STATISTICAL DESIGN OF EXPERIMENTS (DOE) APPLIED TO THE FORMULATION OF TRANSPARENT SINGLE-FIRE FRITS

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ABSTRACT

In view of the importance of the frit, glaze, and ceramic colour manufacturing sector in the ceramic tile production chain, this paper seeks to identify the influence of the chemical composition of ceramic frits for porous single firing on glazes formulated with these frits in order to provide information for formulating frits capable of achieving the performance required by today's glazed tile manufacturing sector.

Nowadays, porous single-fire frits are the main ingredients for glazes used to manufacture ceramic tiles in Brazil. Their basic characteristics are a high softening temperature and low viscosity at high temperatures. This behaviour encourages the removal of gases from the body in single-firing processes and leads to the formation of layers of high-gloss glaze, with minimum roughness and excellent fit to the ceramic body.

For the purposes of this study, different transparent frit compositions for porous single firing were formulated by varying the contents of the main oxide constituents, especially the network modifiers (CaO, ZnO, and K_2O). Statistical design of experiment (DOE) techniques for mixtures were used to determine the effect of these oxides on cost, real density, transparency, flow, thermal expansion, and viscosity of the suspensions formulated from each frit.

The results obtained illustrate the importance of using statistical design of experiment techniques to develop formulations with appropriate technical properties. Furthermore, the method of analysis used revealed the significance of each oxide on the behaviour of each type of frit and allowed composition ranges to be identified that enabled frit performance to be optimised from the point of view of quality ceramic tile manufacturing.

1. INTRODUCTION

The dizzying growth in ceramic tile production in Brazil, which took place mainly in the second half of the last decade, has brought with it a series of challenges for the frit, glaze, and ceramic colour manufacturing sector responsible for supplying frits and pigments to the ceramic wall and floor tile industry. In view of the fact that Brazilian ceramic tile output grew by over 100% in a period of just 10 years [1, 2], frit, glaze, and ceramic colour manufacturers have had to come to terms with the demand from tile manufacturers and to increase the number of manufacturing plants throughout Brazil. Apart from more traditional companies already present in the country, who undertook significant extensions of their production capacity, several new colour manufacturers, using both domestic and foreign capital, have set up inside Brazil.

The competition generated throughout the sector, where different companies fight for segments of an increasingly demanding market, has led to colour manufacturers developing new products – in search of differentiation – by continuing to strengthen the efficiency of their present services with increased quality and cost-cutting, more customised provision of services or by establishing new marketing policies.

Nowadays, ceramic frits [3, 4] produced by these colour manufacturers are used as the main raw materials for glazes applied to ceramic tiles. On the industrial scale, a significant number of the frit formulations used in Brazil come from imported recipes developed abroad – especially in Spain and Italy. Specialised scientific literature on the subject is also rather scarce and only a small number of studies have appeared that deal directly with frit formulation. Therefore, frit development work currently undertaken by colour manufacturers in the country is limited to using imported recipes (not necessarily the most suitable for the raw materials and particular characteristics of the Brazilian ceramic tile industry), for which local sector technicians make empirical adjustments to existing formulations.

Transparent, glossy frits for porous single firing – the subject of this paper - are the most widely used type of frits in the Brazilian ceramic tile industry. The fast single firing process has spread rapidly in recent years and calls for the development of frits suitable for the requirements of the process. Frits for porous single firing are characterised by having high permeability at high temperatures, which enables the gases from the reactions taking place in the ceramic body during firing to be eliminated. Furthermore, after the surface softening and subsequently water-proofing, they need to have high rate of viscosity reduction in order to provide smooth, glossy surfaces in short time and temperature ranges of the fast firing cycles currently used in the Brazilian ceramic tile industry. In order to guarantee such behaviour, frits for porous single firing are generally poor in alkaline elements – which act as vigorous network modifiers - and are rich in alkaline-earth elements. Calcium and zinc oxides are the main network modifiers in this type of frit [3].

Ceramic frits need to be formulated in such a way as to be able to simultaneously provide a specific series of characteristics that guarantee their manufacture at the colour producer and their performance during usage, i.e. during the obtainment of the glaze in ceramic tile manufacture, as shown in Figure 1. Thus, successful frit manufacture can only be guaranteed through the frit formulation, which needs to take several parameters into account, such as ease of raw material transport, low toxicity of the composition, low release of corrosive vapours, high productivity, stability during manufacture, and reasonable costs. Likewise, when used by the ceramic tile industry, the frit needs to guarantee performance during milling, not cause any adhesion problems on the ceramic tile before firing, form stable suspensions with suitable rheological properties for glaze application [5] and drying times compatible with production line requirements.

