INVESTIGATION INTO THE EFFECT OF ALKALINE AND ALKALINE EARTH RATIOS ON COLOUR DEVELOPMENT OF MALAYAITE-BASED CERAMIC INK

Sumeyra Guven(1), Umit Engin Anil(1), Fahriye Altindal(1), Suleyman Onder Varisli(1), Bunyamin Ozturk(1), Selcuk Bulut Yazan(1) , Ferhat Kara(2)

(1)Akcoat R&D Center, Ceramic Coatings Division, 2nd IZ, 54300, Sakarya, Turkiye
(2)Eskisehir Technical University, Department of Materials Science and Engineering, 26555, Eskisehir, Turkiye

ABSTRACT

In this study, pink colour development was investigated by systemically changing the alkaline and alkaline earth ratios of the developed glaze (Na_2O/CaO, Na_2O/MgO, Na_2O/BaO), and characterising the compositional variations. Colorimetric values (L*, a*, b*) of the compositions were measured by a spectrophotometer according to CIELab space. The crystal phases were examined by X-ray diffraction (XRD) method to understand their effects on colour behaviour. The microstructural and compositional evaluations of the test specimens were characterized by using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). According to the results, an improvement in pink colour intensity was observed when the alkali/alkaline earth ratio decreased from 0.89 to 0.38. It can be said that the pink colour development regarding the a* (redness) value may be related to the amount of malayaite, cassiterite (SnO_2) phases and the bar-shaped BaO-CaO-Al_2O_3-SiO_2 crystals occurring in the microstructure.

1. INTRODUCTION

The term 'pigment' originates from the Latin word 'pigmentum,' which translates to 'colour' or 'paint.' This term is also employed to describe the colouring agents used in paint, whether in dry or liquid form [1,2]. In traditional ceramic manufacturing, complex inorganic colour pigments (CICPs) are used to colour glaze or body slurry. These ceramic pigments consist of metal transition complex oxides and are manufactured through a calcination process [3]. CICPs are particularly valuable in high-temperature applications, where colour stability and resistance to chemical attacks are essential requirements. Therefore, they are well-suited for use in the production of ceramic materials.[4-6]

In the ceramic tile industry, digital inkjet printing technology has emerged as the most innovative decoration method for decoration in recent times [5,6]. Digital ceramic inks are mixtures of finely ground inorganic pigment, organic-based solvents, and other additives (dispersants, electrolytes etc.). Ceramic inks are applied to the tile surface prior to firing using a printing head. [6-10]

Malayaite-structured inorganic pigments are employed within the ceramic industry to achieve various shades of pink, purple, and red. This type of pigment consists of Cr_2O_3-SnO_2-CaO-SiO_2 composition, and it provides reddish tones. [11,12]. Malayaite belongs to the allochromatic pigments family and the colour stems from a dopant in a colourless matrix. Chromium is responsible for colour development due to its entrance into the octahedral structure in the form of Cr (III) [13,14]. There are some studies investigating the mechanism behind the colour loss of this pigment in certain type of glazes. [15,16].

Many studies may be found on the interactions between ceramic pigments and glazes in the literature. However, studies on how glaze/frit compositions affect the colour behaviour of pink ceramic ink for digital printing are limited.

In this paper, pink ceramic ink colour development was investigated by systemically changing the alkaline/ alkaline earth ratios of the developed glaze. The crystal phases were examined by X-ray diffraction (XRD) to understand the effect of the colour mechanism. The variations of the chromatic coordinates were evaluated by a spectrophotometer, and a scanning electron microscope (SEM) was used to corroborate the crystal formation in the glaze microstructure.

2. MATERIALS AND METHODS

Industrial grade kaolin (Kaolin, Bulgaria), clay (Etili, Türkiye), albite (Matel, Türkiye), high purity alumina (99%, Eti, Türkiye), quartz (Esan, Türkiye), Zircon (Bitossi, Italy), Wollastonite (Imerys, France), magnesite (Akınsır, Türkiye), barium carbonate (Enpar, Türkiye), a commercial opaque frit (Akcoat, Türkiye) and a commercial ceramic pink ink (Akcoat, Spain) were used to prepare an opaque glaze. The oxide composition of the frit and other raw materials is given in Table 1. The XRD graph of the pink ink based on (Cr)CaO.SnO2.SiO2 (malayaite) is shown in Figure 1 and the particle size distribution values can be seen in Table 2.

