



The effect of the addition of bismuth (III) oxide on the properties of low-melting boron frits: part 1

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Abstract

Low-melting frits are most often applied in the form of coatings for ceramic building materials, i.e., roof tiles and brick façade. A thin layer of glaze or sintered engobe improves decorative and functional properties of the final product. The roof tiles are fired in the low temperature range (1000–1200 °C). There are expected solutions which will allow obtaining a smooth layer of glaze without deteriorating mechanical and chemical properties. Thus, it is important to find a solution that meets the above requirements. The aim of this study was to analyze the effect of bismuth (III) oxide on the properties of low-melting different commercial frits used as a main component of glaze for ceramic roof tiles. Three commercial frits were modified with the addition of bismuth (III) oxide in the amount of 5 and 10 wt%. In the first stage, the results of the dilatometric and high-temperature microscopy analysis are shown.

Keywords Low-melting frits · Ceramic roof tiles · Low-melting glaze · Bismuth (III) oxide Bi_2O_3

Introduction

One of the most important parameters of low-melting glazes and sintered engobes is to match the coefficient of thermal expansion to the ceramic body and a good spread of glaze on the modified surface. Typically, glazes have lower values of thermal expansion coefficients than ceramic materials and therefore various defects (cracks) occur. Usually, thermal expansion coefficient values of low-melting frits range from 6 to $9 \times 10^{-6} \text{ K}^{-1}$ [1–3]. It is expected that these values are $< 6 \times 10^{-6} \text{ K}^{-1}$. Lithium and bismuth compounds are unique substances with inversion of thermal expansion. Moreover, many bismuth alloys have a low melting point and increased mechanical strength [4–6]. On the other hand, due to the limitation of the use of heavy metals that negatively affect humans and the environment, bismuth and boron, among others, try to replace lead in glazes, especially for red ceramics (majolica) [1].

Low-melting ceramic frits are usually compositions of glass network formers: B_2O_3 - SiO_2 - Al_2O_3 . Other oxides applied in boron frits are Na_2O , K_2O , CaO , ZrO_2 , Li_2O , TiO_2 , etc. [7–9]. There is a continuous increase in the requirements for the improvement of technological and aesthetic properties of glazes and enamels. Each “new” frit should have a wide range of firing temperatures and contain environmentally friendly substances while maintaining appropriate technological properties, such as thermal expansion, mechanical strength, chemical resistance, and aesthetic values.

Low-melting boron frits are used as the main components of glazes, for example, for ceramic roof tiles. In addition to aesthetic values, the low-melting layer of glaze has a beneficial effect on the functional properties of the roof cover. It reduces the adhesiveness of smutting, increases the tile’s resistance to changing weather conditions and inhibits moss expansion. Roof tiles are fired in the low temperature range (to 1100 °C). In such firing conditions, it is difficult to obtain a smooth layer of glaze without deteriorating chemical resistance, especially thermal shock resistance. Obtaining the expected color of the product often becomes a challenge, because the use of the same pigment in configurations with different frits results in products with a different color. In this case, bismuth frits are not sufficiently known yet, although frequently used in the automotive industry as enamels for windscreens and in enameling and electronic industries as

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well [10–16]. There are no references concerning studies on the effect of the addition of bismuth (III) oxide on properties of low-melting frits. The additions of bismuth (III) oxide in the amount of 5 and 10 wt% were selected on the grounds of phase diagrams in $\text{Bi}_2\text{O}_3\text{-SiO}_2$, $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$, and $\text{Bi}_2\text{O}_3\text{-Al}_2\text{O}_3$ systems. The analysis of these diagrams confirmed that the addition of Bi_2O_3 in the range up to 10 wt% brings about the most beneficial effect on the reduction in melting temperature of these systems [17, 18]. The additions of bismuth (III) oxides in the amount of 5 and 10 wt% enable to observe the measurable differences between analyzed systems.

As we know, fritting the glaze mixture brings many advantages. The water-soluble components of the glaze are transformed into insoluble and hence it is possible to apply it to the ceramic body in the form of a water suspension. Fritting also reduces the toxic properties of certain ingredients, e.g., heavy metals, by building them into the glass structure. This also refers to bismuth salts soluble in water. Most of all, the use of fritted glazes reduces the amount of energy necessary to fire products, improves the quality of products and extends the range of their use [1–3]. For this reason, this traditional method of glaze preparation was also used in this study.

