

The development of a Chromium pink glaze coloring

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The research concentrates on producing a range of pink-red colors. The objective of the study is to find a composition that will produce stable colors even at high temperatures. The pink-red color has been high in demand yet it has not been easy to maintain its consistency. The research experiments to produce the pink-red color in both glaze and pigments. The experiment uses Cr_2O_3 , SnO_2 , and CaO . The study has proven that cassiterite and malayaite crystalline formations are the main factors in producing color. The crystals are also engaged by Cr_2O_3 . Furthermore, H_3BO_3 is added as a mineralizer in pigment compounds to accelerate and increase the formation of malayaite. The result of this is then analyzed with the XRD method. The increase in malayaite crystals, results from the reaction caused by malayaite combined with pigment compounds, and an excess amount of Cr_2O_3 is produced, consequently allowing Cr_2O_3 to engage with malayaite. The research has proven to be important for more future experiments in producing other colors. It will contribute to other studies in understanding the color mechanism associated with other chemical components.

Key words: Ceramic pigments, Chromium-pink, SnO_2 .

Introduction

In the production of ceramics, obtaining the true red color from the oxide system has not been an easy matter and because of this difficulty, colors such as pinks, purples, brick reds, maroon shades substitute much of the red tones in a number of different applications [1]. In traditional porcelain wares, copper red glazes were used to achieve a deep red tone but there are drawbacks in this as color development is unreliable due to the volatility of copper oxide that causes the glaze to become most sensitive to the temperature and atmosphere. Therefore, obtaining the pink-red color in highly-fired ceramics is difficult due to the color instability, yet because of the brilliance and attraction of this color for decorative purposes, there is a great demand in finding a method that would produce a consistent pink-red.

The presence of Cr_2O_3 in solids yields to various colorations: pink, red, reddish brown or green [2]. When Cr_2O_3 is used together with SnO_2 CaO in glazes, the pink-red colors are reliably sustained even at high temperatures. Depending on the quantity of added colorants, cinnabar can be substituted and the development of a stable deep purple color is possible. Consequently, it has been proven that colors ranging from purple to pink-red can be achieved by adding both Cr_2O_3 and SnO_2 in a glaze. Reports show that it is the result of the two main crystalline structures cassiterite (SnO_2) and malayaite (CaSnSiO_5) [3] and the effect of Cr_2O_3 .

This research examines Cr_2O_3 in producing the pink-red color. It studies the formation of cassiterite and malayaite crystallites, the primary factors in producing the pink-red color, in relation to the application of Cr_2O_3 to examine its coloring mechanism.

Experimental Procedure

The basic glaze composition of Cr_2O_3 - SnO_2 - CaO and component changes for pink-red

The basic glaze was prepared using the Seger method with the mixed composition of 0.249 KNaO , 0.75 CaO , 0.266-0.516 Al_2O_3 , 2.217-4.717 SiO_2 and 0.16 MgO . The glaze experiments were conducted by adding 0.05 mole of Al_2O_3 and 0.5 mole consecutively, with changes in composition. Here, 0.03 wt% of Cr_2O_3 and 0.9 wt% of SnO_2 were added consistently. The glaze was then fired in a oxidation firing condition for 1 hour at a temperature of 1260 °C. The basic glaze recipe included feldspar, limestone, kaolin, SnO_2 , Cr_2O_3 . 36 glazes were made of which glaze No. 19 produced the most vivid pink-red. Therefore the color mechanism for Glaze No. 19 was examined. The crystalline phase formed in glaze No. 19 was analyzed with XRD. Furthermore, the structural changes in the crystalline phase was studied by firing glaze No. 19 at different temperatures-it was fired at 1000 °C, 1100 °C, 1150 °C, 1200 °C and the results were analyzed again with XRD. In order to understand the effect of Cr_2O_3 and SnO_2 within the glaze, glaze No. 19 was mixed only with Cr_2O_3 (19-Cr), glaze No. 19 mixed only with SnO_2 (19-Sn), glaze No. 19 with no added materials, were tested by firing in an oxidation condition at 1260 °C for 1 hour. After the firing, the results were analyzed using