During firing, the frit has to provide a suitable maturing range at the working temperatures, provide gloss and stretching [6] as well as thermal expansion compatible with the ceramic body in order to prevent any curvatures [7], while also meeting the requirements laid down by technical standards for the finished product, such as surface cleanliness, resistance to scratching, abrasion and chemical attack.

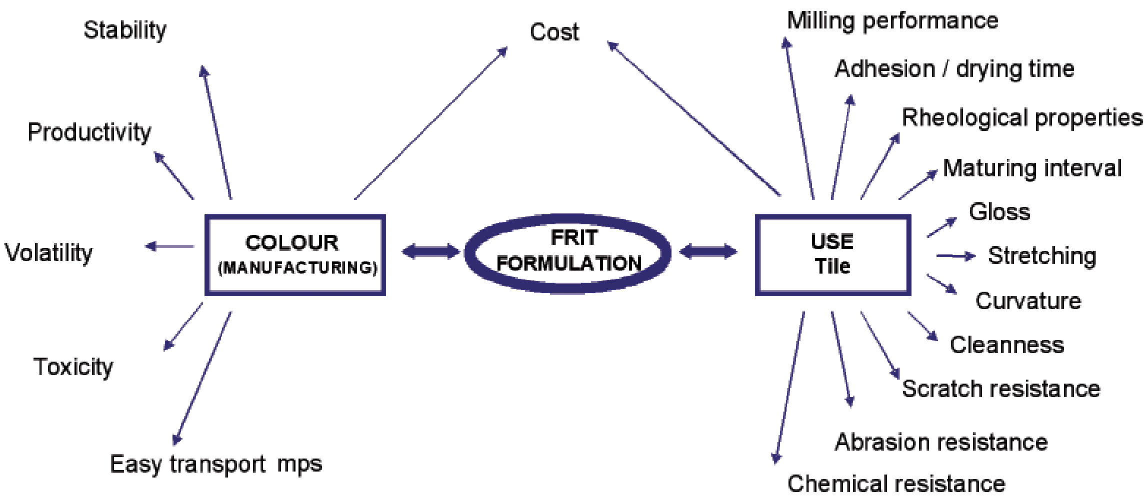

Figure 1. Performance requirements to be taken into account in frit formulation.

Given the large number of requirements that need to be taken into account when formulating transparent frits and the variety of compositions that can be obtained by modifying the proportions of the constituents in the formulation, Statistical Design of Experiments (DOE) gains special relevance as a tool for developing optimised compositions. This tool, already well exploited in other industrial sectors, has been used successfully in recent years to develop formulations in the ceramic sector [8,9]. Thus, the main objectives of this study are:

- To assess the potential of the statistical design of experiments technique for developing formulations of transparent frits for single firing;
- To determine the influence of the main network modifying oxides on transparent frit properties.

- To identify chemical composition ranges that optimise the target properties of transparent frits for single firing.

2. EXPERIMENTAL PROCEDURE

Tables I and II show the frit compositions obtained with Minitab 14.0 software, which were experimentally evaluated. Transparent frit compositions for single firing were formulated by maintaining steady molar proportions of SiO_2, Al_2O_3 and B_2O_3 while varying the content of CaO, ZnO and K_2O. The values shown in Table I are expressed as molar proportions according to the Seger formula [10], while Table II shows the same compositions expressed in oxides by weight percent. For the statistical design, it was decided to vary CaO content between 0,55 and 0,85, ZnO content between 0,00 and 0,35, and K_2O content between 0,05 and 0,25. Figure 2 illustrates the composition ranges evaluated in the study. It is important to observe that compositions E and G are replicas of composition B, required in the statistical design of experiments to determine the experimental deviations associated with each of the properties under evaluation in the study. The raw materials used to obtain the compositions described herein were quartz, potassium feldspar, kaolin, boric acid, limestone, zinc oxide and potassium nitrate.

