

Formation and color properties of vanadium doped ZrSiO_4 ceramic pigments

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Vanadium doped zircon pigments were prepared by a ceramic method from a mixture of monoclinic zirconia and silica with sodium fluoride as a mineralizer and the color properties of the pigments were also investigated. The raw composition was varied in order to optimize the synthesis of the final pigments. The color of synthesized pigments observed in the absence and the presence of the NaF was green and blue, respectively. They were characterized by X-ray diffraction, UV-Vis and Raman spectroscopies. The color changes produced in the samples during heating are discussed in terms of the valence of the vanadium species in the zircon matrix and the yield of the zircon phase. In these zircon pigments, evidence of the intermediate phase (NaVO_3) in an initial step in the synthesis process is observed by Raman spectroscopy. V^{4+} - ZrSiO_4 pigments using rice husk ash give rise to a blue coloration at a low temperature (750 °C) and they became a more intense blue color with holding time and a suitable turquoise blue at high temperature (~1300 °C) glazes for porcelain wares.

Key words: Rice husk ash, V- ZrSiO_4 pigment, Raman internal mode, Formation process.

Introduction

Zircon-doped structures are frequently found in ceramic pigments and are closely related to properties, such as low toxicity, dissolution resistance and tinctorial strength that are desirable for a wide range of industrial applications. The first commercially introduced zircon pigment was "turquoise blue (DCMA 14-42-2)" containing vanadium as a chromophore cation. A yellow zircon pigment containing praseodymium (DCMA 14-43-4) and a pink zircon pigment (DCMA 14-44-5) containing iron are also commercially available [1-6].

Vanadium forms solid solutions and incorporates into the zircon lattice with a form of V^{4+} ions that is the origin of the blue color of this pigment. But there are some contradictory reports about the limit of the solid solution, the valence, location and stabilization of the blue color [7]. Eppler examined the mechanism of formation to elucidate the origin of the coloring by zircon pigments, and also proposed the role played by mineralizers in the reaction kinetics through an ion diffusion model and a vapor transport model [8]. Demiray *et al.* [9] confirmed the existence of V^{4+} in the ZrO_8 position in the zircon structure using crystal field theory through optical spectrum analysis and concluded that V^{4+} ions occupy the octahedral sites since the unit cell parameters in V-doped zircon are the same as those in undoped zircon.

Structural research [10] of the V- ZrSiO_4 system indicates that the V^{4+} cation which forms a solid solution with the zircon lattice by substituting for both Si^{4+} and Zr^{4+} cations

and flux additions (NaF) increased the solubility and thermal stability of V^{4+} in zircon but did not affect the valence and coordination. Raman spectra have been proposed [11-13] to try to obtain information concerning the position of vanadium(IV) in the zircon lattice. De Waal *et al.* [11] used for the calculation of V-O bond distances in vanadium(IV) compounds the equation of Hardcastle and Waches [13], and indicated that the $\text{Si}^{4+}(4b)$ positions accommodate the chromophores as V^{4+} from Raman spectra.

In a previous study [14], rice husk ash was used as a source of silica in the preparation of pr- ZrSiO_4 solid solutions to produce a yellow powder in which a degree of high reactivity allows a significant increase in the efficiency of the process at a lower temperature. Currently in Korea, the estimated production of rice husk is approximately 800,000 tons per year. Research is continuing to determine the feasibility of using rice husk ash which remains as waste after burning, as an industrial raw material [15-17].

In the present study, the raw composition of vanadium contents and firing conditions were varied in order to optimize the synthesis of the final pigments and the Raman spectrum of undoped zircon powder was compared to that of the V-doped zircon pigments using rice husk ash and SiO_2 as a source of silica in order to elucidate the state of vanadium ions in the formation process by means of a low temperature processing route.