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Table 1. Stoichiometry of samples

Sample	Stoichiometry
1	CaSnSiO_5
2	$\text{CaCr}_{0.04}\text{Sn}_{0.97}\text{SiO}_5$
3	$\text{CaCr}_{0.16}\text{Sn}_{0.88}\text{SiO}_5$
4	$\text{CaCr}_{0.32}\text{Sn}_{0.76}\text{SiO}_5$
5	$\text{CaCr}_{0.48}\text{Sn}_{0.64}\text{SiO}_5$

Table 2. Stoichiometry of samples with H_3BO_3 (2 wt%)

Sample	Stoichiometry- H_3BO_3 (2 wt%)
1H	$\text{CaSnSiO}_5\text{-H}_3\text{BO}_3$ (2 wt%)
2H	$\text{CaCr}_{0.04}\text{Sn}_{0.97}\text{SiO}_5\text{-H}_3\text{BO}_3$ (2 wt%)
3H	$\text{CaCr}_{0.16}\text{Sn}_{0.88}\text{SiO}_5\text{-H}_3\text{BO}_3$ (2 wt%)
4H	$\text{CaCr}_{0.32}\text{Sn}_{0.76}\text{SiO}_5\text{-H}_3\text{BO}_3$ (2 wt%)
5H	$\text{CaCr}_{0.48}\text{Sn}_{0.64}\text{SiO}_5\text{-H}_3\text{BO}_3$ (2 wt%)

XRD, FT-IR. X-ray diffraction (XRD) using XRD-7000, Shimadzu, Japan and FT-IR analysis using IR-Prestige-21, Shimadzu, Japan.

Malayaite crystal composition and component changes

It is important to understand the engaged reaction of the malayaite crystalline phase, the primary factor in producing color, with Cr_2O_3 , malayaite was synthesized as shown in Table 1. The components were fired in an oxidation condition at 1300 °C for 2 hours. The crystalline phase of the synthesized pigment was analyzed with XRD and then 6 wt% was added consecutively to a lime base glaze. This was then fired in an oxidation firing environment at 1260 °C for 1 hour. The color was later checked. The formation of the malayaite crystalline phase was accelerated as shown in Table 2. The 2 wt% of H_3BO_3 was added consecutively as a mineralizer [2] to the samples of Table 1. The components were fired in an oxidation condition at 1300 °C for 2 hours. The synthesized pigment was analyzed with XRD, FT-IR and then 6 wt% was added consecutively to a lime base glaze fired in an oxidation condition at 1260 °C for 1 hour. The changes in the crystalline structure and color were examined. The engaged reactions by Cr_2O_3 to the two crystalline

structures were revealed. The amount of Cr_2O_3 in malayaite was analyzed with Raman spectroscopy. Pigments 2, 3H, 4H were selected through XRD analysis presenting comparative results in the two crystalline phases and also showing a wide change in color variation. The particle size and grain morphology of the pigments were measured and recorded individually by TEM and SEM.

Results and Discussion

The chromium pink-red glaze

The pink-red color resulted in being stable to all aspects of the experiments. The glaze was made according to the Seger method and fired in an oxidation condition at 1260 °C for 1 hour. Figure 1 shows the changes in fusing and coloring, with reference to the different glaze compositions. Where the SiO_2 quantity was large, the glaze remained partially in the insoluble state. Where the Al_2O_3 quantity was low, the glaze became matt, and when the Al_2O_3 amount was increased considerably, the glaze became opaque. Glaze No. 19 showed the most vivid pink-red color with a high-level of transparency. In this composition Al_2O_3 was 0.316 mole and SiO_2 , 2.217 mole. Therefore glaze No. 19 was selected as the basic glaze for experimentation due to its vivid pink-red color.

