

Effect of the Synthesis Conditions of Cobalt Aluminate Nano-Sized Powder on the Melting Behaviour of Transparent Glaze

Sh. Salem¹, S.H. Jazayeri¹, F. Bondioli², A. Allahverdi^{*1}, M. Shirvani¹

¹School of Chemical Engineering, Iran University of Science and Technology, Tehran 16846 – 13114, Iran

²Department of Material and Environmental Engineering, University of Modena e Reggio Emilia, Modena 41100, Italy

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Abstract

The effect of the conditions applied for the synthesis of cobalt aluminate powder on the thermal behaviour of a typical transparent frit was investigated. The nano-sized cobalt aluminate spinels were prepared with the combustion method. The powders were synthesized at a pH of 2.5, 7.0, 10.5 and a fuel ratio of 0.56 and 0.75 using cobalt and aluminium nitrates and glycine as fuel. The obtained gels were calcined at 800 and 1000 °C. 2 wt% calcined powders were added to an industrial transparent frit and the thermal behaviour of the modified glazes was studied by means of hot stage microscopy (HSM). The thermal properties are described in terms of height percentage and contact angle. All samples began to shrink close to 700 °C and reached a minimum value at around 1330 °C. The synthesis of powder at acidic and neutral pH with a low content of fuel led to a significant change in the height percentage and an expansion was observed between 940 and 1040 °C. The HSM data were analyzed with the Vogel-Fulcher-Tamman equation and the influence of the synthesis conditions on the molten viscosity was evaluated. The results indicated that the synthesis of cobalt aluminate gel at neutral pH in the presence of a low fuel ratio and calcination at 1000 °C provides the best conditions from an industrial point of view.

Keywords: Cobalt aluminate, glaze; melting, hot stage microscopy, viscosity

I. Introduction

Cobalt aluminate powder is widely used in the ceramic, glass, paint and enamel industries as well as in colour television tubes as a contrast-enhancing luminescent pigment to produce Thenard's blue^{1,2}. This material is preferred for use in ceramic glazes because of the attractive colour produced when it is prepared in nano-size^{3,4}. The properties of cobalt aluminate spinel depend on the mineralogy and particle size distribution of the powder, which determine the quality of the final product.

The theoretical formula for spinels is generally $A^{2+}B_2^{3+}O_4$ in which the crystalline structure is classified as cubic, the anions being arranged in a cubic close-packed lattice. In addition, the A and B cations occupy some or all of the octahedral and tetrahedral sites in the lattice⁵. There are two ideal structures: the normal spinel structure which is usually identified by cubic close-packed oxides with one octahedral and two tetrahedral sites for each oxide anion. The tetrahedral interstices are smaller than the octahedrals therefore; the B^{3+} ions occupy half of the octahedral holes whereas A^{2+} ions occupy 1/8th of the tetrahedral holes because of a charge factor. The lattice energy is maximized when the diameter of ions is similar^{6,7}. On the other hand, the inverse spinel structure is slightly different owing to

the presence of transition metals in the crystal field. If the A^{2+} ions have a strong preference for the octahedral sites, they displace half of the B^{3+} ions from the octahedral sites to the tetrahedral ones. If the B^{3+} ions have low or zero octahedral site stabilization energy, then they have no preference and adopt the tetrahedral site¹.

One of the most frequently used spinels with regard to the cobalt aluminate system is $Co^{II}Co^{III}_xAl_{2-x}O_4$ in which the x value is between zero and two. The chemical analysis of cobalt aluminate spinels is more like Co_3O_4 , Co_2AlO_4 and $CoAl_2O_4$ ^{8,9}. The coordination of Co^{2+} is one of the most important factors affecting the colorant performance of cobalt pigment^{10,11}. Control of its composition is therefore necessary to ensure reliable performance in industrial applications. On the other hand, the glaze composition, containing frit and pigment should provide sufficient melting properties to support the hot rheological characteristics and suitable surface tension during firing with the substrate. Regardless of the above properties, cobalt aluminate powder should exhibit the normal thermal behaviour in order to achieve suitable properties.

The most commonly applied process for the commercial production of $CoAl_2O_4$ with effective colorant behaviour on industrial scale is based on a solid-state reaction in which the oxides are mechanically ground at high calcination temperatures of about 1300 °C for a long time.

* Corresponding author: ali.allahverdi@iust.ac.ir

Although this process is relatively inexpensive, the product may not be of acceptable quality. The inferior quality can be attributed to a lack of homogeneity, with relatively large and uneven grains as a result of a poor control of stoichiometry^{11,12}. Recently spinels have been synthesized using several wet-chemical techniques such as sol-gel^{13–15}, emulsion precipitation¹⁶, hydrothermal crystallization^{12,17} and co-precipitation^{18,19}. Regardless of the available solution chemistry routes, the combustion technique is an inexpensive method permitting the preparation of high-purity, nano-sized crystalline powders at lower calcination temperatures in a significantly shorter time^{20–22}.

Synthesis of cobalt aluminate powder by means of the combustion method is an important application step. The solution is prepared in an intermittently or continuously stirred tank at room temperature. To obtain favourable properties of cobalt aluminate powder in glazes, it is necessary to study the effect of the powder synthesis conditions on the melting behaviour of glaze. Consequently, there is great interest in studying the effect of the solution pH, fuel ratio and powder calcination temperature on the melting behaviour of glaze based on the determination of the hot viscosity and surface tension. In this way, it is possible to determine the optimal conditions to ensure acceptable thermal behaviour following the addition of the pigment into the glaze.

Hot stage microscopy provides useful data for characterizing the melting behaviour of glaze^{23–25}. It enables monitoring of the thermal behaviour of glaze from the sintering to the melting stages. The application of this technique to study the sintering of different ceramic substrates has been reported by a number of researchers^{26–28}. Hot stage microscopy enables assessment of the shrinkage of glaze or ceramic body. The compact sample was made from powder with the uniaxial compaction technique.

Hot stage microscopy is a standard, well-known device in the ceramic and glaze fields. Traditionally, the instrument has been mainly applied to assess thermal behaviour, particularly to determine the softening and melting temperatures of glazes, ceramics and other silicate materials²⁹. The cylindrical powder samples are obtained by pressing in a die at room temperature, usually without the addition of any binder²⁸. For non-isothermal experiments, the furnace of the microscope is heated to the maximum temperature usually at a constant heating rate. The samples are placed on a small ceramic plate with the longitudinal axis coinciding with the vertical direction. By measuring the changes in length and diameter of the samples during the sintering process, either by taking photographs of the sample at pre-defined time intervals during the sintering process or by video recording the whole experiment, it is possible to ascertain the axial and radial shrinkage. The height and diameter of the photographed or video-recorded sample images can be measured with a relative error < 1 % on suitable enlargement.