In order to make this article as clear as possible, it was divided into two parts. The first part is dedicated to technological properties of frits. It presents the results of the dilatometric and high-temperature microscopy analysis. Structural properties of frits will be the subject of the second part of the article.

Subject matter

The aim of this study is to determine the effect of the addition of bismuth (III) oxide on the properties of low-melting boron frits applied for the production of ceramic roof tiles. Three different oxide compositions of frits dedicated to firing in the low temperature range are compared, including the conditions in which the typical technological process is carried out. To assess the effect of bismuth (III) oxide, the following frits were used: boron-calcium (A), boron-sodium-calcium (B), and alkali-boron (K, Na, Li) (C). Compositions of basic frits are presented in Table 1.

Taking chemical resistance into account, frits with a small amount of alkali were selected. Al_2O_3 content should improve the mechanical, chemical, and thermal properties of the glaze.

A large amount of B_2O_3 increases the melting kinetics without deteriorating chemical resistance and reduces the tendency to crystallize. ZrO_2 (in the case of non-transparent glazes) increases the resistance to thermal shock [2].

Experimental procedure

Oxide compositions were modified with the addition of bismuth (III) oxide in the amount of 5 and 10 wt%. Homogenization was conducted in a ball mill in two steps. At first, the basic frits were wet milled for 20 min and then dried. At the second step, basic frits were dry milled for 4 min with the addition of Bi_2O_3 in the amount of 5 and 10 wt% to homogenize. Each time, 300 g of each frit composition was milled. The homogenized compositions were melted in platinum crucibles with a lid at 1300 °C for 4 h and then the melt was rapidly cooled by pouring onto a steel plate.

The study of thermal expansion was determined by dilatometry (Netzsch DIL 402CD). The test samples were prepared by cutting the frits (dimensions $25 \times 3 \times 3$ mm), which were heated at the rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ within the temperature range of 30–1230 °C under synthetic air atmosphere. The values of softening points and linear thermal expansion coefficients for each frit were determined in 20–300 °C. Averaged results of three measurements are presented in Table 2. The standard deviation for glass transition temperature was $\pm 1 \text{ }^\circ\text{C}$ and for softening temperature was $\pm 1 \text{ }^\circ\text{C}$. The Mayer-Havas calculation results are presented for comparison [19].

The study of fusibility and other technological properties was carried out by means of a Misura HSM high-temperature microscope. The test samples were prepared using the ground frits with the grain size below 63 μm . The next step was to press the pellets of a cylindrical shape ($\varnothing=2$ mm) and 3 mm in height. The measurement was taken at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ within the temperature range from 30 °C until the sample was melted. The measurement with a high-temperature microscope for each sample was performed once.

During these measurements, the following parameters were determined:

- The beginning of volume shrinkage,
- The maximum volume shrinkage (to softening point),

Table 1 Compositions of basic frits

Frit	Chemical composition (wt%)											
	Li_2O	Na_2O	K_2O	MgO	CaO	SrO	BaO	ZnO	Al_2O_3	B_2O_3	SiO_2	ZrO_2
A	–	–	–	–	10.0	–	–	–	10.0	26.0	51.0	3.0
B	–	8.0	–	–	3.0	–	–	–	2.0	36.0	51.0	–
C	1.0	2.0	3.0	1.0	9.0	2.0	1.0	–	12.0	13.0	56.0	–

Table 2 The results of the dilatometric analysis of basic and modified frits

Frit	Bi ₂ O ₃ content (wt%)	Softening point (°C)	Glass transition temperature (°C)	Linear thermal expansion coefficient	
				Dilatometer (20–300 °C) × 10 ⁻⁶ (K ⁻¹)	By Mayer-Havas (10–150 °C) × 10 ⁻⁶ (K ⁻¹)
A	0	747	651	3.40	14.97
	5	694	643	5.08	15.47
	10	683	629	4.68	15.97
B	0	529	499	4.72	15.34
	5	547	501	6.19	15.82
	10	558	502	6.57	16.30
C	0	647	599	5.95	20.57
	5	650	601	6.67	20.79
	10	633	590	6.82	21.01

- The softening point (corner rounding),
- Melting temperature I (sphere effect, when width of the sample is equal to its height),
- Melting temperature II (hemisphere effect, when the base length is equal to 200% of the sample height),
- The flow temperature (temperature at which the base length is equal to 300% of the sample height),
- The sintering interval (the temperature of corner rounding and it is equal to the temperature of shrinkage),
- The softening interval (the temperature of the hemisphere and it is equal to the softening temperature),
- The melting interval (sphere temperature and it is equal to the flow temperature),
- The flow interval (the temperature of the hemisphere and it is equal to the flow temperature).