The result of the XRD analysis of glaze No. 19 is shown in Fig. 2. The analysis was conducted after firing glaze No. 19 in an oxidation condition, at 1260 °C for 1 hour. According to Fig. 2. the main crystalline phase in the glaze proved to be malayaite but cassiterite, quartz and anorthite crystalline formations were also found [4, 5]. It is evident that the crystalline structures of quartz and anorthite are part of the basic glaze components, while malayaite and cassiterite are responsible for the glaze color. Therefore in order to observe the temperature at which malayaite crystals form in the glaze, glaze No. 19 was fired at different temperatures of 1000 °C, 1100 °C, 1150 °C, 1200 °C. The firings were done in an oxidation condition and the results of the malayaite crystalline formations were compared as shown in Fig. 2.

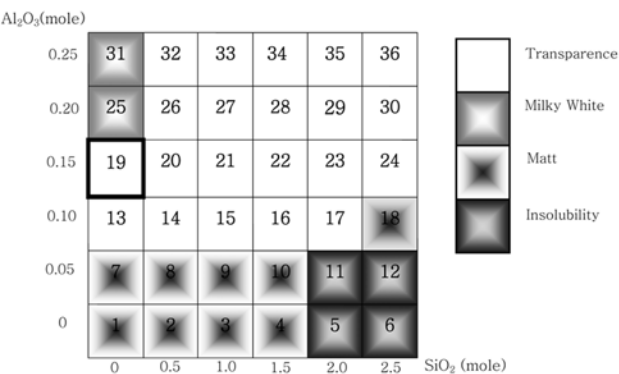


Fig. 1. $\text{Al}_2\text{O}_3\text{-SiO}_2$ changes by binary system.

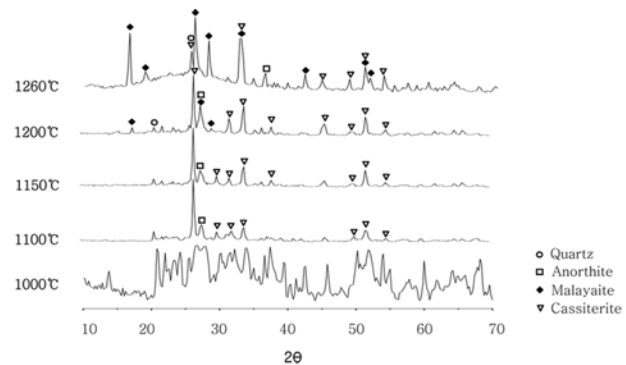


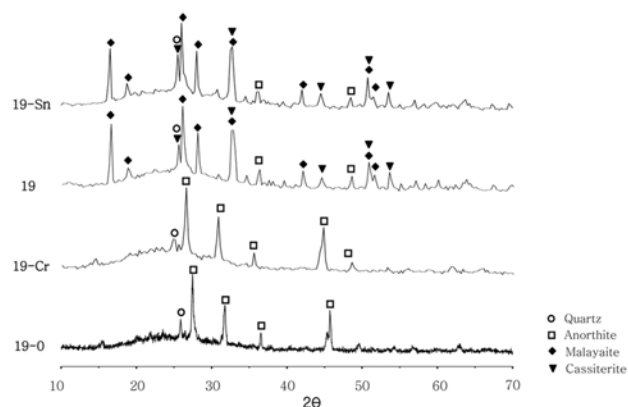
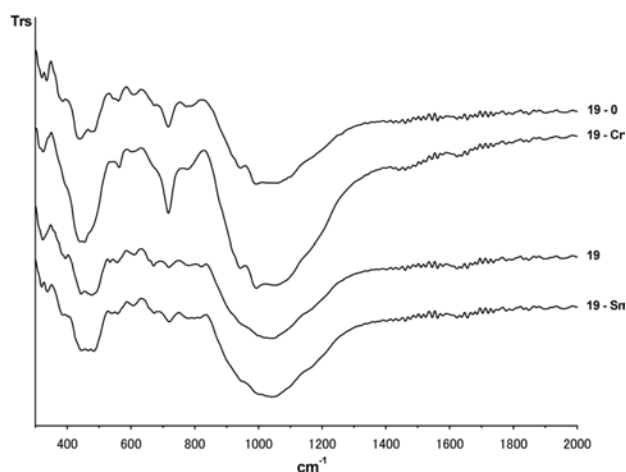
Fig. 2. XRD patterns of glaze No. 19 fired at 1000 °C, 1100 °C, 1150 °C, 1200 °C, 1260 °C.