At high temperatures glaze behaves as a fluid and its viscosity falls with increasing temperature. In the temperature range between the vitreous transition temperature and the melting point, glaze behaves visco-elastically. In oth-

er words, a certain amount of time is needed for viscous flow to ensue, but if it is subjected to a short and intense stress, the glaze reacts elastically. When the temperature is increased, the glaze reaches the vitreous transition temperature, T_g , in which the viscosity is about 10^{12} Pa·s. A further increase in the temperature causes the viscosity to fall progressively down to $10^3 - 10^4$ Pa·s, when the melting point is reached²³. The variation in viscosity over the temperature range applied in industrial processes is therefore extremely wide, more than ten orders of magnitude.

Vogel-Fulcher-Tamman developed a model to estimate the viscosity of molten glass as a function of temperature. They predicted the hot viscosity based on three constant parameters according to the following equation:

$$\log \eta = A + \frac{B}{T - T_0} \quad (1)$$

where A , B and T_0 are the constant parameters of equation. T_0 is an empirical constant which is used to linearize the viscosity curve. This parameter defines the degree of association of the ceramic structure and depends on the type of glaze and viscosity range. Moreover, the model parameter, A , is related to the theoretical viscosity of completely free particles. It means that no activation energy is required for mobility of particles into viscous flow and it is possible to obtain this theoretical viscosity at an infinitely high temperature. Parameter T_0 is related to changes that occur in matrix of glaze. This parameter is very important since the value of T_0 determines the association of the silicate structure. B essentially influences the prediction correlations because of appearing in power. If B equals zero, the viscosity is temperature-independent. To calculate the three unknown constants A , B and T_0 , it is necessary to input the three reference temperatures into the VFT equation. A reference value of 10^{12} Pa·s is widely accepted for viscosity at T_g for all types of glasses. Also, the value of viscosity at half sphere shape has been selected as another reference temperature. $T_{1/2}$ is the temperature in which a sample forms a half sphere shape during HSM analysis^{30,31}. This temperature is obtained when the height of the sample is half of width corresponding to the contact angle 90° . Scholze studied the viscosity of nine types of pressed powder samples at $T_{1/2}$ and reported the average value of $10^{3.55}$ Pa·s³⁰. The measured viscosity at $T_{1/2}$ temperature provided some important information and it is easily distinguishable during HSM measurement. The viscosity of multi-oxide silicate and frits at sintering temperature, T_s , was determined by several investigators. The obtained results showed the value of $10^{9.25}$ Pa·s^{23,30,31}. The constant parameters of Eq. (1) can be easily calculated by substituting the value of viscosity at corresponding temperatures and the results are summarized as the following equations:

$$T_0 = \frac{12T_g - 3.55T_{1/2} + (9.25T_s - 12T_g) \frac{T_{1/2} - T_g}{T_s - T_g}}{8.45 - 2.75 \frac{T_{1/2} - T_g}{T_s - T_g}} \quad (2)$$

$$A = \frac{9.25T_s - 12T_g + 2.75T_0}{T_s - T_g} \quad (3)$$

$$B = (T_g - T_0)(12 - A) \quad (4)$$

Extensive literature is available on the synthesis of cobalt aluminate powder, which can be useful to understand the structural changes in the powder properties. Unfortunately, information on the effect of the conditions for the synthesis of cobalt aluminate on the thermal behaviour of glaze does not exist for estimating hot viscosity and surface tension to achieve optimum conditions. The aim of this study is to quantify the viscosity changes as a function of the powder synthesis conditions. The laboratory investigation was conducted to determine the shrinkage as a function of temperature for a typical transparent frit and the glazes modified with 2.0 wt% synthesized pigment by means of hot stage microscopy. This paper reports on the findings of this study on hot viscosity and surface tension, which were conducted based on pH, fuel ratio and calcination temperature.

II. Materials and Methods

(1) Sample preparation

The experiments were conducted by dissolving two materials in de-ionized water at room temperature. The solutions were prepared with the addition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (both from Merck, 99% minimum) and glycine as a fuel. The molar ratio of Co/Al was 1:2. Two appropriate amounts of glycine were added to adjust the G/ NO_3 molar ratio to 0.56 and 0.75. Subsequently, ammonia was added to control the pH level at around 7 and the final pH of the solution was adjusted to 2.5, 7, and 10.5 by adding the required amount of either HNO_3 or liquid ammonia. Precursor solutions with a pH of 2.5 were completely homogeneous but precipitations were observed in solutions prepared with a pH of 7 and 10.5. The temperatures of the solutions were maintained at 298 K.

In order to obtain a viscous gel, the mixed solution was heated on a hot plate kept at a steady temperature of 110 °C. The viscous precursor materials were then heated rapidly in a pre-heated furnace kept at 500 °C. During smouldering combustion, which lasted longer than 7 min, the material underwent foaming followed by decomposition, generating a large volume of gases. The voluminous and foamy combustion ashes obtained were easily crushed to produce the powders. The crushed powders were further calcined at 800 and 1000 °C for 1 h to study their thermal behaviour. The powders calcined at 800 and 1000 °C produced dark and bright blue colours respectively.

(2) Sample characterization

The experiments were conducted on small scale. For this purpose, a typical transparent frit was used. The chemical analysis of the frit, expressed in mass percent, was determined as follows: SiO_2 : 61.95, Al_2O_3 : 11.80, Na_2O : 0.93, K_2O : 1.03, CaO : 12.40, MgO : 10.40, Fe_2O_3 : 0.30, TiO_2 : 0.46 and SnO_2 : 0.70. To evaluate the effect of the synthesis conditions of the cobalt spinel on the melting behaviour of the frit, 2.0 wt% calcined pigments were replaced with the same amount of frit. All samples were prepared by dispersing the materials in acetone followed by milling to obtain homogenous powders. Test specimens in the shape of bars

(3 mm height \times 2 mm diameter) were prepared by means of uniaxial pressing.

The HSM tests were performed on the specimens at a constant heating rate of 50 °C/min. The HSM instrument used (Misura ODHT-HSM, Expert Systems Srl, Modena, Italy) consists of three principal units mounted on a 1.5-m-long optical bench. A halogen lamp as the light source, an electronic furnace and a carriage for the specimen were used in the equipment. The system was also equipped with a microscope for observation of the shape changes. Other data collected using HSM are the percent of specimen height and contact angle curves. The percent of initial height plots indicate the balance of three forces acting on the glaze, i.e. gravity, viscous and tension forces. The contact angle plots relate to the interfacial tension between the molten glaze and substrate. To further investigate the effect of subsequent pigment synthesis conditions on the melting behaviour of the frit used, the HSM tests were performed on the specimens containing the pigments calcined at 800 and 1000 °C respectively and the results compared with the thermal characteristics of the frit. The HSM experiments were repeated twice for the frit and prepared glazes to substantiate the repetition of experimental data. The maximum difference observed in the percent of initial height plots was 5 °C.