Oxides	A	B	C	D	E*	F	G*	H	I
SiO_2	2,50	2,50	2,50	2,50	2,50	2,50	2,50	2,50	2,50
B_2O_3	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15
Al_2O_3	0,20	0,20	0,20	0,20	0,20	0,20	0,20	0,20	0,20
CaO	0,85	0,69	0,75	0,60	0,69	0,85	0,69	0,55	0,55
ZnO	0,10	0,17	-	0,35	0,17	-	0,17	0,20	0,35
K_2O	0,05	0,14	0,25	0,05	0,14	0,15	0,14	0,25	0,10

Table I. Compositions used in the study expressed in accordance with the Seger formula.

Oxides	A	B	C	D	E*	F	G*	H	I
SiO_2	62,3	61,1	61,4	60,7	61,1	62,1	61,1	60,1	60,3
B_2O_3	4,3	4,2	4,3	4,2	4,2	4,3	4,2	4,2	4,2
Al_2O_3	8,5	8,3	8,3	8,2	8,3	8,4	8,3	8,2	8,2
CaO	19,8	15,8	17,2	13,6	15,8	19,7	15,8	12,3	12,4
ZnO	3,4	5,5	-	11,5	5,5	-	5,5	6,5	11,4
K_2O	1,8	5,0	8,9	1,8	5,0	5,4	5,0	8,7	3,5

Table II. Compositions used in the study expressed by weight percent

The frits were fused in zirconium-aluminium-silica crucibles at 1500 °C, maintained for 30 minutes at this temperature and then quenched in water. After that, glazes were prepared using 94% of the frit composition and 6% kaolin. 0,2% CMC, 0,2% TPP and 40% water were added for laboratory milling for a sufficient period of time to obtain 2% and 4% residue on a 44 µm mesh. The glazes thus obtained with each frit were characterised in the following ways:

- Real density, as per Helium gas pycnometer, by using the dry glaze in an electric furnace and disaggregation until it passed through a 177µm mesh;
- Apparent suspension viscosity, which was determined by a Brookfield rotational viscometer at a set shear rate;
- High temperature viscosity – by stretching of buttons pressed in the same conditions and fired on a laboratory sloping-base muffle furnace at 1130 °C for 40 minutes.
- Transparency – after applying the glazes with a slider with an aperture of 0,4 mm on a ceramic body, through the chromatic coordinate L* as determined by a Minolta CM-2600d spectrophotometer.
- Thermal linear expansion index calculated from 25 to 325 °C by means of dilatometer analysis of previously pressed samples fired in a laboratory muffle furnace at 1000 °C.

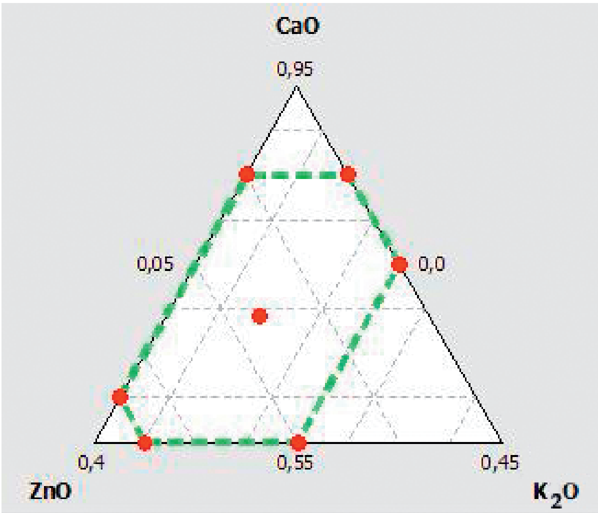

Figure 2. Graphic illustration of the composition ranges evaluated in this study

3. ANALYSIS AND DISCUSSION OF RESULTS

Figure 3 depicts the modelling of the cost of frits for single firing within the range of compositions preset for the study. It shows that the cost of the frits can vary significantly depending on the proportion of raw materials used, with certain compositions having a cost nearly 300% higher than the lowest cost compositions.