Table 3. Coloring agent changes in glaze compound

Sample	Cr ₂ O ₃ (wt%)	SnO ₂ (wt%)
19-0	-	-
19-Cr	0.03	-
19-Sn	-	0.9
19	0.03	0.9

The crystalline phase appeared clearly from 1100 °C where the crystalline formation of cassiterite, quartz and anorthite initiated. At 1150 °C, only cassiterite, quartz and anorthite crystals remained and in such cases the color was near to white. Malayaite crystals began forming at 1200 °C. At this stage the glaze was still unmelted and remained more-or-less in the solid state with a deep turpid pink color. In order to examine the effect of malayaite and its engaged component Cr₂O₃, coloring agents were added to the glaze compounds of glaze No. 19 as show in Table 3.

The glaze for Table 3 was fired in an oxidation condition at 1260 °C for 1 hour and then analyzed by XRD. The result for this is shown in Fig. 3. In Fig. 3. the XRD patterns divide clearly into two forms-where there is a high level of SnO₂ content and where there is no SnO₂ content glaze No. 19-0, containing no added components, and glaze No. 19-Cr, containing only Cr₂O₃, both showed similar XRD patterns with the main crystals being quartz and anorthite. Although their XRD patterns are quite similar, after firing they proved to have a distinct difference in color-one was white and the other was green. In the case of glaze No. 19-Sn, containing SnO₂ and glaze No. 19, containing all components, the main crystals were cassiterite and malayaite. However they also contained quartz and anorthite crystalline formations. Again although the two glazes showed to have similar XRD patterns, their colors differed. One was whitish-pink and the other was a deep purple color. After comparing the colors from the experiments, it was possible to see that Cr₂O₃ and SnO₂ should be added to all the glazes. Again cassiterite and malayaite proved to be the main crystals responsible for producing color. Here it is

**Fig. 3.** XRD patterns of samples No. 19, 19-0, 19-Sn, 19-Cr fired at 1260 °C.**Fig. 4.** FT-IR spectra of No. 19-0, 19-Cr, 19, 19-Sn fired at 1260 °C/1 h.

speculated that Cr₂O₃ is engaged to produce the pink-red color range but the engaging state of Cr₂O₃ are not detected by XRD analysis.

To understand the engagement of Cr₂O₃ in the crystalline phase, XRD analysis was conducted as shown in Fig. 3. The glazes were measured with FT-IR and this is shown in the patterns of Fig. 4. Similar to the XRD analysis, the FT-IR method could only distinguish two patterns relating to the content of SnO₂ in the glaze. No other definite distinctions were found. Malayaite crystals, the main cause of color, were examined comparatively with the difference in color created by pigments through the stoichiometry calculation as analysis proved to be difficult due to the small content of Cr₂O₃ within the compound.

Adding chromium pink-red pigment

Color pigments were added to the composition as shown in Table 1, simultaneously with studying the engaged effect of Cr₂O₃ with malayaite crystalline formation. Malayaite the main cause in producing the pink-red color was composed according to the stoichiometry calculation. The different compounds of pigments as shown in Table 1, were fired in an oxidation condition at 1300 °C, for 2 hours. The results of the pigment compounds in the glaze are shown in Fig. 5. Malayaite crystals were measured according to the stoichiometry calculation and the XRD analysis proved that the main crystalline phase was cassiterite. Malayaite and cristobalite crystals were subsidiary but they co-exited with cassiterite. With pigments No. 1, No. 2 there were calcium tin oxide crystals. In pigments No. 3, No. 4, No. 5, the content of Cr₂O₃ was increased and the samples contained Cr₃O₄ crystals. To observe the color effect of pigments, 6 wt% was added to a lime glaze and then fired at 1260 °C in an oxidation condition.