Simultaneous differential thermal analysis (DTA-TG, Model 409, Netzsch, Germany) of the gel was conducted with a heating rate of 10 °C/min.

The nature of the chemical functional groups of the synthesized powder was determined by means of Raman spectroscopy (Horiba Jobin-Yvon, Longjumeau, France). The Raman spectra were recorded using the excitation wavelength (632.81 nm) provided by helium and neon. The laser power was set to 20 mW.

The morphology of the calcined particles was analyzed by means of transmission electron microscopy (TEM, JEM 2010, JEOL, Tokyo, Japan). For this purpose, the specimens were prepared by dispersing the powders in distilled water and then placing a drop of suspension on a copper grid with a transparent polymer followed by drying in laboratory oven. Approximately, 100 crystals were considered in the evaluation of the crystal size.

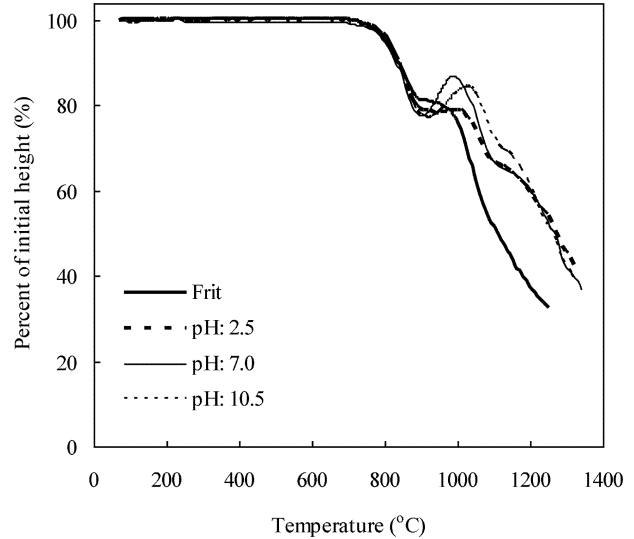
III. Results and Discussion

The initial height percent of the glazes containing the pigments prepared at different pH and calcined at 800 °C are plotted in Fig. 1. The glazes have been studied non-isothermally from 70 to 1330 °C. The results presented in Fig. 1(a) show the height of glazes prepared with the fuel ratio of 0.56. Sintering of the frit used begins at 720 °C. The nature of the curve is similar to that published in the literature on glazes^{23, 24}. In the non-isotherm curve no significant shrinkage was measured at the temperature less than 720 °C. The decrease in height begins at 720 °C, corresponding to the sintering temperature of the frit. In the initial stage, the areas of contact between adjacent particles form and grow. In the intermediate stage, growing necks merge and the large number of small particles is replaced by a smaller number of large particles. In the final stage of sintering, the pore spaces become bro-

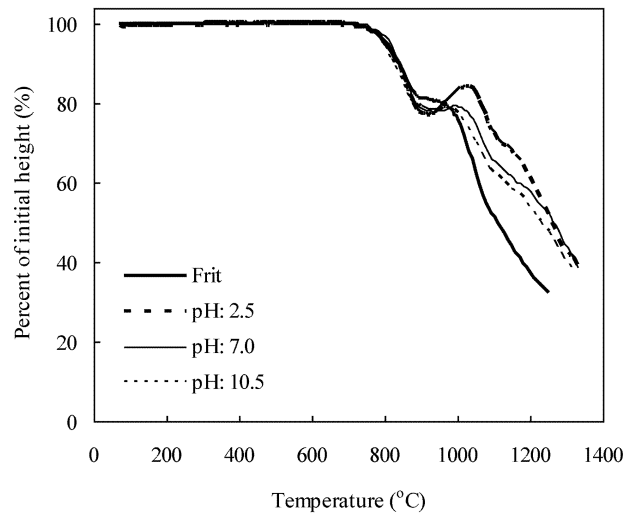
ken up with isolated closed pores and shrinkage is observed as densification proceeds. At 892 °C, the softening temperature, the specimen height does not change any more. In this case, the final shrinkage is about 20 %. The softening temperature measured using the heating microscope represents the temperature at which the liquid phase prevails over the solid phase and at this temperature the specimen becomes completely impermeable to the passage of gas formation on the surface of the specimen. For the temperatures above 990 °C, the height of sample decreases exponentially with temperature as shown in Fig. 1(a). It should be noted that the shape of sample was changed to a sphere at 1080 °C. Above 1080 °C significant height reduction is observed. When the temperature reaches 1162 °C, the sample appears like a half sphere. Between 1162 °C and 1242 °C, the frit begins to melt and finally coats the substrate at 1242 °C. The variation in sample shapes of frit is illustrated in Fig. 2 as a function of temperature.

The effect of the synthesis pH on the thermal behaviour of glaze containing 2.0 wt% pigment is also presented in Fig. 1(a). It is obvious that the sample height undergoes different changes than those observed in the frit used. From the curves for compositions prepared at different pH, it can be seen that the shrinkage rate decreases to a minimum with an addition of cobalt aluminate powder. The change in pH negligibly decreases the sintering rate. When shrinkage reaches 20 % at about 900 °C, the height variation is affected by the pH. The height is observed to increase until a maximum value when powder is synthesized at a pH of 7 and 10.5. From 1000 °C and 1040 °C onward, the expansion rate gradually decreases and melting starts at 1050 °C and 1070 °C corresponding to a pH of 7 and 10.5. From these temperatures the height decreases in an exponential form with temperature. The value of critical temperatures, such as the glass transmission temperature determined with an optical dilatometer, T_g , the sintering temperature evaluated by thermal microscopy, T_s , the temperature at which sphere shape is obtained, T_{sp} , the temperature in which half of sphere is formed, $T_{1/2}$ and melting point, T_m , are summarized in Table 1 as a function of the pH. It is clearly observed that the value of T_g remains approximately constant for modified glazes. Also T_s does not substantially change with the pH whilst $T_{1/2}$ and T_m increase considerably compared to those for the frit. Although, for the synthesis of cobalt aluminate powder in acidic environment, a pH of 2.5 favours the thermal behaviour, obtaining a normal variation from sinter-

ing point to melting temperature, the precursor prepared at a pH of 2.5 presents a flaming combustion type. In contrast precursors prepared at a pH of 7 and 10.5 exhibit smouldering combustion type. Therefore, from an industrial point of view the preparation of powder in an acidic environment is not suitable for the synthesis of cobalt aluminate powder.