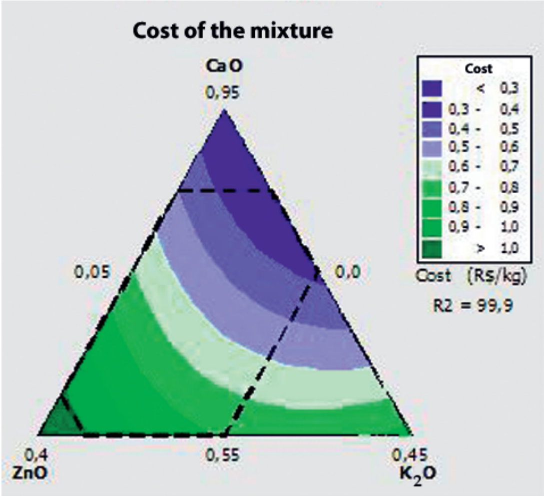

Figure 3. Cost modelling of the frit compositions over the studied sample space.

Frits with the highest concentrations of ZnO are the most costly as a result of the high price of zinc oxide. Compositions with a high concentration of K_2O are also in the upper cost range due to the need to include potassium nitrate in the formulations in order to achieve the required proportions of K_2O. Frits rich in CaO are the least costly within the range of compositions used in the study.

Figure 4 represents the variation in real density of the frits in the range of compositions under study when using statistical design of experiments. Real density has to be taken into consideration in order to define the working density of the ceramic tile glaze suspensions, given that changes in the proportions of the different oxides present in the compositions can lead to significant variations in the specific weight of the frits thus obtained. Real density of ceramic frits is mainly determined by the concentration and nature of network modifiers in the silica glasses [11]. The higher the concentration of network modifiers in silicate glasses is, the greater the density. In this case, as the molar concentration of silicon and boron oxides was kept constant in all the frits under study, the only variable responsible for altering the density of the frits was the nature of the network modifiers used.

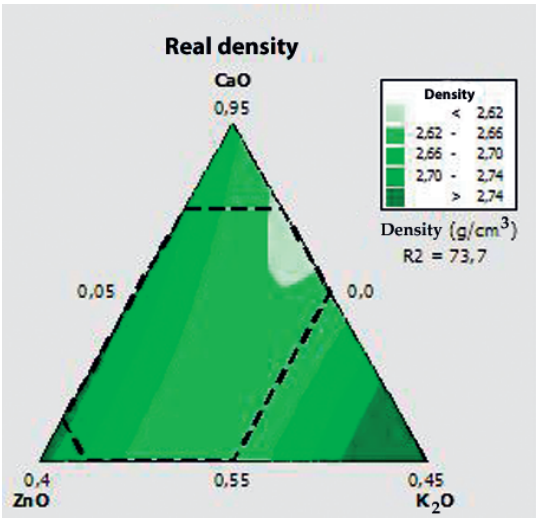

Figure 4. Modelling of real density of the frit compositions in the studied sample space.

It can be seen from Figure 4 that the frits with the highest density were obtained from the compositions with the highest ZnO content and lowest K_2O content. The atomic weight and radius of the network modifier cations determine their capacity to penetrate inside the interstitial holes in the vitreous structure. Figure 5 shows a comparison of the experimental results obtained with the frits in Tables I and II together with theoretical density values calculated using the Schott factor [12]. It can be seen that, although a certain correlation exists between the theoretical and experimental data, the sample space analysed reveals a good degree of scatter.

Figure 6 presents an evaluation of the viscosity of the suspensions obtained with each of the frits and the modelling of this variable using statistical design of experiments techniques. Once again it can be seen that the presence of ZnO in detriment of K_2O significantly affects the behaviour of the frits during firing. Generally, the suspensions formed from frits located in the area of the diagram that depicts the compositions with the greatest ZnO content present the lowest viscosity within the study range. Likewise, all the compositions rich in K_2O led to higher viscosity glazes. These results can be explained by two main factors: the volumetric concentration of solids in the suspensions, which is higher in frits with lower real density when the amount of water used for milling the glazes is pre-determined as a % by weight, and secondly, because frits rich in K_2O have a greater tendency to solubilise, which allows for more cations to be released into the suspension, thereby affecting its rheological properties.