Experimental

Sample preparation

The preparation of the vanadium-doped zircon pigments was carried out using traditional ceramic procedures. High-purity reagent-grade monoclinic zirconia (Yakuri), rice husk ash and SiO_2 as a source of silica, V_2O_5 (99.0% Junsei),

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as well as a mineralizer NaF (Duksan) were selected as the raw materials in the preparation of the pigments. The rice husk ash used was obtained by the slowest possible burning at 1000 °C. After burning it was washed repeatedly with water to remove as much alkali as possible. The average particle size was 0.56 µm. ZrO₂ and SiO₂ were mixed to an equimolar concentration. 0.1–0.2 mol% of V₂O₅, 0.5 mol% of NaF were added to the mixture and this was then milled in acetone. The resulting dried powders were finally homogenized in an agate mortar and samples of the mixture were placed in alumina crucibles. In order to allow the V-ZrSiO₄ pigment to be formed in a solid-state reaction, the dried powders were fired in an electric furnace at temperatures ranging between 600 and 1000 °C for 3 h. To produce an intense blue pigment and lower the synthesis temperature, the firing conditions were designed with holding schedules which were varied from 3 h to 10 h at 750 °C. Also to investigate the formation process in this pigment, the holding schedules were varied from 0 h to 10 h at 700 °C.

Characteristics of V-ZrSiO₄ pigments

To measure the silica content in the rice husk ash, an analysis was carried out using XRF (Shimadzu, XRF -1800). A particle size analyzer (Shimadzu, SALD-7101) was used for an analysis of the particle size. Characterization of the calcined samples was done using an X-ray diffractometer with Ni-filtered Cu Kα radiation (Shimadzu, XRD 7000). For a qualitative analysis, the patterns were recorded on ground samples in the 10–70 2θ range at room temperature at a scanning rate of 10°/minute and a step size of 0.2°. 10 wt% of corundum was added to all samples as an internal standard. The fraction of ZrSiO₄ (α -ZrSiO₄ = $I_{ZS(200)} + I_{M(11\bar{1})} + I_{M(111)} + I_{T(111)}$) was obtained based on the relative intensity calculated using the four peak areas of ZrSiO₄ (200), (monoclinic) m-ZrO₂ (11 $\bar{1}$, 111) and (tetragonal) t-ZrO₂ (111) that appeared in the 2θ range of 26–32° in the X-ray diffraction patterns of the sample powders heat-treated at each temperature [18].

The oxidation state of the vanadium in the pigments synthesized at various calcination temperatures was analyzed using UV-Vis spectra (Shimadzu, UV-2410 PC). Assignment of the zircon frequency and doped V-O bonding frequency was confirmed using Raman spectroscopy (Dimention D2, Lambda Solution, Inc, U.S.A.). The Raman spectra were excited with a semiconductor laser operating at 532 nm and vertical scattered reflection light was analyzed using a CCD dispersive Raman spectrometer at a spectral resolution of 3 cm⁻¹. Raman spectra were recorded at room temperature using a vector Raman probe (RP532-US). The UV-Vis spectra were obtained in the absorption mode in the range of 200–800 nm. The colors of the synthesized pigments and their coloring in a lime-barium glaze were analyzed via UV-Vis spectra. The results were also obtained numerically by means of UV PC optical color analysis software (Shimadzu, P/N 206-67449) using the CIE $L^*a^*b^*$ color system.

Application of glazes under high-temperature firing

The scope of application of the V-ZrSiO₄ pigments synthesized in the present study is the range of the ceramics created by high-temperature firing (SK 8–10). For the final evaluation of the coloring of the synthesized pigments, experiments were conducted by applying the pigments to lime-barium glazes used in a ceramic made by high-temperature firing. Its Seger formula is as follows:

0.297 KNaO
0.157 CaO 0.734 Al₂O₃ 4.682 SiO₂
0.018 MgO
0.528 BaO

Each of the synthesized pigments was added to lime-barium glazes (10%) by wet-mixing. Firing was done in an electric furnace by raising the temperature to 1265 °C for 30 minute at a rate of 3 K·minute⁻¹. The samples were then cooled. The characteristics of the colors of the high-temperature fired glazes using the synthesized V-ZrSiO₄ pigments were measured by UV-Vis spectroscopy, and these values were then expressed numerically based on the CIE $L^*a^*b^*$ color order system.