	SiO_2	Al_2O_3	CaO	MgO	ZrO	K_2O	Na_2O	TiO_2	BaO	LOI
Opaque Frit	48-53	17-20	4-6	0-2	10-12	0.00	14-16	0.00	0.00	
Kaolin	52.4	32.6	0.15	0.22	0.00	1.09	0.22	0.19	0.00	13.2
Clay	51.8	26.6	0.27	0.00	0.00	1.49	0.15	1.17	0.00	18.4
Na-feldspar	70.3	17.5	0.88	0.00	0.00	0.00	10.9	0.00	0.00	0.41
Zircon	34.7	2.48	0.00	0.00	62.6	0.00	0.24	0.00	0.00	0.00
Quartz	99.3	0.42	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.14
Alumina	0.07	99.2	0.00	0.00	0.00	0.00	0.64	0.00	0.00	0.06
Wollastonite	46.22	0.1	51.9	1.12	00.0	0.00	0.00	0.00	0.00	1.45
Barium Carbonate	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.08	76,87	0.81
Magnesite	3.15	0.15	2.09	44.7	0.00	0.00	0.00	0.00	0.00	48.1

Table 1. *Oxide (wt.%) content for frit and raw materials*

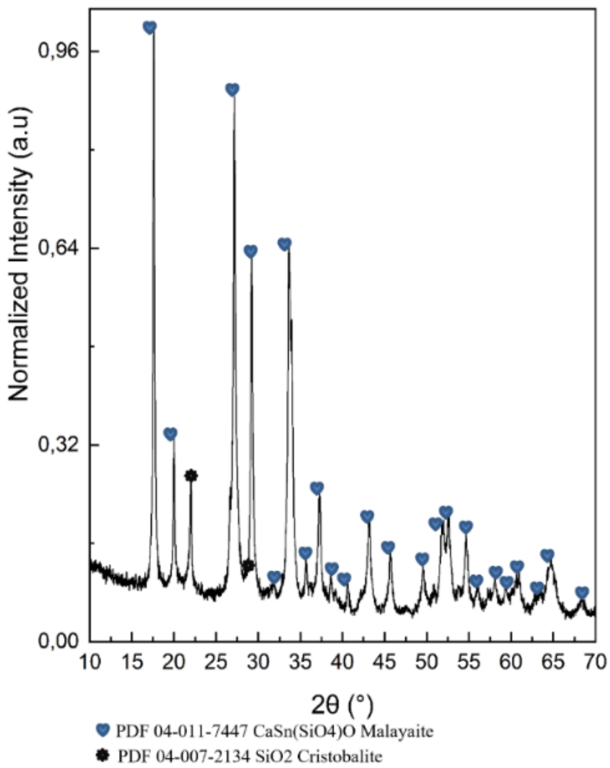

Figure 1: *XRD patterns of malayaite-based pink ink*

	D_{10}(μm)	D_{50}(μm)	D_{90}(μm)
Pink ink based on (Cr)$CaO.SnO_2.SiO_2$	0.241	0.366	0.547

Table 2. *Particle size distribution of malayaite-based pink ink*

2.1. COMPOSITION DESIGN

Glazes were designed to investigate the effect of alkaline/alkaline earth oxides on colour development. In the compositions, Na_2O was systematically decreased and the alkaline earth oxide ratios were increased in a limited range to maintain a constant SiO_2/Al_2O_3 value. The composition references were chosen to reflect the decreasing and increasing oxides, as shown in Table 3.