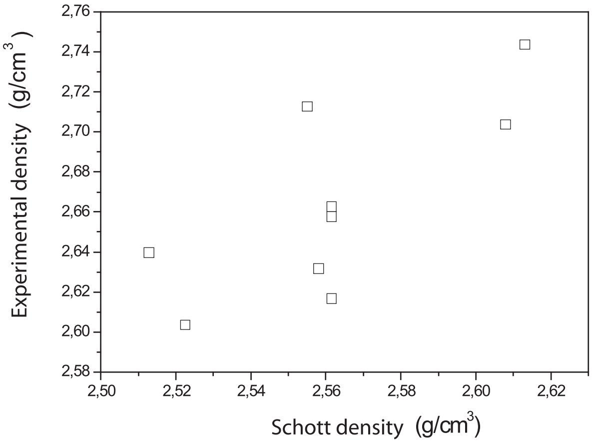

Figure 5. Comparison of the experimental results with the theoretical results obtained using Schott factors to calculate frit density

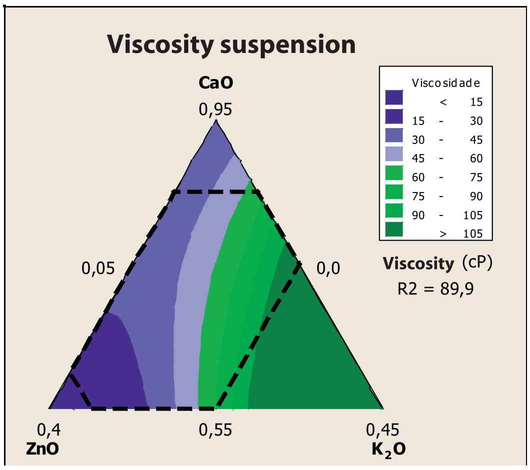

Figure 6. Modelling of apparent viscosity of the glaze suspensions obtained from the frits in the studied sample space.

Figures 7, 8 and 9 present the modelling of the characteristics during firing of the frits under evaluation in this study, with diagrams that show how the chemical composition of the frits affects their transparency, viscosity (as evaluated by means of their flow capacity) and their coefficient of thermal expansion.

Frit transparency was evaluated using the L* chromatic coordinate measured by spectrophotometry on glazes applied by a slider on unglazed bodies. The higher the L* parameter, the whiter the frits become, which indicates that they have lower transparency and greater milkiness. On the other hand, the lower the L* parameter, the more transparent the frits are, as they allow dark colours in the ceramic base to be clearly observed through the glazed surface.

Figure 7 shows that frits free of ZnO were the ones with the greatest milkiness. Above molar concentrations of 0,15 ZnO (expressed according to Seger formula), the frits become highly transparent. Frits with a high K_2O content display the greatest milkiness, while in compositions rich in K_2O and ZnO, transparency attains acceptable values.

The loss of transparency in some frit compositions for single firing is caused by the presence of phases with different refractive indices in the formed glaze. In this sense, possible hypotheses that may justify the loss of homogeneity in the glass are the presence of air bubbles, the formation of crystalline phases and glassy phase separation phenomenon. Glasses rich in alkaline-earth elements (especially MgO and CaO) have a greater tendency to phase separation [11,13]. An alternative to prevent this phenomenon is to increase Al_2O_3 content in the compositions, although this option was not pursued as it did not fall within the scope of this study.

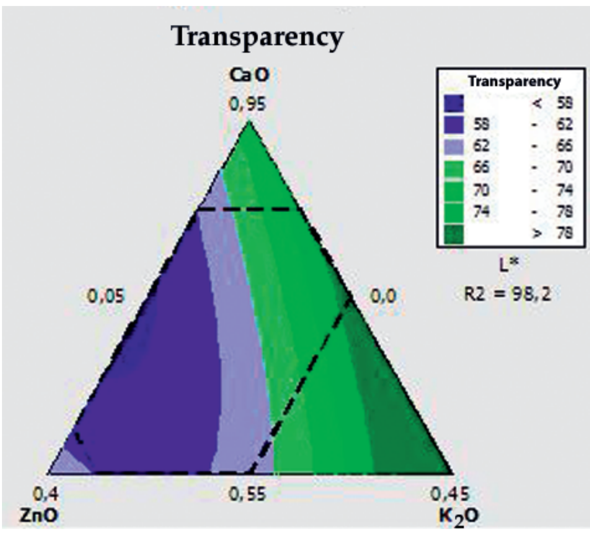

Figure 7. Modelling of transparency in the frit compositions included in the studied sample space

The viscosity of the frits in the range of compositions under study was measured by assessing the flowability at high temperature of buttons made from the same frits. Figure 8 shows that the CaO content in the frits is the parameter which most significantly influences this property. Frits with a high CaO content were the ones that had the lowest flow at high temperatures. It is interesting to observe in the diagram in Figure 8 that there is an area where the compositions with the lowest viscosity and, therefore, the highest flow are concentrated. This area is related to the compositions with low CaO content, high K_2O content, and intermediate levels of ZnO. It can also be seen that frits rich in ZnO and poor in K_2O do not display low viscosity even when the concentration of CaO is low. In this sense, the importance of alkaline network modifiers as the means of obtaining low viscosity frits for single firing should be underlined.