Measurements of characteristic temperatures of frits were performed three times. The averaged values are presented in Table 2.

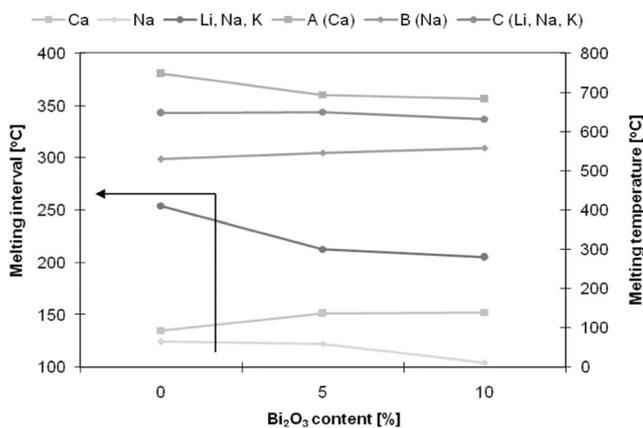


Fig. 1 The softening temperature and melting interval as a function of Bi₂O₃ concentration of basic frits

Also, the changes in frits’ viscosity are determined based on changes in the sample geometry. The values were calculated by the Vogel-Fulcher-Tamman relation:

$$\log \eta = A + \frac{T}{T - T_0} \tag{1}$$

where:

- η is the viscosity coefficient (Pa·s),
- A, B, and T₀ are constants dependent on the chemical composition of frits,
- T is the temperature (K).

The values of constants A, B, T₀ were determined based on three viscosity coefficients which correspond to temperatures of softening and transformation (dilatometer determination) and melting (microscope determination of the sphere) [5]. The results are presented in Figs. 1, 2, and 3.

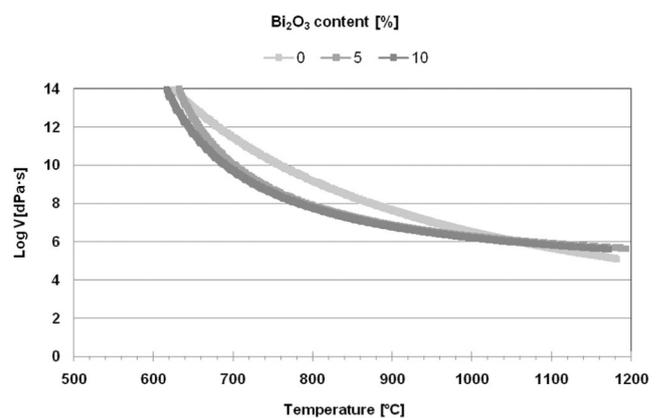


Fig. 2 The viscosity of boron-calcium frits versus temperature

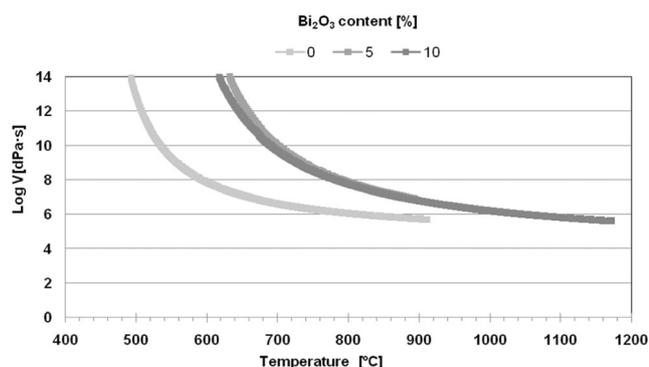


Fig. 3 The viscosity of boron-sodium frits versus temperature

Results and discussion

Figure 1 shows the changes in the melting point (dilatometry) of frits and melting interval as a function of Bi_2O_3 concentration of basic frits.