	Na_2O	CaO	MgO	BaO	SiO_2/Al_2O_3	Alkaline/Alkaline Earth
STD	0.41	0.41	0.05	0.00	6.70	0.89
NC1	0.34	0.50	0.05	0.00	6.84	0.62
NC2	0.28	0.57	0.05	0.00	6.99	0.45
NC3	0.23	0.64	0.05	0.00	7.17	0.33
NM1	0.36	0.43	0.10	0.00	6.75	0.68
NM2	0.29	0.43	0.15	0.00	6.82	0.50
NM3	0.25	0.46	0.20	0.00	6.89	0.38
NB1	0.35	0.42	0.05	0.06	6.75	0.66
NB2	0.29	0.43	0.04	0.13	6.81	0.48
NB3	0.24	0.43	0.04	0.20	6.88	0.36

Table 3. *Seger ratios of the designed compositions*

2.2. SAMPLE PREPARATION

Glaze compositions were wet milled with alumina balls for 20 min to yield a particle size of less than 45 µm. Malayaite-based pink ink was added at 3 wt% to the glaze slurry. Glaze slurry samples were dried at 200 °C for 10 min. in a laboratory scale dryer. The samples were dried and sieved through a 500 µm sieve. The powder was used to form circular pellets by a laboratory type press with diameter of 40 mm, which were fired with a fast cycle (60 min. cold to cold) at a maximum temperature of 1190 °C in a laboratory type electrical kiln (Nabertherm). The colour coordinates of the samples were measured using a spectrophotometer (Konica Minolta, CM 700d) with D65 and 10° according to CIELab space. XRD analysis with CuKα radiation, scanning range (2θ) of 10°–70° (Bruker D8 Advanced) was performed on fired pellet powders. The microstructural and compositional evaluations of the compositions were characterized by using scanning electron microscopy (SEM, FEI Quanta FEG 450) with a magnification range between 25kX and 80kX, and by energy dispersive spectroscopy (EDS). Specimens were sputtered coated with gold, and signals were collected using backscattered electrons.

3. RESULTS AND DISCUSSION

Pink colour is characterized by having high a* and low b* values in the CIELab system [2].The a* value varied linearly depending on the changes of alkaline and earth alkaline ratios compared to the standard sample. Na_2O is the main decreasing oxide while the others increase. The findings show that the effect of each earth alkaline oxide on colour development is different. CaO, BaO and MgO have a higher a* value than STD. The colour development behaviour of CaO and BaO is similar, as shown in Figure 2, whereas the BaO ratio is lower than CaO in NB3. Figure 2 shows the L, a*, b* values and representative colour tones for each composition.

	L	a*	b *	Colour Tones
STD	83.80	6.03	1.79	
NC.1	77.47	12.97	2.02	
NC.2	74.81	15.02	1.91	
NC.3	74.22	15.82	1.97	
NM.1	79.48	10.24	1.25	
NM.2	80.72	9.34	0.87	
NM.3	81.03	8.48	0.72	
NB.1	77.27	12.88	1.41	
NB.2	75.39	13.77	1.21	
NB.3	72.13	15.66	1.39	

***Figure 2**. Colorimetric values of the developed glazes*

XRD analysis was used to determine the crystal structure of the glaze in order to understand the colour development of the ink. The third sample of each composition was analysed to clearly see the effect of oxide variation.