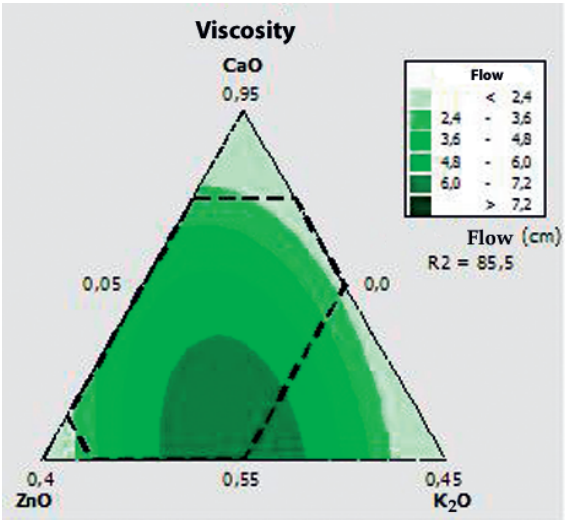

Figure 8. Modelling of high temperature viscosity in the frit compositions in the studied sample space.

An analysis of thermal expansion coefficients in frits for porous single firing is shown in Figure 9. It can be seen that this type of frit generally displays low thermal expansion. While the compositions with the lowest thermal expansion coefficients are to be found in the central areas of the studied sample space, the frits with the highest K_2O content presented thermal expansion rates of over 68,0 x 10^{-7} $^oC^{-1}$, as well as the frits with the lowest content of this element.

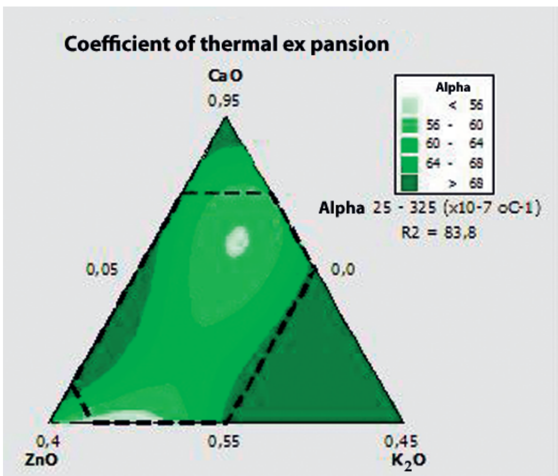

Figure 9. Modelling of the coefficient of thermal expansion in the frit compositions included in the studied sample space.

4. CONCLUSIONS

Statistical design of experiments methods can be successfully used to obtain formulations of frits for single firing, as well as to indicate the influence played by each of the main oxide constituents on the technological properties of interest. A large number of important characteristics for frits for single firing can be evaluated using this technique, through experimental characterisation of a small number of formulations within a very ample sample space. Statistical models allow for the unknown characteristics of the compositions to be reliably designed, thereby economising on time and resources in the frit development stage.

The results indicated that the technological properties of frits for single firing vary significantly within the range of compositions under study, in which the relative proportion of network modifying oxides was hardly varied. In summary, it can be concluded that:

- The cost of the composition depends highly on its ZnO content;
- Frits with a low K_2O content and high ZnO content have the highest densities;
- Suspensions with the lowest viscosity can be obtained from the compositions with the highest ZnO content;
- Frits free of ZnO and rich in K_2O within the studied range of compositions revealed a loss of transparency;
- The CaO content in the frits has a considerable impact on their viscosity at high temperatures; and
- Thermal expansion coefficients of the single-fire frits can differ considerably depending on their K_2O content.

Depending on the target properties of the frits to be developed, superimposing the diagrams on each other may indicate different compositions capable of meeting the necessary requirements within the context of frit formulation. These results can be even further optimised by introducing other oxides into the system (Na_2O, MgO, BaO, for example) or by controlled varying of the oxide contents that were set in this study (SiO_2, Al_2O_3 and B_2O_3).

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