Results and Discussion

Characterization of raw samples

The results of the chemical analysis of the rice husk ash are shown in Table 1. The loss by ignition of the ground rice husk ash was 25.75% while that of the silica content was 58%. Additionally, the content of the Fe₂O₃, which affects cloth coloring, was extremely low at 1.89%. This value for the content of the alkali was 4.04%.

Optimization of synthesis parameters

Phase changes depending on different calcination temperatures

Regarding the synthesis of V-doped blue zircon pigment using rice husk ash, an investigation was carried out between the relation of the formation of zircon crystals and the coloring of the pigment according to the calcination temperature. Fig. 1 shows the calcination temperature-dependent changes of the crystal phases of the V-ZrSiO₄ pigment synthesized with the addition of 0.2 mol% of V₂O₅. The holding time at each temperature zone for the

Table 1. Chemical analysis of the rice husk ash as received

Oxide	Composition (%)	Oxide	Composition (%)
SiO ₂	58.16	K ₂ O	3.90
Al ₂ O ₃	3.23	P ₂ O ₅	2.31
Fe ₂ O ₃	1.89	MnO	0.26
MgO	1.23		
CaO	2.40	Ig. loss	25.75
Na ₂ O	0.14		

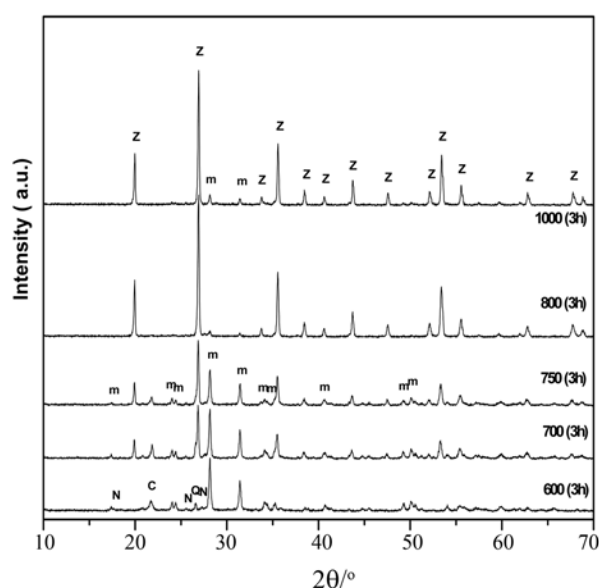


Fig. 1. XRD patterns of samples formed at different temperatures in V-doped ZrSiO₄ pigments. (V₂O₅ 0.2, NaF 0.5 mol%) (600, 700, 750, 800, 1000 °C : 3 h keeping) Z : zircon, m : monoclinic ZrO₂, C : cristobalite. Q : quartz, N : NaVO₃

synthesis of the pigment was 3 hours. In the case where the calcination temperature was 600 °C, the main phase was m-ZrO₂ with traces of unreacted silica and NaVO₃ (sodium vanadium oxide), which is a eutectic of V₂O₅ and NaF were observed (JCPDS : 30-1259). This observation is in agreement with the Raman analysis. Raman analysis was carried out in order to more clearly confirm the presence of NaVO₃ produced at 600 °C, which therefore had been produced before zircon was produced; and the result is shown in Fig. 2. The standard in Fig. 2 represents the result of the analysis of the NaVO₃ synthesized at 650 °C using an equimolar mixture of V₂O₅ and NaF. The result showed that the pigment synthesized at 600 °C showed the appearance of characteristic NaVO₃ bands at 952, 915, 637, 506, 342, 248, 225 and 180 cm⁻¹. Thus it was confirmed that NaVO₃ is the intermediate phase, the first reaction product during the process of the pigment. Also it was confirmed that during the initial period of reaction, vanadium exists as the intermediate phase V⁵⁺, which is a yellow powder. The reaction between m-ZrO₂ and silica began at 700 °C to initiate the active production of zircon crystals. When the temperature reached 750 °C, zircon became the main phase and at 800 °C it showed a rapid growth accompanied by the relative reduction of the M-ZrO₂ to a trace. The Hedvall effect [19] has been well known: that during the synthesis of zircon, the temperature zone for the monoclinic-tetragonal phase transition or quartz-cristobalite phase transition allows a very reactive state, maximizing the reaction rate, and thus resulting in an increase of zircon formation. Fig. 3 shows the changes in the yields of zircon and m-ZrO₂ according to varying the calcination temperature when a V-ZrSiO₄ pigment is synthesized with the addition of 0.2 mol% V₂O₅. The result showed that the