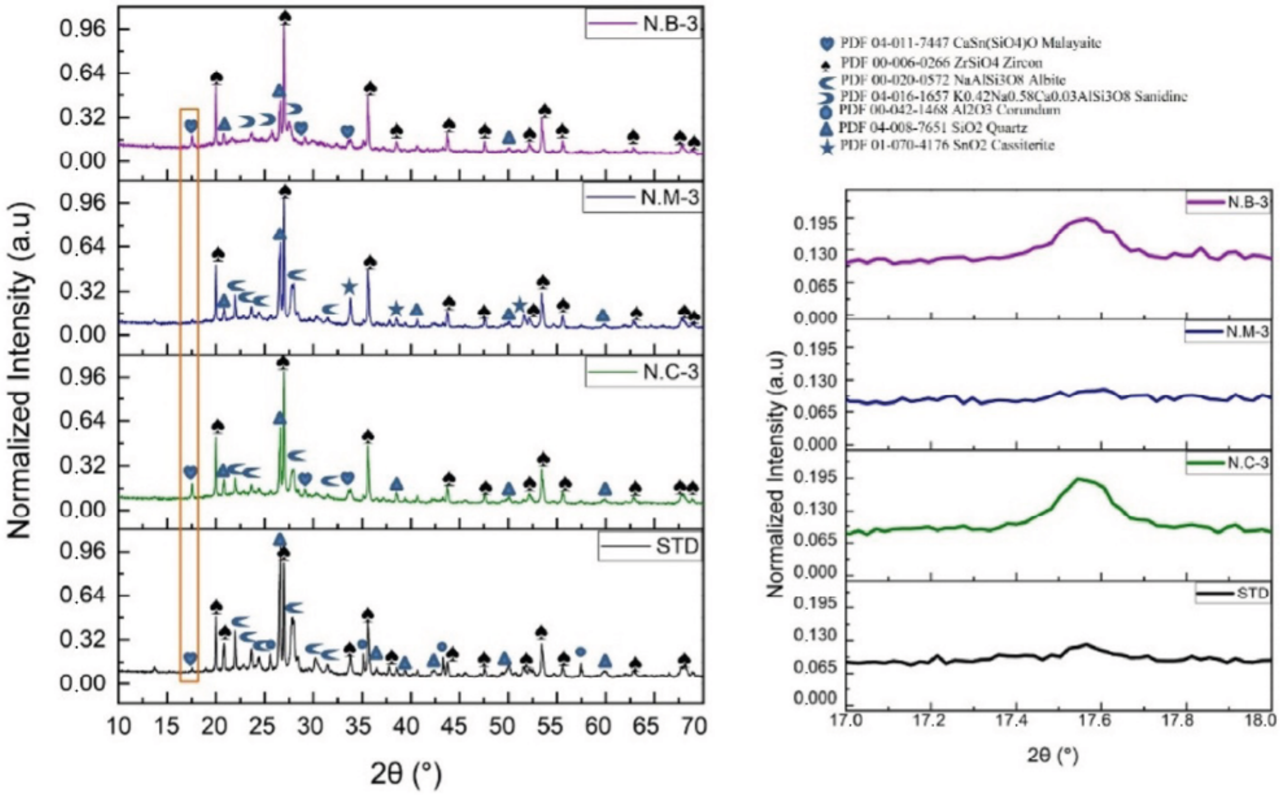

Figure 3: *XRD patterns of Group-1 compositions with 3 wt% pink ink.*

As shown in Figure 3, zircon, quartz, and corundum are common phases for all the compositions. The malayaite phase is observed in all compositions except the composition containing magnesium. As the amount of Na_2O in the compositions decreased and the amount of CaO increased and the alkali/alkaline earth ratio decreased from 0.89 to 0.33, the intensity of the malayaite phase intensity rose in relation to the standard. The magnified XRD patterns in Figure 3(b) exhibited a peak intensity difference among the compositions with low Na_2O content with respect to the STD sample. It was observed that the a* value increased when looking at the optical values. It is known that adding Ca has a favourable impact on the development of the pink coloration [15]. When the SEM images in Figure 4.a are examined, it is seen that less than 1-micron size malayaite crystals are present in the STD composition. In the microstructure of NC3 from Figure 4.b, similar malayaite particles are seen in the albite-poor area. The colour intensity difference between STD and NC3 may be explain with the results from EDX point analysis in Table 4 and Table 5, respectively. The percentage of both Ca and Sn in malayaite crystals of NC3 is higher than those in the STD structure and Na was not detected. In NC3, needle-like albite grains of nearly 1 micron in size can be readily observed. The malayaite particles might be protected from alkaline attack in the region with lack of Na, so that their Ca and Sn content may be enough to keep colour intensity compared to the STD structure.