(a)



(b)

Fig. 1: The initial height percentage of glazes containing the powders prepared at different pH, calcined at 800 °C and a fuel ratio of (a) 0.56, (b) 0.75.

Sintering	Softening	Sphere	Hemisphere	Melting
804°C 94.89%	892°C 81.82%	1086°C 53.98%	1162°C 42.33%	1242°C 32.95%
72°	112°	65°	100°	117°

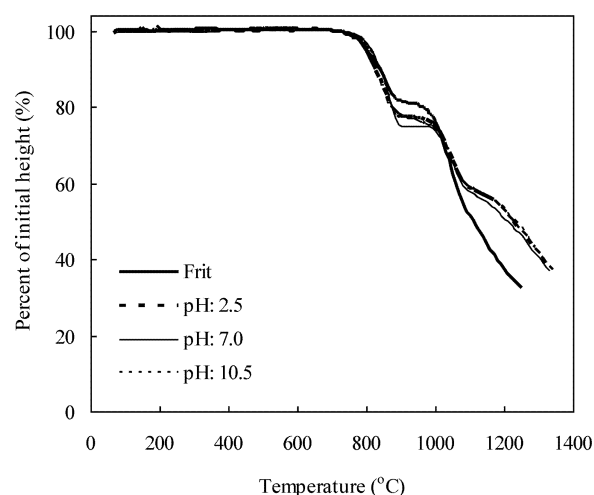
Fig. 2: The sample shapes of frit as a function of temperature.

Table 1: The critical temperatures of the frit and modified compositions used as a function of the synthesis conditions and calcination temperature

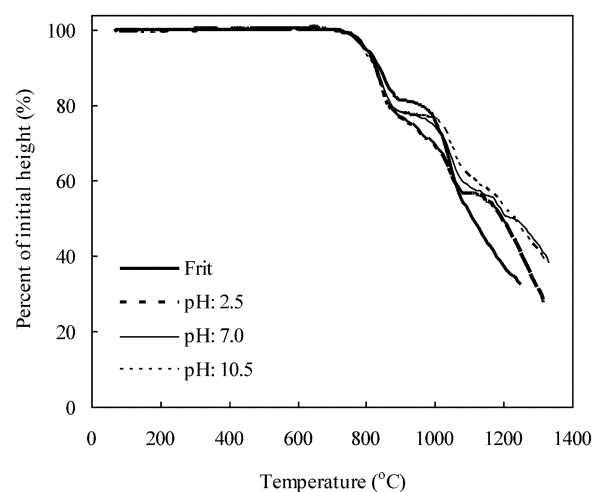
Fuel ratio	Calcination temperature (°C)	pH	Critical temperatures (°C)				
			T_g	T_s	T_{sp}	$T_{1/2}$	T_m
Frit			698	726	1086	1162	1242
0.56	800	2.5	700	726	1100	1260	1328
		7.0	700	732	1152	1258	1328
		10.5	700	736	1084	1246	1314
0.75	800	2.5	700	732	1108	1244	1310
		7.0	732	752	1094	1248	1320
		10.5	706	722	1090	1230	1304
0.56	1000	2.5	694	716	1088	1256	1328
		7.0	710	734	1148	1246	1322
		10.5	716	738	1162	1256	1328
0.75	1000	2.5	704	724	1100	1200	1250
		7.0	708	726	1090	1246	1324
		10.5	704	728	1072	1240	1316

The cobalt aluminate powders were prepared with a fuel ratio of 0.75 at different pH and the obtained powders were calcined at 800 °C. The modified glazes were prepared with addition of 2.0 wt% calcined powder to the frit and the HSM plots shown in Fig. 1(b) refer to the thermal behaviour of the above-mentioned glazes. All the curves are identical in nature and are characterized by exponential behaviour in sintering and melting regions. This type of behaviour is generally observed in the thermal behaviour of glazes. The results obtained show that the melting temperature increases with addition of the synthesized powders. The composition containing the powder prepared in an acidic environment undergoes rapid expansion between 970 and 1040 °C. First, the decrease in height is a result of the softening of the glaze. As the thermal process progresses, expansion is observed in the sample. Finally, because of the melting of glaze, the height of the sample falls exponentially, leading to the covering of the substrate. It is obvious that the rate of variation decreases as the pH of the synthesis environment rises. The expansion may be related to spinel transformation, which can be observed at 800 °C.

To study the effect of the calcination temperature of the pigment synthesis on the thermal behaviour of modified glazes, the prepared powders were calcined at 1000 °C and the HSM plots of glazes are shown in Fig. 3. The plots describe the starting stage of neck formation as stages of the sintering process. At higher temperatures, densification occurs and shrinkage increases. All the phenomena previously described take place in all studied cases. In solid-state sintering, it is evident that linear shrinkage values do not increase after a certain temperature. It is useful to compare, on the same temperature scale, the HSM plots to determine which composition may affect thermal behaviour. In an analysis of the plots obtained, two prima-



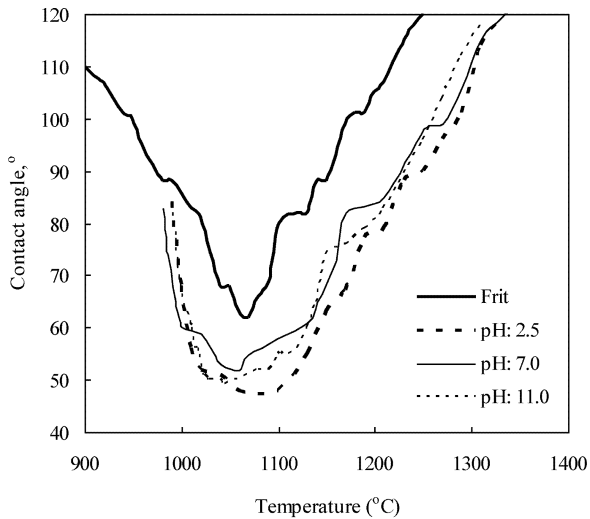
(a)



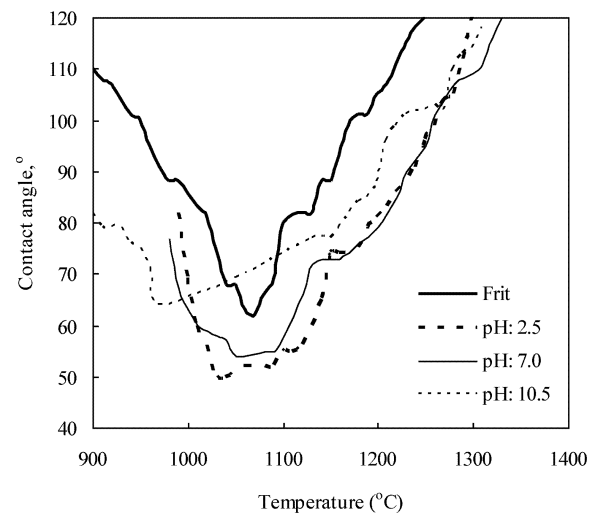
(b)