Boron-sodium frit (B) has the lowest softening point and boron-calcium frit (A) has the highest. A variety of bismuth content effects also is noticed. The higher the softening point of the basic frit is, the stronger the effect of bismuth on the decrease in the softening temperature is noticed. In particular, this property involves the boron-calcium frit. The same relationship is noticed during the assessment of alloys' transformation temperatures.

In the case of frit A, which contains 26 wt% B_2O_3 and a low amount of alkali (up to 0.5 wt%), the addition of Bi_2O_3 reduces the softening point and glass transition temperature. These changes are slight and basically fall within the error limits.

In the case of frit B, which contains the most alkali (about 8 wt%) and B_2O_3 (about 36 wt%) and has the least content of Al_2O_3 (about 2 wt%), the addition of Bi_2O_3 increases the softening point and transformation temperature.

In the case of frit C, which contains 13 wt% B_2O_3 and 12 wt% Al_2O_3 , only 10 wt% addition of Bi_2O_3 slightly reduces the softening point; the glass transition temperature does not change significantly.

The values of the softening points determined by dilatometry correspond at most to the characteristic shrinkage temperatures in the high-temperature microscope (Table 3). Viscosity changes according to Vogel-Fulcher-Tamman are dissimilar and they can be used for comparison purposes only.

The addition of Bi_2O_3 affects the viscosity of low-melting boron frits. The effect depends on the frit composition. In the case of frits with a low content of alkali (a boron-calcium frit), the addition of Bi_2O_3 reduces the alloy softening point and viscosity, especially in the temperature range 650–1000 °C (Fig. 2). This effect decreases with the increase of the amount of alkali.

In the case of a boron-sodium frit, the addition of Bi_2O_3 increases the softening point and the viscosity values over the entire range of the analyzed temperatures (Fig. 3). Furthermore, the addition of Bi_2O_3 to a boron-sodium-potassium-lithium frit does not significantly change both the softening temperature and its viscosity (Fig. 4).

The analyzed frits have linear thermal expansion coefficients at the level $6 \times 10^{-6} \text{ K}^{-1}$. Slightly lower values of this coefficient are obtained for a boron-calcium frit (with a low content of alkali). It was observed that the addition of Bi_2O_3 in each case increases the values of the linear thermal expansion coefficient of low-melting boron frits. For comparison, Table 2 presents the values of linear thermal expansion coefficient calculated on the basis of the Mayer-Havas method. These values are one order of magnitude larger, but the trend of change is similar.

The interpretation of characteristic temperature is noteworthy. The width of the sphere's base in this case depends on the surface tension of the alloy to the standard alundum substrate

Table 3 The characteristics of temperature (high-temperature microscopy) of basic and modified frits

Frit	Bi_2O_3 content (wt%)	Temperature of characteristic points (°C)					Interval (°C)		
		Shrinkage	Rounding	Sphere	Halfsphere	Flow	Sintering	Softening	Flow
A	0	729	1022	1047	1135	1182	293	113	47
	5	779	1028	1040	1146	1191	249	118	45
	10	749	995	1020	1127	1172	246	132	45
B	0	583	754	785	871	909	171	113	42
	5	611	749	775	870	897	138	123	25
	10	584	745	761	826	865	161	81	39
C	0	695	835	899	947	981	140	12	134
	5	677	784	903	1047	1116	107	263	69
	10	673	813	891	1050	1096	140	236	33

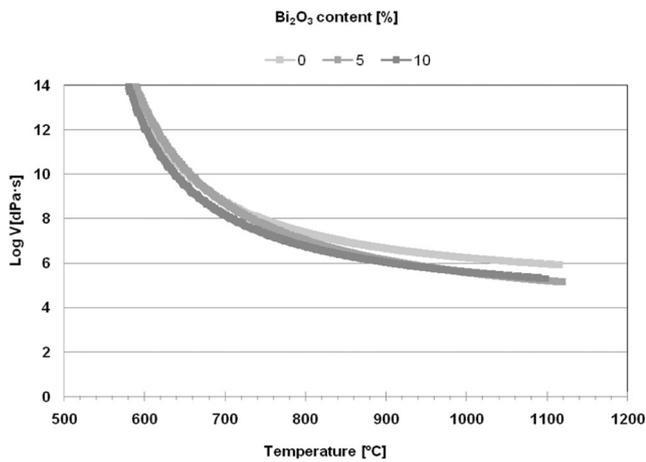


Fig. 4 The viscosity of alkali-boron (K, Na, Li) frits versus temperature

(Fig. 5). The relative width of the base for temperature of sphere is presented in Table 4.