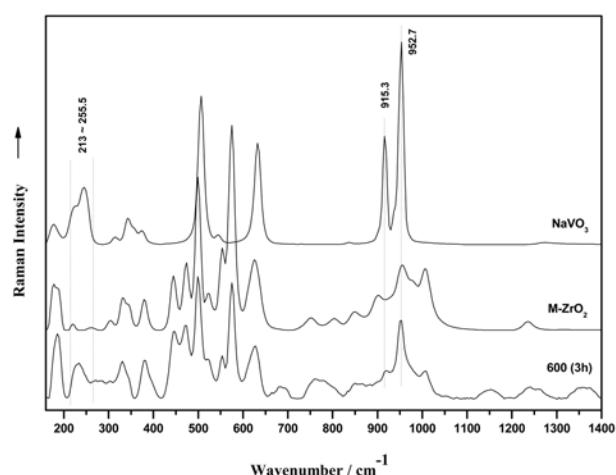


Fig. 2. Raman spectra of vanadium 0.2 mol% doped zircon blue pigments using rice husk ash at 600 °C.

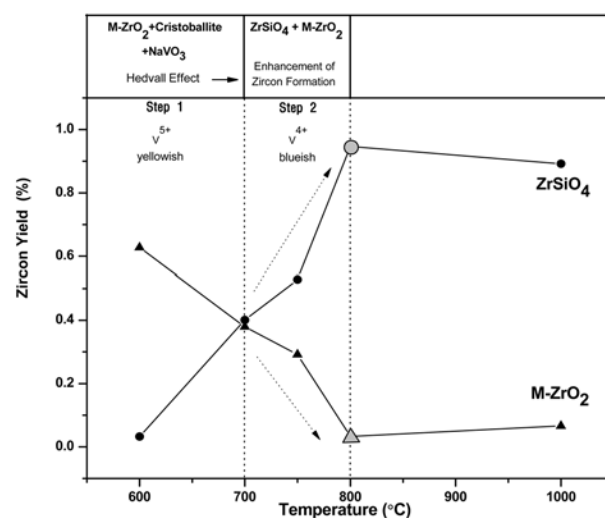


Fig. 3. Zircon and M-ZrO₂ yields with different temperatures of the V doped ZrSiO₄ pigments.

addition of NaF allowed the phase transition of SiO₂ (quartz → cristobalite) at the very low temperature of 600 °C, thereby maximizing the reaction so as to increase in the next step the yield of zircon by the Hedvall effect. In the synthesis of zircon pigment, the temperature at which zircon begins to be synthesized as the main phase is very important because at this stage coloring of the pigment begins as the chromophore is included into the host matrix. The yield of zircon was shown to be highest (94.7%) at 800 °C. The optimum calcination temperature for V 0.2 mol% doped blue pigment was 800 °C for 3 h and the best pigment was synthesized at this temperature as shown in Fig. 3. The color property of this pigment when applied to a glaze was $L^* 62.66$ $a^* -14.66$ $b^* -9.12$ (H 2.0B V/C 6.2/3.8).