Fig. 3: The initial height percent of glazes containing the powders prepared at different pH, calcined at 1000 °C and a fuel ratio of (a) 0.56, (b) 0.75.

ry behaviours are exhibited. The first behaviour describes those cases where the temperature at the end of the final sintering stage remains approximately constant. The glaze powder that presents such behaviour sinters before the melting process begins. The second behaviour describes those cases where the melting temperature increases with addition of the powders. In the studied cases with the pH and fuel ratio of the synthesis conditions, the expansion behaviour seen in Fig. 1 is not observed. All the compositions studied in this work that present the normal thermal behaviour can be considered for the production of cobalt aluminate powder but the selection of a simple method for pigment synthesis is of great importance in the manufacturing process. According to the data in Table 1, no significant changes were observed in T_g and T_s with a change in the synthesis conditions. In fact, below 900 °C no significant change occurred in shrinkage. The melting temperature is approximately constant for the modified glazes and near to 1320 °C with an exception in the composition containing the powder prepared at a pH of 2.5 and a fuel ratio of 0.75.



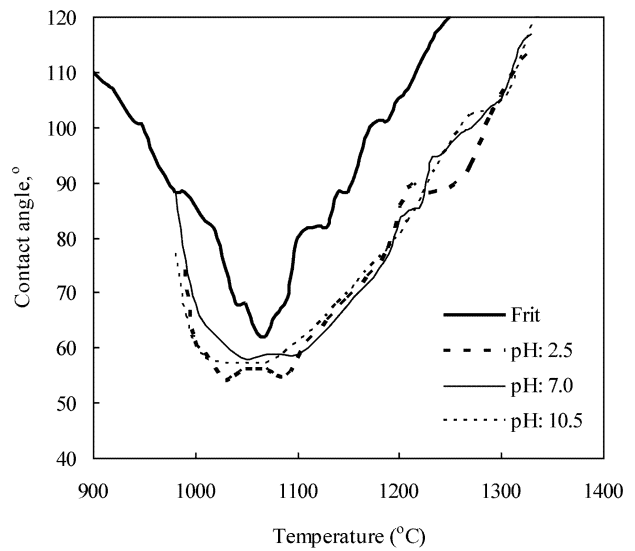
(a)



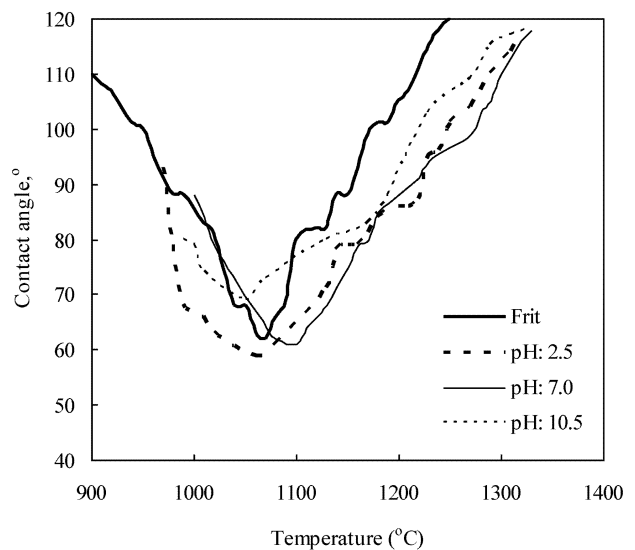
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Fig. 4: The contact angle of glazes containing the powders prepared at different pH, calcined at 800 °C and fuel ratio of (a) 0.56, (b) 0.75.

The good approximation in determination of the optimum synthesis conditions can also be related to surface tension. In order to better understand the influence of the synthesis conditions on thermal behaviour, the contact angle was evaluated as a function of temperature. By comparing contact angle curves, Figs. 4 and 5, it was possible to illustrate how the conditions in the synthesis of cobalt aluminate powder influence the behaviour of glaze. As a general rule, the synthesized powders notably decrease the minimum contact angle. The cobalt aluminate powders usually increase surface tension at around 1080 °C. With rising temperature up to melting temperature, the contact angle increases and reaches 120 ° for frit and modified glazes. When cobalt aluminate powders are introduced into the glaze matrix, they can notably modify the glaze network near the temperature in which the spherical shape is obtained.



(a)



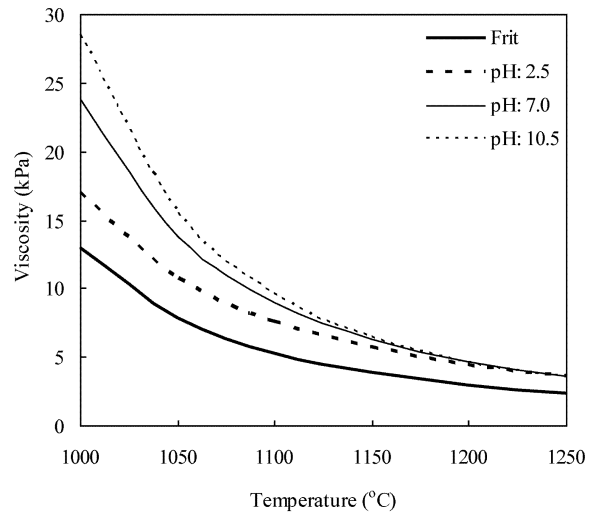
(b)

Fig. 5: The contact angle of glazes containing the powders prepared at different pH, calcined at 1000 °C and fuel ratio of (a) 0.56, (b) 0.75.

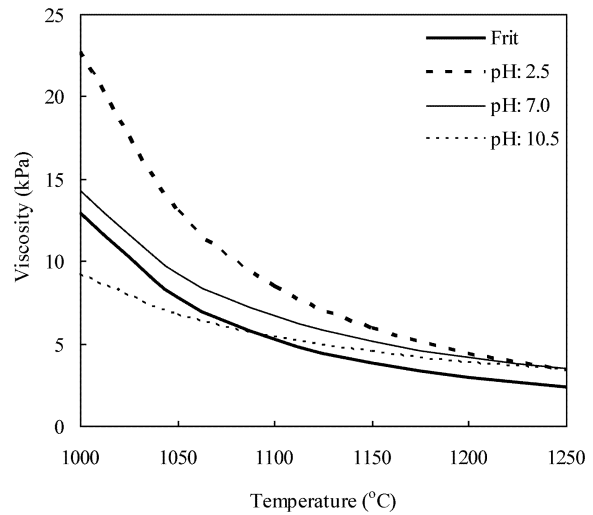
All samples were analyzed with the help of the VFT model to determine the viscosity as a function of temperature for the investigated frit and modified compositions. The effect of the pH on the viscosity of melted glaze is shown in Fig. 6 for samples calcined at 800 °C. The viscosity increases as the pH of the synthesis environment rises. Fig. 6 also shows the effect of the fuel ratio on hot viscosity. As the fuel ratio was increased, a considerable decrease was observed in viscosity. It might be of importance to note that when the fuel ratio was increased, the inverse behaviour was detected compared to Fig. 6(a).

