub>F results in higher expansion coefficient values as compared with that for glass G<sub>5</sub> (MgF<sub>2</sub>-free), figure 6.

#### Thermal expansion data of the glass-ceramics

The thermal expansion data of the glass-ceramics (C<sub>1</sub>-C<sub>5</sub>) and those nucleated by TiO<sub>2</sub> or MgF<sub>2</sub>, C<sub>5</sub>T or C<sub>5</sub>F are given in table 2 and graphically represented in figure 7. The resulting data revealed that considerable increase of the  $\alpha$ -values of the base glass-ceramic are detected by addition of BaO instead of B<sub>2</sub>O<sub>3</sub>, C<sub>2</sub>-C<sub>5</sub>.

With respect to the effect of nucleating agents, it was seen that the addition of TiO<sub>2</sub> decreased the  $\alpha$ -values of sample C<sub>5</sub>T, as compared with that of sample C<sub>5</sub> (TiO<sub>2</sub>-free) while MgF<sub>2</sub> increased the expansion coefficients of sample C<sub>5</sub>F as compared with that of sample C<sub>5</sub> (MgF<sub>2</sub>-free), figure 7.

## DISCUSSION

### Crystallization characteristics

The addition of BaO instead of B<sub>2</sub>O<sub>3</sub> in the base glass decreases the temperature at which the nucleation begins. The DTA data give evidence that the crystalliza-

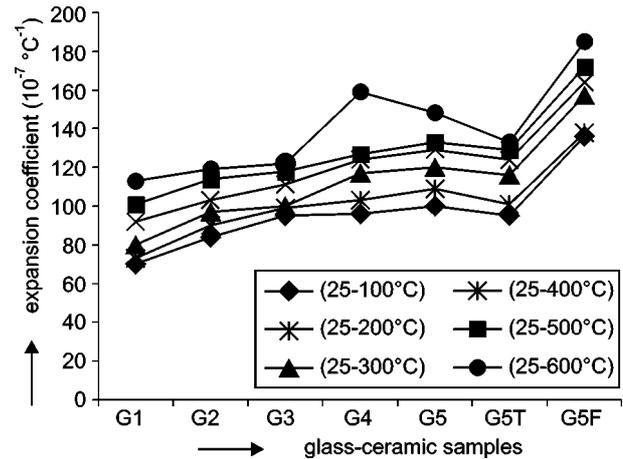


Figure 7. Changes in expansion coefficients of glass-ceramics as a function of composition.

tion characteristics of the glasses were markedly improved by BaO/B<sub>2</sub>O<sub>3</sub> replacements. Both the endothermic dips and the onset of the crystallization exotherms were shifted to lower temperatures by adding BaO instead of B<sub>2</sub>O<sub>3</sub>, i.e. the crystal growth was improved [10]. Oldfield et al [11] showed that B<sub>2</sub>O<sub>3</sub> acts as a diluent in the devitrification process during the DTA run.

The introduction of Ba<sup>2+</sup> into the B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system reduces the melting temperature and viscosity promoting phase separation, which in the ternary barium-borosilicate system is already present in the melt and which in the alkali-borosilicate system can be produced by tempering [12].

On the other hand, the addition of Ba<sup>2+</sup>, a bigger cation, instead of B<sup>3+</sup> a smaller cation, seemed to decrease the SiO<sub>2</sub> chain length of the present glass structure and also increased the number of non-bridging oxygen "NBO" [13]. Thus low viscosity of the glasses is expected [14] which led to enhance crystallization of BaO-containing glasses.

Considering the above-mentioned basis, the crystallization process was easily developed in the heat-treated samples and consequently the crystallization of the glass becomes more apparent with the addition of BaO instead of B<sub>2</sub>O<sub>3</sub>.

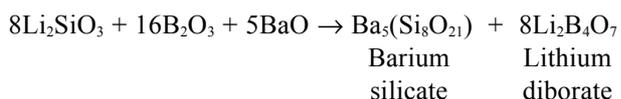
The addition of TiO<sub>2</sub> as a nucleating agent to the glass G<sub>5</sub>T led to shift of the endothermic and exothermic peak temperatures to higher values. This can be ascribed to the role played by TiO<sub>2</sub> in the glass structure, which preferably exhibits a tetrahedral coordination (i.e. TiO<sub>4</sub>) in the glass composition [15].