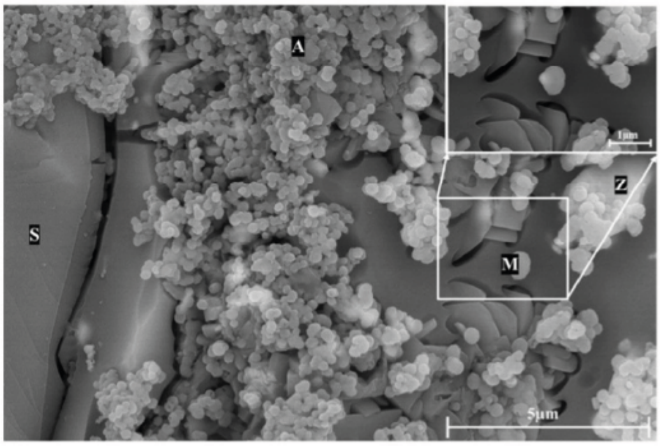

Figure 4.a: Back-scattered SEM image of standard composition (S:Quartz, A:Albite, Z:Zircon, M:Malayite

Table 4. % element weight from EDX

Element	Malayaite crystal
O K	40.26
Na K	6.63
Al K	13.56
Si K	29.09
Sn K	1.32
Ca L	9.14

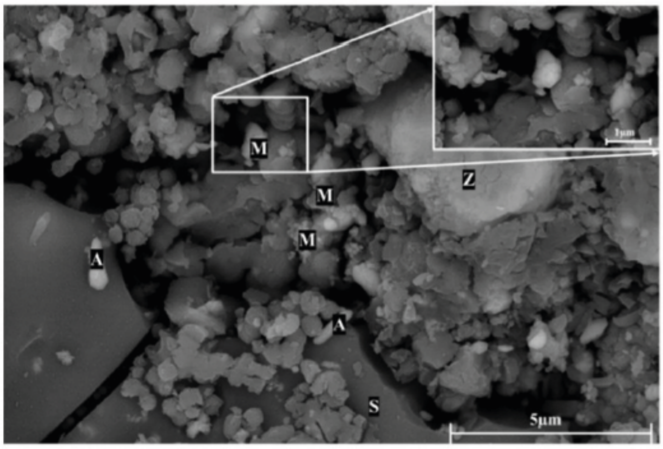

Figure 4.b: Back-scattered SEM image of NC.3 compositions (S:Quartz, A:Albite, Z:Zircon, M:Malayaite)

Table 5. % element weight from EDX

Element	Malayaite crystal
O K	41.72
Al K	13.94
Si K	13.25
Sn K	2.10
Ca L	28.99

Sample NM3 has Cassiterite (SnO_2) phase instead of malayaite, observing sample NC3 and NB3. This situation can be explained by the fact that the firing temperature is high enough for MgO to become a flux and not only a modifier. The increase in the amount of MgO causes the dissolution of the raw materials with decreasing viscosity [18]. MgO may have deteriorated the malayaite phase in the pigment structure and caused the formation of only the cassiterite phase [8]. The SEM image of NM3 in Figure 5 shows that the crystals in the structure are covered with a glassy structure. Results from the EDX point analysis in Table 6 confirms the presence of the cassiterite phase. Albite and MgO in the composition may have increased the amount of glassy phase. Therefore, the crystals remained embedded in the glassy phase. Violet chromium-doped cassiterite is the chromium pigment used in the ceramic industry for colouring glazes and has lower a* and b* values than the chromium-doped malayaite pink pigment. When the compositions containing MgO are examined, it is seen that the a* and b* values are lower. This supports the idea of cassiterite phase formation as the amount of MgO increases [9].

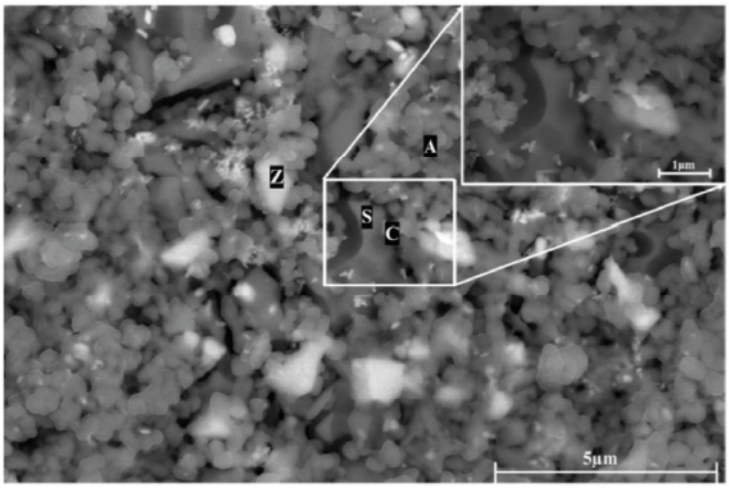

Figure 5: Back-scattered SEM image of NM.3 compositions (S:Quartz, A:Albite, Z:Zircon, C:Cassiterite)