Phase changes depending on the content of V₂O₅ and different holding times

In order to find the optimum V₂O₅ content for the synthesis

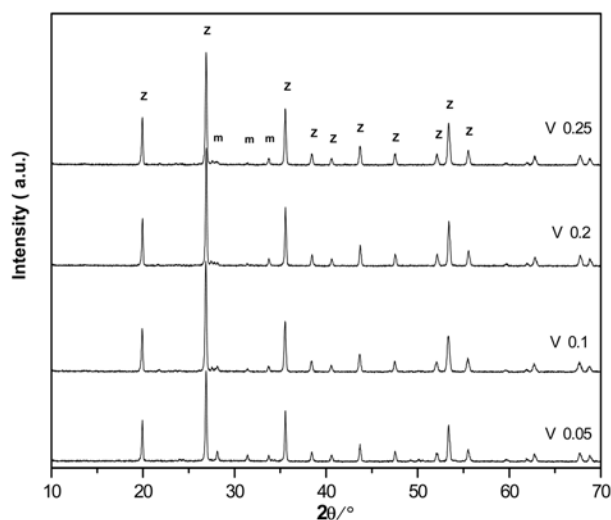


Fig. 4. XRD patterns of content change of V_2O_5 at 800 °C (3 h) in V-doped $ZrSiO_4$ pigments. (V_2O_5 0.2, NaF 0.5 mol%) Z : zircon, m : monoclinic ZrO_2 , Q : low quartz, C : cristobalite, N : $NaVO_3$.

of V-doped blue zircon pigment using rice husk ash, calcination was carried out at 800 °C for 3 hours with the addition of 0.05, 0.1, 0.2 and 0.25 mol% V_2O_5 . The results are shown in Fig. 4. During the synthesis of zircon pigment, vanadium oxide first forms a eutectic by reacting with NaF while it also plays a role as a mineralizer to promote the formation of zircon. In all the samples the main phase was zircon, but the presence of unreacted M- ZrO_2 exerted a subtle effect on the completion of pigment synthesis as well as on the intensity of coloring. The addition of more than 0.1 mol% V_2O_5 allowed a good production of zircon during calcination, resulting in the blue coloring of the synthesized pigment. In this research, the optimum amount of V_2O_5 that resulted in the best blue coloring of the pigment was 0.2 mol% when this pigment was applied to a glaze, the color values were L^* 62.66, a^* -14.66, b^* -9.12 (H 2.0B V/C 6.2/3.8).

The holding time at the final temperature has been reported to be an important synthetic factor that can lower the calcination temperature by reducing the unnecessary 2nd phase and by stabilizing the growth of the 1st phase zircon and that can also increase the intensity of coloring [14]. When pigment samples synthesized at various calcination temperatures were applied to a glaze the best coloring was shown by the sample calcined at 800 °C for 3 hours. Whereas the sample calcined at 750 °C for 3 hours showed a reduction of the 2nd phase (M- ZrO_2) as the zircon grew. Therefore, in order to obtain the optimum calcination condition at 750 °C, samples containing 0.2 mol% V_2O_5 and 0.5 mol% NaF were calcined for varying holding times of 3, 5 and 10 hours. Fig. 5 shows the change of crystal phases according to the change of holding time. The results showed that the highest intensity of zircon was obtained from the sample calcined at 750 °C for 5 hours, also with the best coloring: L^* 58.38, a^* -12.87, b^* -10.63 (H 3.7B V/C 5.7/3.9). The best condition for the synthesis

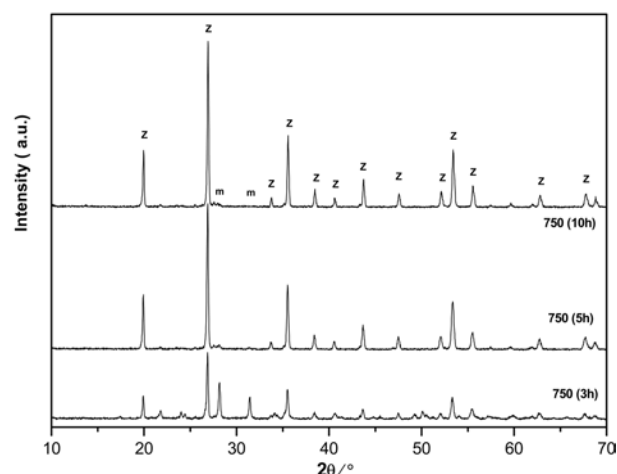


Fig. 5. XRD patterns for different holding times at 750 °C in V-doped $ZrSiO_4$ pigments. (V_2O_5 0.2, NaF 0.5 mol%) Z : zircon, m : monoclinic ZrO_2 .

of the V- $ZrSiO_4$ pigment using rice husk ash was calcination at 750 °C for 5 hours with the addition of 0.2 mol% V_2O_5 and 0.5 mol% NaF. This is because the holding time at 750 °C can stabilize the growth of zircon crystals as well as the inclusion of V ions, resulting in an improvement of the coloring.