The addition of MgF<sub>2</sub> as a nucleating agent to the glass G<sub>5</sub>F, led to shift of the endothermic and exothermic peaks to lower values, this can be attributed to the fact that fluorine replaces bridging oxygen in the glass structure by non-bridging fluorine due to their similar size without causing a great disturbance in the arrange-

ment of the other ions. The lower charge of F<sup>-</sup> compared with O<sup>2-</sup> necessitates compensatory mechanism to occur in the glass structure. This may occur by the breakdown of the strong Si-O-Si linkage in the structure and the terminals of the chains are bound to two fluorine ions, i.e. 2 (≡Si-F), with the result that the glass network structure will be weakened [16]. Therefore, fluorine ions may act as network breaker and their influence on decreasing the viscosity and facilitating crystallization of the glass may depend on this property. Furthermore, the fluorine content of the glass generally enhances amorphous phase separation, leading to bulk crystallization [17].

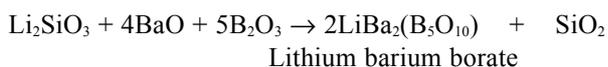
Lithium disilicate was crystallized first as predominant phase together with lithium diborate from the base glass G<sub>1</sub>. However, minor constituents of lithium metasilicate and α-quartz were crystallized as well. Crystallization of meta- and disilicate and their ratios depends on the temperature and duration of the process. Lithium disilicate is formed almost exclusively by low temperature treatment of glasses, while at higher temperature lithium metasilicate appears [18].

It is seen that prolonged thermal treatment would produce secondary phases. These phases developed more slowly and their proportions tended to increase with the duration of heat-treatment [19-20]. Lithium metasilicate-Li<sub>2</sub>SiO<sub>3</sub> was formed at early stage of crystallization in glasses G<sub>2</sub> and G<sub>3</sub> (with 4 and 8 mole % of BaO). However on prolonged heating, lithium diborate, barium silicate-Ba<sub>5</sub>(Si<sub>8</sub>O<sub>21</sub>) and traces of lithium disilicate phases were crystallized as well. This can be explained by considering that a redistribution of the elements of the glass took place through a solid state reaction as shown in the following equation:



The development of traces of lithium disilicate can be explained on the basis that for prolonged heating or long duration the residual silica can combine with lithium metasilicate to form lithium disilicate phase [21].

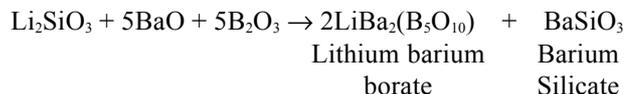
Thermal treatments of glass G<sub>4</sub> (with 12 mole % of BaO) at low temperature led to the formation of lithium metasilicate. However at higher temperature and long duration a redistribution of the B<sub>2</sub>O<sub>3</sub> and BaO in the glass matrix may react with lithium metasilicate to form lithium barium borate and silica (SiO<sub>2</sub>) as follows:



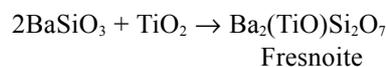
The silica (SiO<sub>2</sub>) formed was crystallized as α-quartz.

LiBa<sub>2</sub>B<sub>5</sub>O<sub>10</sub> is a nonlinear optical material. The structure is comprised of Li and Ba cations and [B<sub>5</sub>O<sub>10</sub>]<sup>5-</sup> anions. [B<sub>5</sub>O<sub>10</sub>]<sup>5-</sup> is a moiety composed of three BO<sub>3</sub> triangles and two BO<sub>4</sub> tetrahedral [22].