Table 6. % element weight from EDX

Element	Cassiterite crystal
O K	33.92
Na K	1.71
Al K	15.21
Si K	27.90
Sn K	21.25

As the amount of Na_2O in the compositions decreased and the amount of BaO increased and the alkali/alkaline earth ratio decreased from 0.89 to 0.36, the intensity of the malayaite phase increased in relation to the standard as shown in Figure 3(b).

Sample NB-3 clearly has the bar-shaped (BaO-CaO-Al_2O_3-SiO_2) and malayaite structures in the SEM image in Figure 6. Some studies can be found that reveal the formation of Pabstite ($BaSnSi_3O_9$) in the case of barium-rich and calcium-poor glazes affecting colour negatively [19].

However, no Pabstite structure was observed in the NB3, possibly because the CaO ratio being higher than the BaO ratio prevented formation of the aforementioned phase. EDX point analysis Table 7 confirms that Ba does not form compounds with Sn.

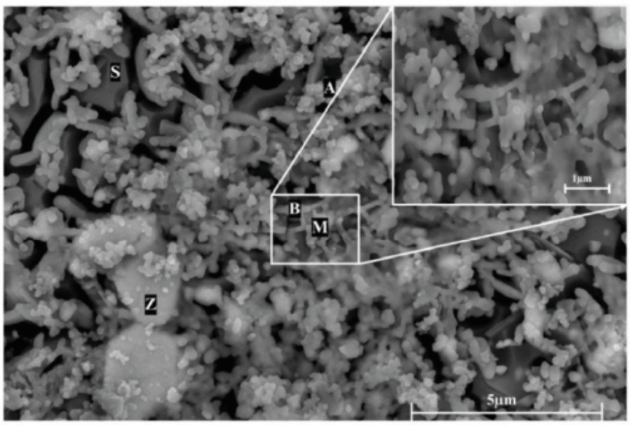

Figure 6: Back-scattered SEM image of NB.3 compositions (S:Quartz, A:Albite, Z:Zircon, M: Malayaite, B: Barium-Calcium-Alumina-Silica)

Table 7. % element weight from EDX

Element	Barium-calcium-alumina-silica crystal
O K	35.36
Na K	3.03
Al K	13.45
Si K	18.11
Zr K	6.27
K K	0.16
Ca K	13.92
Ba K	9.71

4. CONCLUSIONS

- When the alkali/alkaline earth ratio decreases, the a* value and pinkness increase as the alkaline earths Ca and Ba increase in the composition.
- Increasing the amount of CaO and BaO increased the peak intensity of malayaite in XRD analysis and contributed to the redness.
- When the amount of Na_2O in the composition decreased and the amount of MgO increased, it was found that MgO caused the malayaite crystal to dissolve and form Cassiterite phase, producing a violet colour like the Cr-doped cassiterite pigment with a low a* and b* value.

REFERENCES

[1] E. Enríquez, J.J. Reinosa, V. Fuertes, J.F. Fernandez, Advances and challenges of ceramic pigments for inkjet printing, Ceramics International 48 (2022) 31080–31101. https://doi.org/10.1016/j.ceramint.2022.07.155

[2] I. Klöckl, Handbook of Colorants Chemistry Volume 1: Dyes and Pigments Fundamentals, Walter de Gruyter GmbH, Berlin, 2023

[3] Seabright, C.A.: Ceramic Pigments, US Patent., 2, 407-441 (1948)

[4] E. B. Faulkner, R. J. Schwartz, High Performance Pigments, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009.