It is worth noting that the viscosity varies with the calcination temperature of cobalt aluminate powder as shown in Fig. 7. The plots show that the fuel ratio has no pronounced effect on the viscosity when synthesis was performed at a pH of 10.5. Also, significant changes are observable in the viscosity of molten glazes prepared with addition of powders synthesized at a pH of 2.5 and 7.0. Therefore, the pH was found to be an important factor affecting the viscosity of melted glaze in these conditions.

The constant parameters of the VFT equation were determined based on T_g , T_s and $T_{1/2}$. The results obtained are compared in Table 2. The parameters of the VFT equation were used to choose the best synthesis conditions. For the VFT model, the value of the constant T_0 varies from 637 to 606 with changing pH of the synthesis environment, which shows the decreasing association of the silicate structure. The value of B increases regularly from 590 to 926. The change in the value of B , which may be termed the dependence of viscosity on temperature, suggests that the viscosity of molten glaze increases with changing pH. The VFT model was chosen to predict the viscosity. This model appears to have considerable merit in determining the dominant factor influencing viscosity during the melting schedule. This empirical model is in agreement with the viscosity changes for many glass and glaze systems over the melting stage. In the VFT model, the constant B expressed the temperature dependence of the viscosity.



(a)



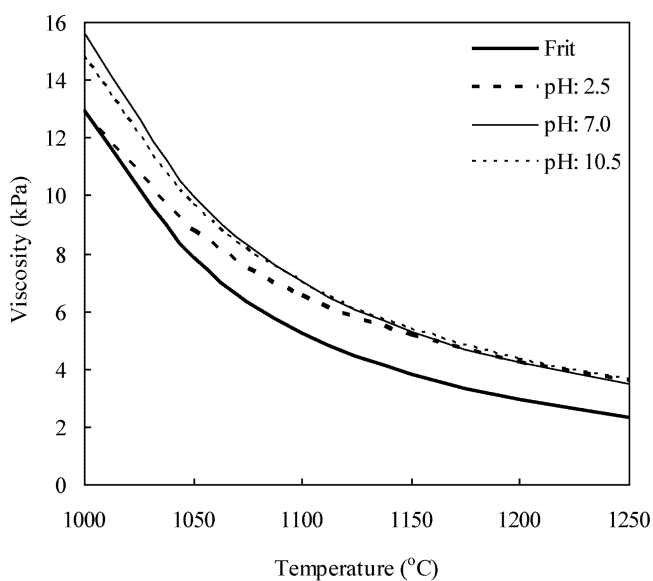
(b)

Fig. 6: The hot viscosity of glazes containing the powders prepared at different pH, calcined at 800 °C and fuel ratio of (a) 0.56, (b) 0.75.

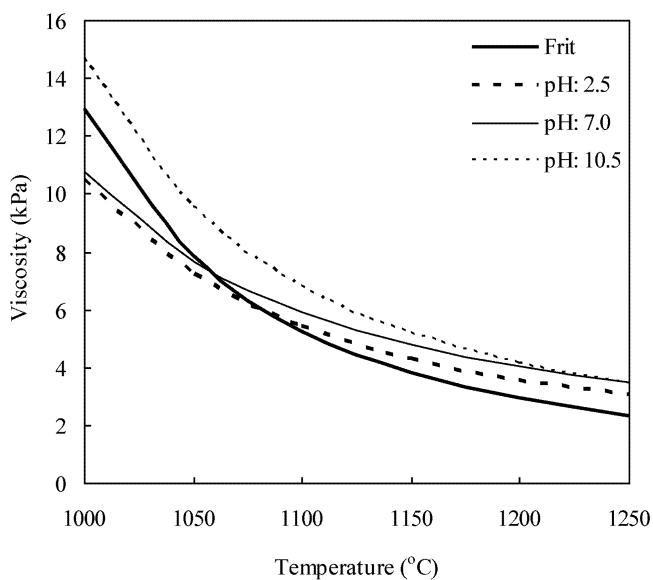
Table 2: The constant parameters of the VFT model for the frit and modified compositions used as a function of the synthesis conditions and calcination temperature

Fuel ratio	Calcination temperature (°C)	pH	A	B	T_0
Frit			2.25	694.5	626.8
0.56	800	2.5	2.60	590.8	637.1
		7.0	2.33	778.5	619.5
		10.5	2.10	926.2	606.4
0.75	800	2.5	2.29	538.8	650.4
		7.0	2.65	433.9	684.9
		10.5	2.96	330.8	669.4
0.56	1000	2.5	2.77	478.4	642.2
		7.0	2.64	539.9	652.3
		10.5	2.73	483.0	663.9
0.75	1000	2.5	2.74	438.0	656.7
		7.0	2.90	378.5	666.4
		10.5	2.64	539.9	646.3

Only the sample in which the resulting HSM demonstrated the normal thermal behaviour was subsequently analyzed from the thermal and structural point of view. The synthesis of cobalt aluminate at a neutral pH with low fuel ratio and calcination of powder at 1000 °C enabled the best results to be achieved from the industrial point of view. The other conditions studied can be considered unacceptable. The presented conditions strongly favour the thermal behaviour, enabling an applicable method to be achieved.



(a)



(b)

Fig. 7: The hot viscosity of glazes containing the powders prepared at different pH, calcined at 1000 °C and fuel ratio of (a) 0.56, (b) 0.75.

The results of simultaneous DTA-TG analyses of gel synthesized at a pH 7 with a fuel ratio of 0.56 are shown in Fig. 8. In the investigated temperature range there are two regions of interest. From 200 to 300 °C glycine is removed from the gel. Between 300 and 400 °C the remaining organ-

ic material is decomposed. The total weight loss was about 55 wt%, corresponding to the content of fuel used in the preparation of the gel.

Fig. 9 shows the Raman spectra of the powder prepared in optimum conditions. The normal spinel characteristics can be distinguished in the Raman spectrum of the powder. The Raman spectra clearly showed that the calcined sample at 1000 °C has the peak intensity at 380 cm⁻¹. The intensity therefore depends directly on the crystallinity of sample, the highest degree of crystallinity appears to be achieved after calcination at 1000 °C^{32, 33}.