On increasing the BaO/B<sub>2</sub>O<sub>3</sub> replacement to 16 %, G<sub>5</sub>, lithium metasilicate was formed at low temperature. At higher temperature for long duration, LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>) and BaSiO<sub>3</sub> were crystallized as well. This can be attributed by assuming that at high temperature lithium metasilicate may react with BaO and B<sub>2</sub>O<sub>3</sub> from glass matrix to form lithium barium borate and barium silicate as follows:



The addition of TiO<sub>2</sub> as nucleating agent in glass with 16 % mole of BaO, G<sub>5</sub>T, led to the formation of lithium metasilicate phase at low temperature. However, on prolonged heating TiO<sub>2</sub> enhances the crystallization of fresnoite -Ba<sub>2</sub>(TiO)Si<sub>2</sub>O<sub>7</sub> phase at the expense of barium silicate-BaSiO<sub>3</sub> as follows:



Keding and Russel [10] showed that fresnoite containing glass-ceramics are mechanically stable and can easily be cut, ground and polished. The coordination of Ti<sup>4+</sup> in this crystal structure is five-fold and thus fairly unusual.

The addition of MgF<sub>2</sub> in the glass composition, G<sub>5</sub>F modified the crystallization kinetics, as expressed by the variation in the peak temperatures (figure 1). This effect may be related to a change in glass viscosity and consequently, led to more mobilization of the glass-forming elements, thus facilitating lithium barium borate-LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>) formation together with lithium metasilicate and MgF<sub>2</sub> phases in glass G<sub>5</sub>F at lower temperatures than that obtained from crystallization of MgF<sub>2</sub>-free glass, G<sub>5</sub>. The retarding effect on BaSiO<sub>3</sub> formation in MgF<sub>2</sub>-containing glass-ceramic, i.e. G<sub>5</sub>F may be explained on the basis that some of Ba<sup>2+</sup> intended to form BaSiO<sub>3</sub> may have been accommodated in the LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>), aided by the presence of F<sup>-</sup> ions.

### Thermal expansion

It is generally accepted that the thermal expansion of glass is not only a function of temperature but is also sensitive to the structure of the glass, for example, degree of cross-linking, type of structural units, the nature and contribution of different cations which occupy either forming or modifying positions in the glass network [23]. The presence of more asymmetrical units in the glass will lead to an increase in the thermal expansion coefficient, while a more coherent network will lead to a decrease in this property [8].

The addition of BaO of lower bond strength (139 kJ/mole) instead of B<sub>2</sub>O<sub>3</sub> of higher bond strength (374-500 kJ/mole) [24] causes a weakening of the glass network structure and consequently, higher  $\alpha$ -values and lower  $T_g$  and  $T_s$  temperatures could be expected in the present glasses.

On the other hand, the addition of TiO<sub>2</sub> to the glass, G<sub>5</sub>T, led to decrease the  $\alpha$ -values. This can be ascribed to the role played by TiO<sub>2</sub> in the glass structure, which preferably exhibits a tetrahedral coordination (TiO<sub>4</sub>) in the glass structure [16]. This in turn will result into a firmer glass structure and led to decrease of the diffusion of different ions and ionic complexes. Therefore, a lower thermal expansion coefficient of the glass and higher  $T_g$  and  $T_s$  values could be expected as compared with the TiO<sub>2</sub>-free glass. However, the presence of MgF<sub>2</sub> in glass G<sub>5</sub>F increased the  $\alpha$ -values and decreased their  $T_g$  and  $T_s$  values. This can be explained on the basis that MgF<sub>2</sub> causes weakening in the glass-network, which led to increase of the diffusion of different ions [16], i.e. higher  $\alpha$ -values and lower  $T_g$  and  $T_s$  values of MgF<sub>2</sub>-containing glasses could be expected.

The thermal expansion coefficients of the glass-ceramics are function of the thermal expansion coefficients and elastic properties of all crystalline phases present including residual glass matrix. The contribution of the residual glassy phase, whose composition is altered from that of the parent glass, must be taken into account [16, 25]. Extremely wide ranges of thermal expansion coefficients are covered by the different crystal types and the development of these phases in appropriate proportions forms the basis of the production of glass-ceramics with controlled thermal expansion coefficient [16].