Color properties of pigments

UV-Vis analysis of pigments with different calcination temperatures

The pigments synthesized at 600-1000 °C with the addition of 0.2 mol% V_2O_5 were added to a lime-barium glaze at a concentration of 10%, for an analysis of the coloring by UV-Vis spectroscopy and the results are shown in Fig. 6. and Table 2. The pigment synthesized at 600 °C gave a yellow color. There was a change in the UV-Vis spectra from 700 °C, the onset temperature of

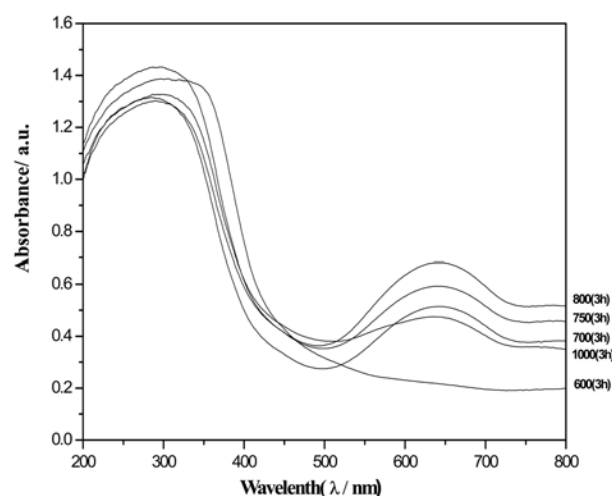


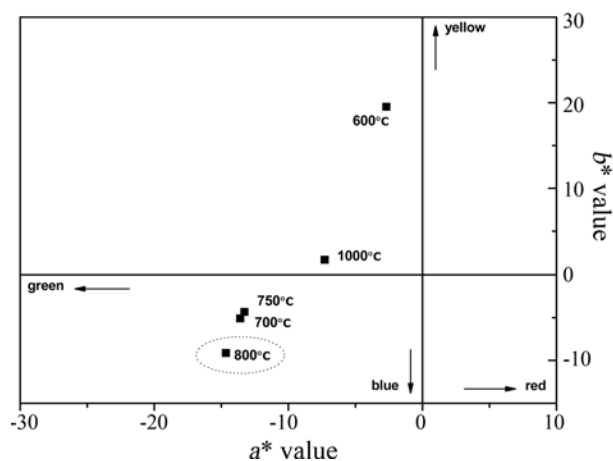
Fig. 6. Optical absorption spectra of glazed samples with V-doped $ZrSiO_4$ pigments. (V_2O_5 0.2, NaF 0.5 mol%) synthesized at different temperatures.

Table 2. Lab parameters of glazed tiles with synthesized samples of V 0.2mol% doped blue pigments with different temperatures

Samples	L^*	a^*	b^*	H	V/C	Color
1000(3 h)	68.29	-7.30	1.78	8.2G	6.7/1.2	Pale Green
800(3 h)	62.66	-14.66	-9.12	2.0B	6.2/3.8	Greenish Blue
750(3 h)	65.99	-13.27	-4.31	8.5BG	6.5/2.9	Light Bluish Green
700(3 h)	71.61	-13.59	-5.08	9.5BG	7.1/3.0	Light Bluish Green
600(3 h)	78.93	-2.69	19.53	5.0Y	7.8/2.6	Grayish Yellow