After the firing, pigment No. 1 not containing any Cr₂O₃, produced a transparent glaze and in the case of pigment No. 2, a dark pink color resulted. With pigments No. 3, No. 4, No. 5, colors ranging from brown to yellow-green, and greens were produced when the Cr₂O₃ content was

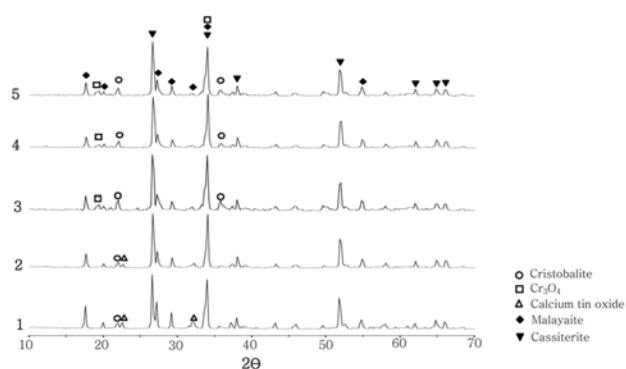


Fig. 5. XRD patterns of samples fired at 1300 °C/2 h.

increased. Therefore the result comes from malayaite engaged with Cr_2O_3 , with control of the quantity of Cr_2O_3 . After a while, it becomes difficult to produce the pink color range if the quantity is too great.

To accelerate the formation of malayaite crystals and to examine its effect on color, 2 wt% of H_3BO_3 was added as a mineralizer to the pigment compounds as shown in Table 1. The compounds were made by the same method as explained above and then the effect of crystals were compared to the color. Table 2 shows the result after adding the mineralizer to the pigments. The same result can be seen from the XRD patterns, in Fig. 6. In all of the compounds, the addition of the mineralizer H_3BO_3 precipitated the formation of malayaite crystals. Although the main crystalline phase was malayaite, cassiterite and cristobalite crystals also formed. Unlike Table 1, no calcium tin oxide crystals appeared in pigments No. 1H and No. 2H. In the case of No. 3H, no Cr_3O_4 crystals formation took place, but malayaite crystals increased in number. In pigments No. 4H and No. 5H, where the amount of Cr_2O_3 was increased, the crystalline formation of chromium, referred to as eskolaite, appeared. According to Fig. 5, in pigment No. 3, the excess amount of Cr_2O_3 crystals did not take place in No. 3H. This means that the quantity of chromium engaged in malayaite increases as more malayaite crystalline structures develop.

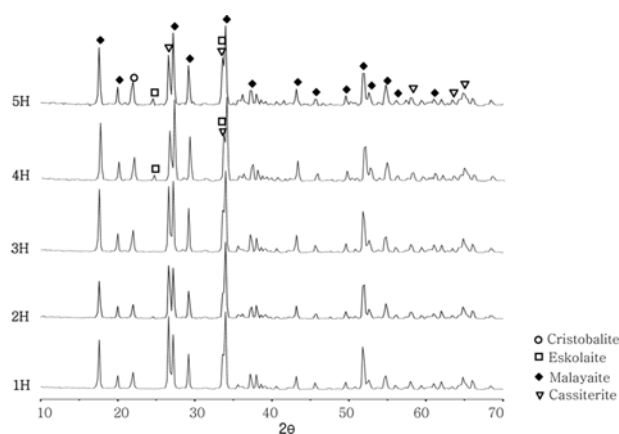


Fig. 6. XRD patterns of samples with H_3BO_3 (2 wt% in weight), fired at 1300 °C/2 h.

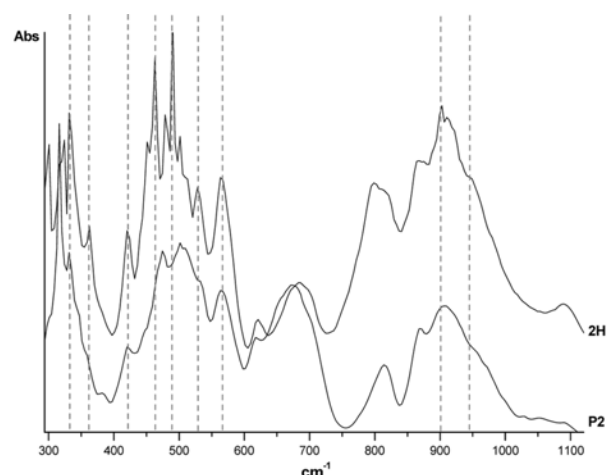


Fig. 7. FT-IR spectra of synthesized samples fired at 1300 °C/2 h (P2 : $\text{CaCr}_{0.04}\text{Sn}_{0.97}\text{SiO}_5$, 2H : P2- H_3BO_3 (2% in weight)).