The expansion coefficient of lithium diborate has a high positive value of  $138 \times 10^{-7}/^\circ\text{C}$  (300-600°C) [26]. Lithium disilicate also has a value of  $110 \times 10^{-7}/^\circ\text{C}$  (20-600°C) [25]. Fresnoite (Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>) has a value of  $(46-171) \times 10^{-7}/^\circ\text{C}$  (300-700°C) [10]. MgF<sub>2</sub> has a high  $\alpha$ -value  $137 \times 10^{-7}/^\circ\text{C}$  [27]. There is no available data on the other Ba-containing phases, e.g. Ba<sub>5</sub>(Si<sub>8</sub>O<sub>21</sub>), BaSiO<sub>3</sub> and LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>). But the obtained results revealed that Ba-containing phases exhibit high  $\alpha$ -values. Also the development of high expansion lithium diborate and/or lithium silicate phases among the crystallization products led to increase of the expansion coefficient of the glass-ceramics (C<sub>1</sub>-C<sub>5</sub>). However the  $\alpha$ -values of glass-ceramic C<sub>5</sub>T are slightly lower than C<sub>5</sub>, which may be attributed to the formation of fresnoite phases instead of barium silicate phase. The thermal expansion coefficient of fresnoite is strongly anisotropic: that attributed to the c-axis is more than three times larger than that related to the a-axis [10]. On the other hand, the  $\alpha$ -values of sample C<sub>5</sub>F were higher than the MgF<sub>2</sub>-free glass-ceramic, C<sub>5</sub>. This can be attributed to the formation of high expansion MgF<sub>2</sub> phase among the crystallization products of sample C<sub>5</sub>F.

## CONCLUSIONS

Varieties of barium-containing phases, e.g. Ba<sub>5</sub>(Si<sub>8</sub>O<sub>21</sub>), BaSiO<sub>3</sub> and LiBa<sub>2</sub>(B<sub>5</sub>O<sub>10</sub>) could be obtained together with lithium meta-, disilicate and  $\alpha$ -quartz phases by adding BaO instead of B<sub>2</sub>O<sub>3</sub> in the crystallized glasses based on Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. The nucleants influenced the type of resulting crystalline phases. Fresnoite (Ba<sub>2</sub>(TiO)Si<sub>2</sub>O<sub>7</sub>) phase was developed on adding TiO<sub>2</sub> as a nucleating agent to the high BaO-containing glass. While, on adding MgF<sub>2</sub> as a nucleating agent, MgF<sub>2</sub> phase was crystallized among the crystallization products of the glasses. The types of the crystallized phases are discussed in relation to the compositional variation of the glasses and thermal treatment used.

The thermal expansion characteristics of the glasses and their crystalline solids have been investigated. The data of the glasses were correlated to the local structure changes induced by BaO/B<sub>2</sub>O<sub>3</sub> replacements and the role of TiO<sub>2</sub> or MgF<sub>2</sub> added as nucleating agents and their contributions to the thermal expansion property of the glasses. However, the results of the crystalline solids were explained in relation to the nature, composition and concentration of all crystalline phases formed including the residual glass matrix.

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KRYSTALIZACE A CHARAKTERISTIKY TEPLOTNÍ  
EXPANZE LITNO-BARNATÝCH BORITOKŘEMIČITÝCH  
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Diferenční termickou analýzou, rentgenovou difrakční analýzou a řádkovací elektronovou mikroskopií (SEM) byl zkoumán vliv BaO na průběh a výsledek krystalizace při ohřevu Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> skel. Byly detekovány různé barnaté krystalické fáze zahrnující křemičitany barnaté, boritany litno-barnaté, meta- a dikřemičitany litné a v některých případech malá množství α-křemene. SEM snímky ukázaly, že BaO podporuje objemovou krystalizaci studovaných skel. Přídavek TiO<sub>2</sub> a MgF<sub>2</sub> jako nukleačních činidel do skel s vysokým obsahem BaO vedl k tvorbě fresnoitu a fází fluoridu hořečnatého. Byly sledovány charakteristiky teplotní expanze skel a jejich krystalických modifikací. Data pro skla byla korelována na lokální strukturní změny vyvolané BaO, TiO<sub>2</sub> nebo MgF<sub>2</sub> a na jejich příspěvky k teplotní expanzi skel. Výsledky byly diskutovány ve vztahu k povaze, složení a koncentraci všech fází zahrnujících zbytkovou skelnou matici.