synthesis at which active production of zircon begins. That is, the characteristic absorption band for a yellow color at 435–480 nm moved towards short wavelengths while the band at long wavelengths around 650 nm became more intensive. From above 700 °C, the characteristic absorption band of V^{4+} at 640 nm [20] was observed along with a clear change in the coloring to blue of the pigment applied to the glaze and the blue coloring was more enhanced as this characteristic band became more intense. This is due to the conversion of the V^{5+} species, which is prevalent in the initial step of pigment synthesis, to V^{4+} in the final step. The coloring of the pigment showed an increase of the blue color property from 750 °C when zircon begins to grow rapidly and the best blue color was obtained at 800 °C with a b^* value of -9.12. There has been literature reporting that the characteristic absorption bands of V^{4+} appeared at 290 nm and 640 nm. They reported that the band [21] at 290 nm was due to $2\text{B}_1 \rightarrow 2\text{A}$ (the dodecahedral transition) and that the band at 640 nm is related to $2\text{B}_1 \rightarrow 2\text{E}$ (the dodecahedral and tetrahedral transition) this is in agreement with the result of the present research. It has been confirmed that in the synthesis of the V-doped zircon pigment using rice husk ash the characteristic absorption bands of V^{4+} which is the major cause for coloring appears at 290 and 640 nm due to a valence electron transition.

Fig. 7 and Table 2 show the $L^*a^*b^*$ values. When

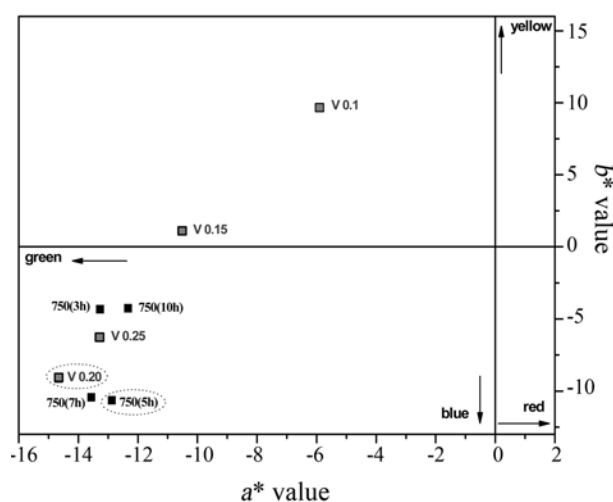
**Fig. 7.** a^*b^* plots of the glazed sample with V-doped ZrSiO_4 pigments (V_2O_5 0.2, NaF 0.5 mol%) different temperatures.

added to a lime-barium glaze the pigments synthesized at 600–1000 °C with the addition of 0.2 mol% V_2O_5 showed the following coloring. The vanadium ion in the pigment synthesized at 600 °C is in the state of V^{5+} (NaVO_3) which has a yellow color so when it was applied to a glaze the b^* value was 19.53 giving a grayish yellow color. The application of the pigment synthesized at 700 °C to a glaze resulted in a negative a^* value (-13.59) and b^* value (-5.08), giving a weak blue color. Whereas the application of the pigment synthesized at 750 °C to a glaze resulted in a^* and b^* values that are similar to those of the pigment synthesized at 700 °C giving a light bluish green color but with an increase of the L^* value to 65.99. As shown in Fig. 3, the pigment synthesized at a higher calcination temperature showed a higher yield of zircon resulting in bluer color property. The pigment synthesized at 800 °C showed the highest yield of zircon and when applied to a glaze it also showed the highest $-b^*$ value of -9.12. In the mean time, its H/V/C value was 2.0B 6.2/3.8 giving the best greenish blue color. The pigment synthesized at 1000 °C showed a somewhat poor yield of zircon with a re-increase of the M- ZrO_2 yield the coloring of the pigment applied to a glaze also became poor to a pale green color.

Thus the results of applying the pigments synthesized at various calcination temperatures to glazes showed that the optimum condition was 800 °C for 3 hours. The pigment synthesized under this condition showed the best greenish blue color (L^* 62.66, a^* -14.66, b^* -9.12, Hue value 2.0B).