6 wt% of the pigment compounds were added consecutively to a lime glaze, and then fired at 1260 °C in an oxidation condition. The result showed that the glaze with pigment No. 1H was transparent, No. 2H brown, No. 3H deep pink-red, No. 4H and No. 5H greenish-brown and green. In pigment No. 3H, with the amount of Cr_2O_3 engaged in malayaite crystals increased, different tones of pink resulted, and in all compounds, the color tones were deeper in comparison to the ones found in Table 1. Consequently, Cr_2O_3 engages in malayaite crystals. The increase of malayaite crystals engaged with Cr_2O_3 deepens the color tones.

The effect of the mineralizer H_3BO_3 increases the malayaite crystals which was also confirmed by FT-IR spectra. In Fig. 7, the bands at 331 cm^{-1} , 362 cm^{-1} , 420 cm^{-1} , 462 cm^{-1} , 489 cm^{-1} , 533 cm^{-1} , 563 cm^{-1} , 902 cm^{-1} , 941 cm^{-1} showed the changes of intensity increased the malayaite which engaged chromium [12]. The quantity of malayaite and cassiterite crystals, the main contributors in producing the pink-red color, was studied in order to understand the quantitative requirement necessary for producing an

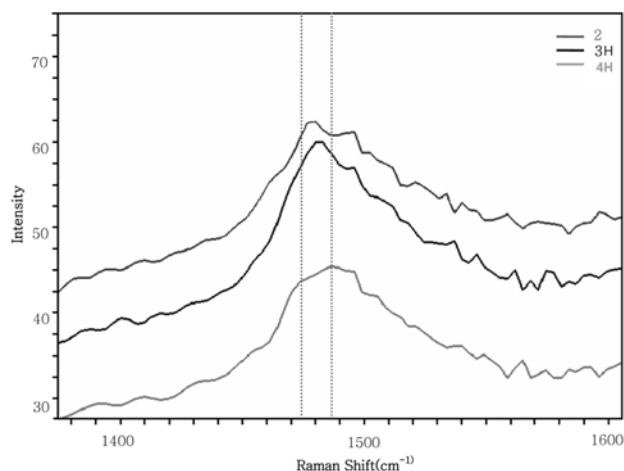


Fig. 8. Raman spectroscopy of sample 2, 3H, 4H in 1380-1600 (cm^{-1}).

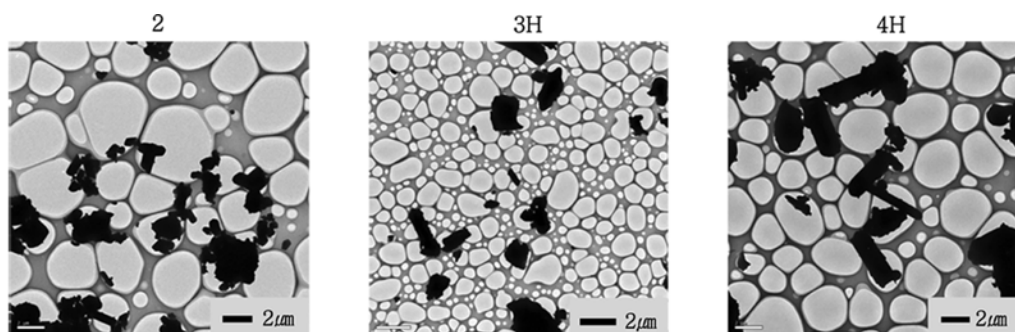


Fig. 9. TEM images of pigments 2, 3H, 4H.