The studies have shown that the addition of Bi₂O₃ increases the contact angle of melted frits, which is associated with an increase in the alloy surface tension in accordance with the Young-Dupre equation [12]. The effect of increasing the value of the contact angle may be the shrinkage of the glaze if the critical value is exceeded relative to the bed. In particular, this feature concerns a boron-sodium-potassium-lithium frit and boron-calcium frit.

In the case of a boron-sodium-potassium-lithium frit, as the Bi₂O₃ content increases, the values of the sphere's contact angles increased from 119 to 142°. The comparison of the sphere's contact angles determined in a high-temperature microscope relative to the alundum bed confirms this case (Table 4). In the case of a boron-calcium frit (without alkali), the contact angle of the sphere has a smaller value at around 100°. This value does not change significantly; however, it increases gradually as the content of bismuth increases. In turn, the boron-sodium frit shows intermediate values of the contact angle at the characteristic temperature of the sphere (about 120°).

A high-temperature microscope enables also to measure the boundary (greatest) values of the contact angle of the frit to the alundum bed (Fig. 6). It can be observed that the highest (boundary) values of contact angles occur at slightly higher temperatures (by approximately 20 °C) than at the characteristic temperatures of the sphere. However, the trend of change is similar in all cases (Table 4).

The relative width of the base also decreases as the addition of Bi₂O₃ increases, which indicates an increase in the surface tension of the alloys with its addition.

The values of surface tension calculated on the basis of properties of specific frit ingredients (oxides) according to Appen [14] depend more on their types (A, B, C) than the addition of Bi₂O₃. Generally, the addition of Bi₂O₃