[5] P.M.T. Cavalcante, M. Dondi, G. Guarini, M. Raimondo, G. Baldi, Colour performance of ceramic nano-pigments, Dyes and Pigments 80 (2009) 226–232. https://doi.org/10.1016/j.dyepig.2008.07.004

[6] E. Enríquez, J.J. Reinosa, V. Fuertes, J.F. Fernandez, Advances and challenges of ceramic pigments for inkjet printing, Ceramics International 48 (2022) 31080–31101. https://doi.org/10.1016/j.ceramint.2022.07.155

[7] Z. Pan, Y. Wang, H. Huang, Z. Ling, Y. Dai, S. Ke, Recent development on preparation of ceramic inks in ink-jet printing, Ceramics International, 41 (2015) 12515-12528. https://doi.org/10.1016/j.ceramint.2015.06.124

[8] G. Ferrari, P. Zannini, Thermal behavior of vehicles and digital inks for inkjet decoration of ceramic tiles, Thermochimica Acta, 639 (2016) 41-46. https://doi.org/10.1016/j.tca.2016.07.002

[9] G.L. Güngör, A. Kara, D. Gardini, M. Blosi, M. Dondi, C. Zanelli, Ink-jet printability of aqueous ceramic inks for digital decoration of ceramic tiles, Dyes and Pigments 127 (2016) 148-154. https://doi.org/10.1016/j.dyepig.2015.12.018

[10] J.H. Kim, H.G. Noh, U.S. Kim, W.S. Cho, J.H. Choi, Y.O. Lee, Recent Advances in the Ink-Jet Printing Ceramic Tile Using Colorant Ceramic-Ink, Journal of the Korean Ceramic Society, 50 (2013) 498–503. doi:10.4191/kcers.2013.50.6.498.

[11] M. Dondi, M. Blosi, D. Gardini, C. Zanelli, Ceramic pigments for digital decoration inks: An overview, Qualicer (2012) 1-12.

[12] H.S. Lee, B.H. Lee, Synthesis of Sphene (CaSnSiO5)-Pink Pigments with CrCl3, Journal of the Korean Ceramic Society, 46 (2009) 405-412, 2009. 10.4191/KCERS.2009.46.4.405

[13] V. Harisanov, R.S. Pavlov, I.T. Marinova, V. Kozhukharova, J.B. Carda, Influence of crystallinity on chromatic parameters of enamels coloured with malayaite pink pigments, Journal of the European Ceramic Society 23 (2003) 429–435. https://doi.org/10.1016/S0955-2219(02)00090-0

[14] S.T. Blachere, Chrome-Tin Pink Glazes, American Ceramic Society Bulletin, 68 (1989) 81-84. https://doi.org/10.1002/9780470310526.ch9

[15] C. J. Byrne, S.G. Kutney, R.A. Pipoly, The Effect of Glaze Composition on the Color and Stability of Chrome Tin Pink Pigments, Ceram. Eng. Sci. Proc. 15 (1994) 206-223.

[16] A. Escardino, S. Mestre, A. Barba, M. Monzo, P. Jodar, L. Diaz, Estability of the pink pigment (Cr)CaSnSiO5. Interaction with ceramic materials, Qualicer (2002) 271-282.

[17] V. Harisanov, R.S. Pavlov, I.T. Marinova, V. Kozhukharova, J.B. Carda, Influence of crystallinity on chromatic parameters of enamels coloured with malayaite pink pigments, Journal of the European Ceramic Society 23 (2003) 429–435. https://doi.org/10.1016/S0955-2219(02)00090-0

[18] Kronberg, T., Hupa L., "The Impact of Wollastonite and Dolomite on Chemical Durability of Matte Fast-Fired Raw Glazes", Journal of the European Ceramic Society, 2020, 40: 3327-3337. https://doi.org/10.1016/j.jeurceramsoc.2020.03.033

[19] C. Zanelli, G.L. Güngör, A. Kara, M. Blosi, D. Gardini, G. Guarini, M. Dondi, Micronizing ceramic pigments for inkjet printing: Part II. Effect on phase composition and color, Ceramics International, 41 (2015) 6507-6517. https://doi.org/10.1016/j.ceramint.2015.01.158