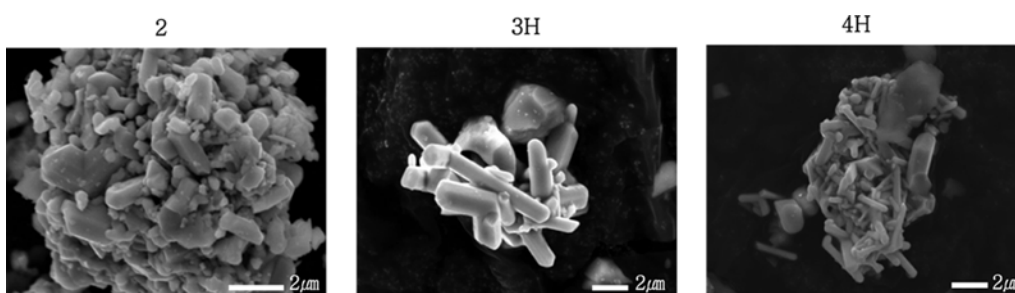


Fig. 10. SEM images of pigments 2, 3H, 4H.

effective color with Raman Spectroscopy. The result from this is presented in Fig. 8. In the pigment compounds the main crystalline phase was cassiterite and the pink resulting from the glaze, pigment No. 2, the intensity of cassiterite and malayaite was the same. Pigment No. 3H gave a deep pink tone, No. 4H, produced a green color with the main crystalline phase being malayaite engaged with Cr_2O_3 . With pigment No. 2, the intensity of line cassiterite peak, 1478 cm^{-1} is greater than the intensity of the malayaite peak, 1498 cm^{-1} . But with pigment No. 3H the peak from cassiterite and malayaite in its intensity, is almost the same, 1480 cm^{-1} , appearing as one single peak. In the case of pigment No. 4H, the intensity of the cassiterite peak is less while the malayaite peak is greater showing a shift towards the right. This shows the acceleration of Cr_2O_3 content engaged in malayaite, is causing a shift to take place. The Raman Spectroscopy results unify effectively with the XRD analysis.

It is evident that the increase of malaysite crystal contents, more than the cassiterite crystals, effect the pink-red color in the condition that Cr_2O_3 crystals are eliminated. When there is more cassiterite crystal content than malayaite, pink colors are produced. If there is more malayaite crystals than cassiterite along with Cr_2O_3 crystals, then the color becomes green.

The particle sizes and shapes of crystals that appear in the crystalline phases within the pigment compounds, were measured individually with TEM and SEM. The results are recorded in Fig. 9. and Fig. 10. The particle sizes in the compounds are different, generally being within $2\text{--}7\text{ }\mu\text{m}$. In pigment No. 2, the main crystals of

cassiterite, the shapes and sizes of the crystals were irregular and inconsistent. In pigment No. 3H, the crystals were disordered with both irregular and bar shapes appearing simultaneously. Here the main crystals are cassiterite and malayaite. With pigment 4H, the main crystalline phase is malayaite. Its crystals are mostly in a bar shape although there are irregular shapes placed in a disorderly away.

Through this it is possible to estimate that with the cassiterite crystals, the shapes and sizes are irregular. The malayaite crystals are mostly bar shaped.

Conclusions

It was possible to produce a stable range of pink-red colors using glazes and pigments with $\text{Cr}_2\text{O}_3\text{--SnO}_2$.

1. To produce the pink-red color, cassiterite and malayaite crystals must exist engaged together with Cr_2O_3 .

2. H_3BO_3 is added as the mineralizer in order to accelerate the formation of malayaite crystals. Through this the non-reactive Cr_2O_3 becomes engaged with malayaite. This enables the glaze to acquire a deeper tone in color.

3. If Cr_2O_3 exists as a non-reactive component within the pigment compound, having no association with the quantity of cassiterite and malayaite crystals, green tones are produced in the glaze.

4. Cassiterite crystals come in an irregular disordered form, while malayaite crystals appear in an ordered structure in bar shapes.

In order to produce a pink-red color with a rich red tone, there should be an excess increase of malayaite crystals that are engaged with chromium oxide.

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