A TEM micrograph of the powders after calcination at 1000 °C is shown in Fig. 10. The microstructure of the particles is observed to be almost spherical, with a particle size in the range 50–70 nm.

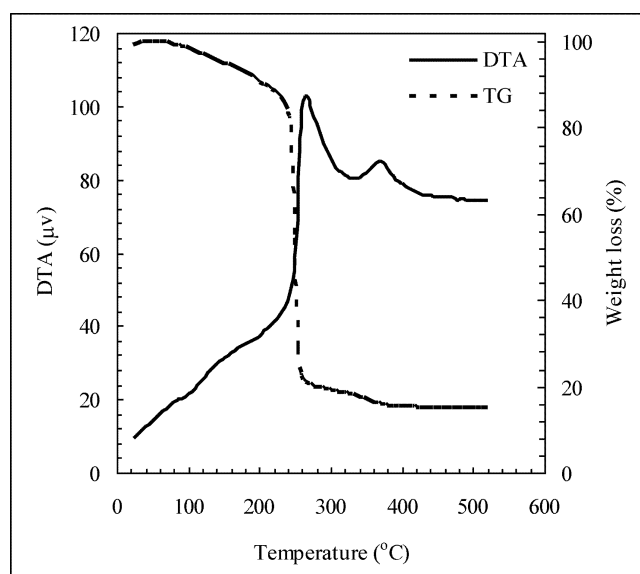


Fig. 8: The DTA-TG curves of gel synthesized at a pH of 7 with a fuel ratio of 0.56.

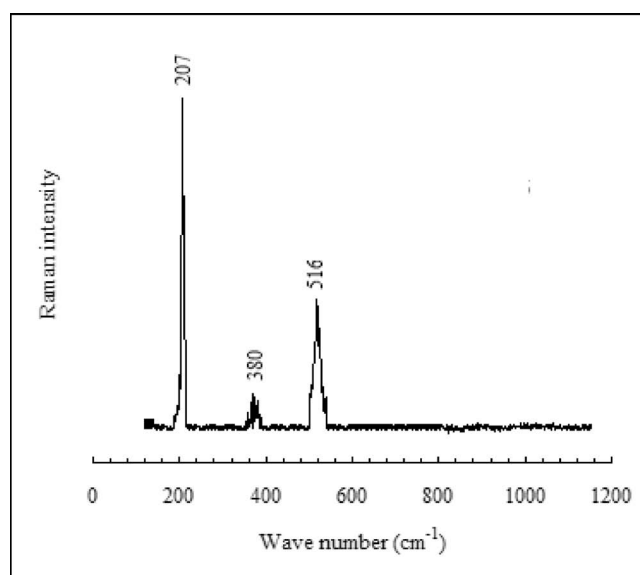


Fig. 9: The Raman spectra of the powder prepared in optimum conditions.

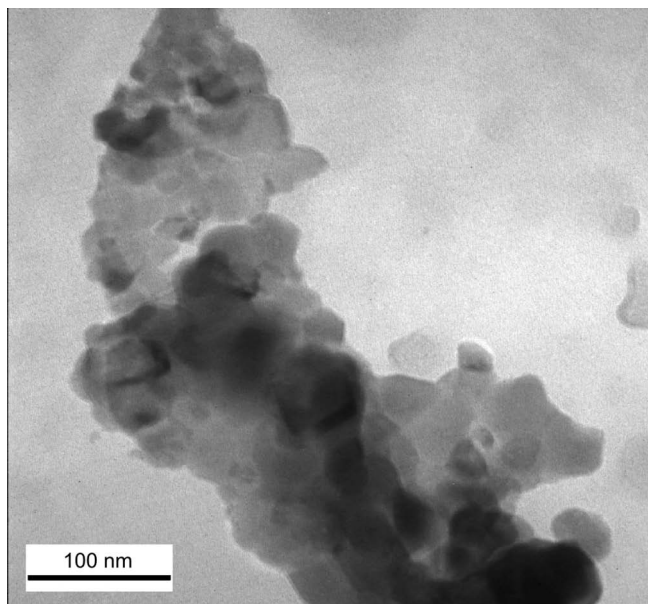


Fig. 10: The TEM micrograph of the powder prepared in optimum conditions.

IV. Conclusions

The thermal behaviour of glazes containing 2.0 wt% cobalt aluminate powders was investigated as a function of the synthesis conditions of the pigment used by means of hot stage microscopy. In all studied cases, significant changes in the height percentage were observed versus the temperature. The modified glazes begin to shrink near 720 °C and reach a minimum value at 1330 °C. The variation in the thermal process was investigated and compared with the behaviour of the transparent frit used, which takes into account a base material. The results showed that the addition of powders synthesized at a low fuel ratio and calcined at 800 °C leads to an expansion between 940 and 1040 °C and beyond this range, the height percentage decreases normally. The results of this study have shown that the fuel ratio is efficient in the thermal behaviour of modified glaze. However, when fuel ratio was 0.75, the expansion region was disappeared with an exception in the glaze containing the powder synthesized in an acidic environment.

The Vogel-Fulcher-Tamman model was used to understand the effect of the synthesis conditions on the viscosity of the molten phase. This equation provides evidence that the pigment synthesis conditions affect the firing curve. The synthesis of powder at a high fuel ratio, 0.75, or calcination of pigment at 1000 °C produces the optimum conditions. Finally, powder synthesis at the neutral pH permits the best results to be obtained. The other methods used in this investigation are unacceptable from practical and engineering points of view.