Fig. 5 The shapes cross of sphere characteristic temperature

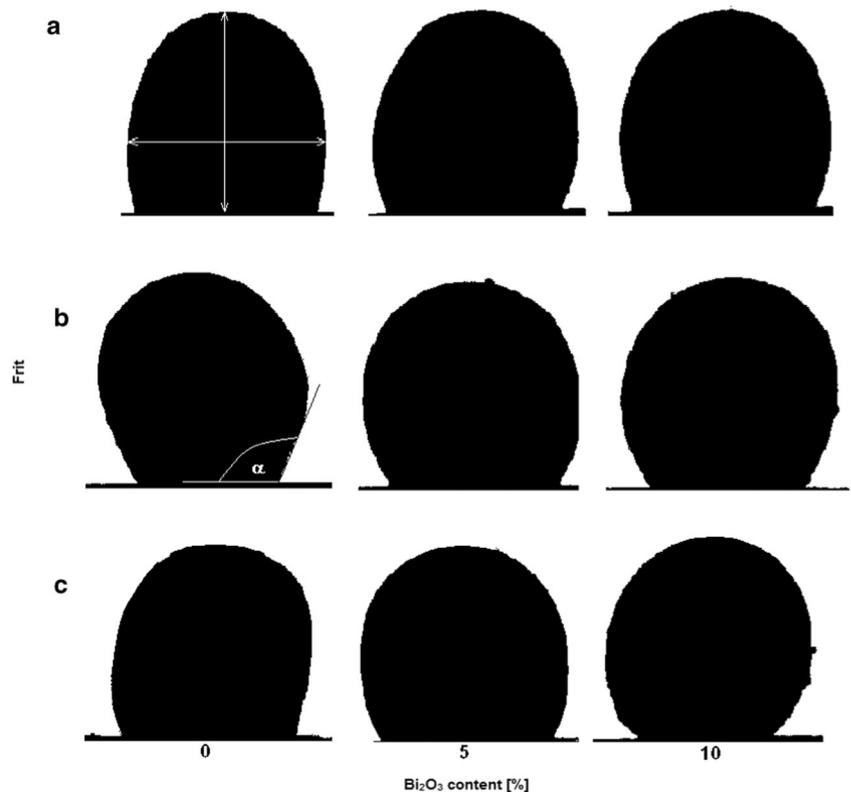


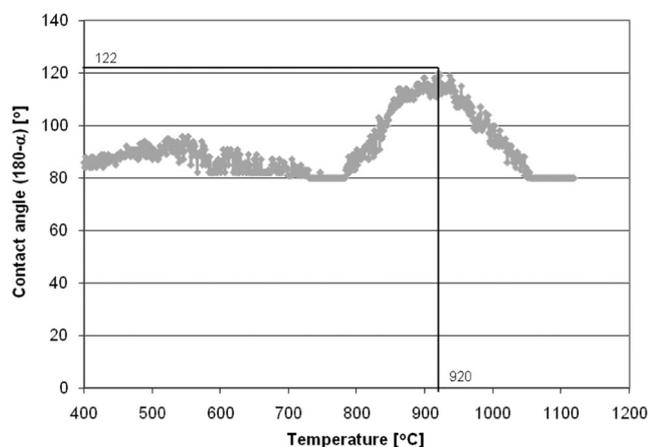
Table 4 Surface tension and contact angle of frits relative to the alundum base in a high-temperature microscope

Frit	Bi ₂ O ₃ content (%)	Surface tension by Mayer-Havas (1300 °C) (N·m ⁻¹)	Sphere			Terminal angle value	
			Relative width of the base	Contact angle (°)	Temperature (°C)	Contact angle (°)	Temperature (°C)
A	0	28.82	0.95	101	1047	117	1060
	5	27.88	0.86	110	1040	122	1062
	10	26.94	0.86	110	1020	125	1036
B	0	22.72	0.86	119	785	130	807
	5	22.08	0.85	120	775	141	823
	10	21.45	0.79	122	761	127	769
C	0	31.87	0.95	119	899	120	978
	5	30.78	0.81	121	903	122	920
	10	29.68	0.79	142	891	147	890

successively reduces the surface tension of boron frits, which is contradictory to the results of studies in a high-temperature microscope (Table 4). At the addition of the Bi₂O₃ in the amount of 10 and 5 wt%, the surface tension, regardless of the type of frit, decreases respectively by approximately 7 wt% and approximately 3 wt%. The alloy viscosity as well as surface tension is important parameters from the point of view of use. The high surface tension value “smooths” (smooth mirror-like finish) the surface, while the high viscosity hinders its melting.

Conclusions

The results discussed above indicate that the addition of bismuth (III) oxide to low-melting boron frits may contribute to improving or degrading their application properties. Their oxide composition has a significant effect.

**Fig. 6** Contact angle limit of a alkali-boron frit with 5% Bi₂O₃

The addition of Bi₂O₃ to a low-melting boron-calcium frit with high melting temperature and low melting interval is beneficial as it lowers the softening temperature and widens the melting interval. Moreover, the low value of thermal expansion and large value of the contact angle of such frits may contribute to the good “coverage” of the glaze on the products.

A low-melting boron-sodium frit modified with Bi₂O₃ with low melting temperature and a small melting interval yields an increase in the softening point and narrowing the melting interval of the frit. It also helps to increase the thermal expansion coefficient, and increases the contact angle value, which facilitates the good coverage of glaze on the products.

Low-melting alkali-boron frits containing sodium, potassium, and lithium doped with Bi₂O₃ with a dilatometric softening point at 600 °C do not significantly change this value; however, it strongly expands the melting interval of such frits. The increased value of the thermal expansion coefficient and the small contact angle contribute to the shrinkage of glaze on the products. This kind of frit is unfavorable to the modification of ceramic glazes, but it should be preferred as a flux for low-sintering ceramic materials.

The proposed mechanism is that Bi₂O₃ in low-melting frits is presumably a glass network modifier that fills in the holes of the network and weakens the bonding. In this connection, it can be added only to a certain extent; otherwise, the whole structure may convert into a crystalline state [3, 20–23].

Moreover, the amount of the Bi₂O₃ addition (5 wt% or 10 wt%) matters and it is associated with the basic frit composition.

To sum up, dilatometric studies in relation to the high-temperature microscopy allow good characteristics of technological properties of low-melting frits. However, they require the accurate analysis of all characteristic temperatures (e.g., sphere, hemisphere, softening) and sintering, softening, melting, and flowing intervals. The methods of Mayer-Havas,

Appen, etc. as well as Vogel-Fulcher-Tamman should only be used for comparison purposes. In the case of low-melting frits, their values can vary significantly which may not be reflected in the industrial practice.

The first stage of research aimed to assess that Bi_2O_3 addition bismuth oxide reduces the melting temperature of frits. In order to gain precise explanation of mechanism of Bi_2O_3 in low melting frits, it is necessary to conduct infrared spectroscopy and additional analysis.

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