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References

- Burdett, J.K., Price, G.L., Price, S.L.: Role of the Crystal-Field Theory in Determining the Structures of Spinel, *J. Am. Chem. Soc.*, **104**, 92–95, (1982).
- Li, W., Li, J., Guo, J.: Synthesis and Characterization of Nano-Crystalline CoAl_2O_4 Spinel Powder by Low-Temperature Combustion, *J. Eur. Ceram. Soc.*, **23**, 2289–2295, (2003).
- Ouahdi, N., Guillemet, S., Demai, J.J., Durand, B., Rakho, L.E., Moussa, R., Samdi, A.: Investigation of the Reactivity of AlCl_3 and CoCl_2 toward Molten Alkali-Metal Nitrates in Order to Synthesize CoAl_2O_4 , *J. Mater. Lett.*, **59**, 334–340, (2005).
- Chen, Z.Z., Shi, E.W., Li, W.J., Zheng, Y.Q., Zhuang, J.Y., Xiao, B., Tang, L.A.: Preparation of Nano-Sized Cobalt Aluminate Powders by a Hydrothermal Method, *J. Mater. Sci. Eng.*, **107**, 217–223, (2004).
- Melo, D.M.A., Cunha, J.D., Fernandes, J.D.G., Bernardi, M.I., Melo, M.A.F., Martinelli, A.E.: Evaluation of CoAl_2O_4 as Ceramic Pigments, *J. Mater. Res. Bull.*, **38**, 1559–1564, (2003).
- Souza, L.K.C., Zamian, J.R., Rocha F.G.N., Soledade L.E.B., Santos, I.M.G., Souza, A.G., Scheller, T., Angelica, R.S., Costa, C.E.F.: Blue Pigments Based on $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ Spinel Synthesized by the Polymeric Precursor Method, *Dyes Pigments*, **81**, 187–192, (2009).
- Sickafus K.E., Wills, J.M.: Structure of Spinel, *J. Am. Ceram. Soc.*, **82**, 3279–3292, (1999).
- Nakatsuka, A., Ikeda, Y., Yamasaki, Y., Nakayama, N., Mizota, T.: Cation Distribution and Bond Lengths in CoAl_2O_4 Spinel, *J. Solid State Commun.*, **128**, 85–90, (2003).
- Wang, C., Liu, S., Liu, L., Bai, X.: Synthesis of Cobalt-Aluminate Spinel via Glycine Chelated Precursors, *J. Mater. Chem. Phys.*, **96**, 361–370, (2006).
- Ahmed, I.S., Dessouki, H.A., Ali, A.A.: Synthesis and Characterization of New Nano-Particles as Blue Ceramic Pigment, *Spectrochim Acta A*, **71**, 616–620, (2008).
- Mimani, T., Ghosh, S.: Combustion Synthesis of Cobalt Pigments: Blue and Pink, *Curr. Sci. India*, **78**, 892–896, (2000).
- Chen, Z., Shi, E., Li, W., Zheng, Y., Zhong, W.: Hydrothermal Synthesis and Optical Property of Nano-Sized CoAl_2O_4 Pigment, *Mater. Lett.*, **55**, 281–284, (2002).
- Niasari, M.S., Khouzani, M.F., Davar, F.: Bright Blue Pigment CoAl_2O_4 Nano-Crystals Prepared by Modified Sol-Gel Method, *J. Sol-Gel Sci. Technol.*, **52**, 321–327, (2009).
- Segal, D.: Chemical Synthesis of Ceramic Materials, *J. Mater. Chem.*, **7**, 1297–1305, (1997).
- Yu, F., Yang, J., Ma, J., Du, J., Zhou, Y.: Preparation of Nano-Sized CoAl_2O_4 Powders by Sol-Gel and Sol-Gel-Hydrothermal Methods, *J. Alloys and Compd.*, **468**, 443–446, (2009).
- Lade, M., Mays, H., Schmidt, J., Willumeit, R., Schomacker, R.: On the Nano-Particle Synthesis in Microemulsions: Detailed Characterization of an Applied Reaction Mixture, *Colloid Surface*, **163**, 3–15, (2000).
- Suchanek, W.L., Riman, R.E.: Hydrothermal Synthesis of Advanced Ceramic Powders, *Adv. Sci. Tech.*, **45**, 184–193, (2006).
- Chokkaram, S., Srinivasan, R., Milburn, D.R., Davis, B.H.: Conversion of 2-Octanol over Nickel-Alumina, Cobalt-Alumina, and Alumina Catalysts, *J. Mol. Catal. A-Chem.*, **121**, 157–169, (1997).
- Britto, S., Radha, A.V., Ravishankar, N., Vishnu, K.P.: Solution Decomposition of the Layered Double Hydroxide (LDH) of Zn with Al, *Solid State Sci.*, **9**, 279–286, (2007).
- Purohit, R.D., Saha, S., Tyagi, A.K.: Powder Characteristics and Sinterability of Ceria Powders Prepared through Different Routes, *Ceram. Int.*, **32**, 143–146, (2006).
- Peng, T., Liu, X., Dai, K., Xiao, J., Song, H.: Effect of Acidity on the Glycine-Nitrate Combustion Synthesis of Nano-Crys-

- talline Alumina Powder, *Mater. Res. Bull.*, **41**, 1638–1645, (2006).
- 22 Lima, M.D., Bonadimann, R., Andrade, M.J., Toniolo, J.C., Bergmann, C.P.: Nanocrystalline Cr_2O_3 and Amorphous CrO_3 Produced by Solution Combustion Synthesis, *J. Eur. Ceram. Soc.*, **26**, 1213–1220, (2006).
- 23 Ahmed, M., Earl, D.A.: Characterizing Glaze Melting Behaviour via HSM, *Am. Ceram. Soc. Bull.*, **81** (3), 47–51, (2002).
- 24 Froberg, L., Kronberg, T., Hupa, L., Hupa, M.: Influence of Firing Parameters on Phase Composition of Raw Glazes, *J. Eur. Ceram. Soc.*, **27**, 1671–1675, (2007).
- 25 Siligardi, C., D'Arrigo, M.C., Leonelli, C.: Sintering Behaviour of Glass-Ceramic Frits, *Am. Ceram. Soc. Bull.*, **79** (8), 89–93, (2000).
- 26 Funk, J.E.: Designing the Optimum Firing Curve for Porcelains, *Am. Ceram. Soc. Bull.*, **62** (6), 632–635, 1982.
- 27 Salem, A., Jazayeri, S.H., Rastelli, E., Timellini, G.: Dilatometric Study of Shrinkage during Sintering Process for Porcelain Stoneware Body in Presence of Nepheline Senate, *J. Mater. Process. Tech.*, **209**, 1240–1246, (2009).
- 28 Boccaccini, A.R., Hamann, B.: Review In Situ High-Temperature Optical Microscopy, *J. Mater. Sci.*, **34**, 5419–5436, (1999).
- 29 Paganelli, M., Sighinolfi, D.: Understanding the Behaviour of Glazes with the Automatic Heating Microscope, *cfi/Ber. DKG*, **85** (5), E63–67, (2008).
- 30 Scholze, H.: The influence of viscosity and surface tension on heating microscope measurements on glasses, (in German), *Ber. DKG*, **39**, 63–68, (1962).
- 31 Engels, M., Link, S.: Bubble Control in Ceramic Glazes, *Interceram*, **55** (3), 152–156, (2006).
- 32 Waal, D.: Raman Investigation of Ceramics from 16th and 17th Century Portuguese Shipwrecks, *J. Raman Spectrosc.*, **35**, 646–649, (2004).
- 33 Kock, L.D., Waal, D.: Raman Studies of the Underglaze Blue Pigment on Ceramic Artefacts of the Ming Dynasty and of Unknown Origins, *J. Raman Spectrosc.*, **38**, 1480–1487, (2007).