Color changes depending on the content of V_2O_5 and different holding times

The pigments synthesized at 800 °C for 3 hours with varying V_2O_5 contents (0.1, 0.15, 0.2 and 0.25 mol%) were added to a lime-barium glaze for an analysis by UV-Vis spectroscopy the result is shown in Fig. 8. The

**Fig. 8.** a^*b^* plots of glazed samples with V-doped ZrSiO_4 pigments (NaF 0.5 mol%) with different V_2O_5 contents (mol%) at 800 °C and with different holding times at 750 °C (V_2O_5 0.2, NaF 0.5 mol%).

pigment sample synthesized with the addition of 0.1 mol% V_2O_5 and applied to a glaze gave a grayish yellow green color. Where the V_2O_5 content was increased to 0.15 mol% there was a remarkable increase of the blue color property along with a decrease of the b^* value to 1.08. however, the L^* value was still 70.88 giving a pale green color of a fairly bright and weak tone. The application of the pigment synthesized with the addition of 0.2 mol% V_2O_5 to a glaze resulted in a big change of color. That is, the color became darker along with an increase of the blue color property resulting in a light greenish blue color. In the case of 0.25 mol% V_2O_5 the color became rather brighter to a light blue color. Thus in the experiment with varying V_2O_5 contents, the optimum V_2O_5 content for an excellent blue coloring was 0.2 mol% which is also in agreement with the result of XRD in Fig. 1.

The pigments synthesized with the addition of 0.2 mol% V_2O_5 at 750 °C for various holding times of 3, 5, 7, and 10 hours were applied to a lime-barium glaze for an analysis by UV-Vis spectroscopy and the results are shown in Figs. 8 and 9. In the experiment with varying holding times at 750 °C, the sample with 5 hours holding time showed a better blue color property than the sample with 3 hours holding time at the same temperature and also than the sample with 3 hours holding time at 800 °C. The sample with 7 hours holding time showed almost the same coloring as the sample with 5 hours holding time but with a propensity for higher brightness resulting in a L^* value of 61.16 and when the holding time was 10 hours, there was again an increase of the b^* value to -4.25, resulting in an even brighter color. The result of the experiments with varying holding times showed that the optimum condition for pigment synthesis was 750 °C with 5 hours holding time. The effect of holding time on the synthesis was not so great in the case of the V-ZrSiO₄ pigment compared to the ZrSiO₄ pigment, however it was possible to lower the highest calcination temperature from 800 °C down to 750 °C as well as to more effectively improve the blue color property.

This could be understood as shown in Fig. 9 by the further stabilization of the V ion to the state of 4+ which maximizes the blue coloring of the pigment. In these experiments, the optimum calcination conditions for the synthesis of the zircon pigment with the addition of 0.2 mol% V_2O_5 was 750 °C for 5 hours and application of this pigment to a glaze gave the most vivid and intense light greenish blue color (L^* 58.38, a^* -12.87, b^* -10.63).

Raman spectra of ZrSiO₄ : V⁴⁺ pigments

Raman analysis was carried out in order to investigate the effect of rice husk ash and the calcination temperature on the zircon frequency and doped V-O bonding frequency during the synthesis of V-ZrSiO₄ pigment and the results are shown in Fig. 10 and Table 3. Assignments were made with the results of the researches conducted by Syme *et al.* [22] and Knittle and Williams [23] as well as with the zircon and V-O vibration Raman modes of the

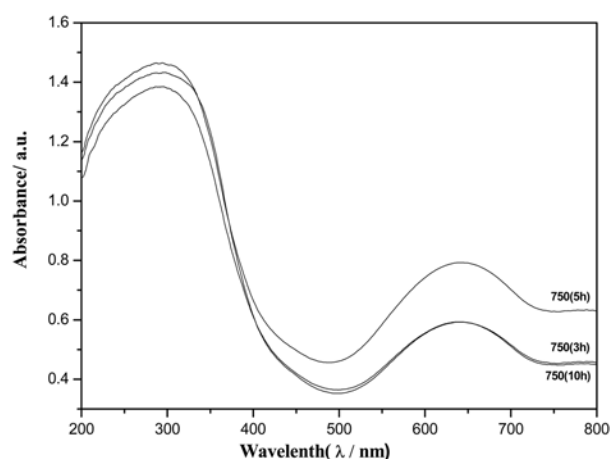


Fig. 9. Optical absorption spectrum of a glazed sample with V-doped ZrSiO₄ pigments. (V₂O₅ 0.2, NaF 0.5 mol%) different holding time at 750 °C.

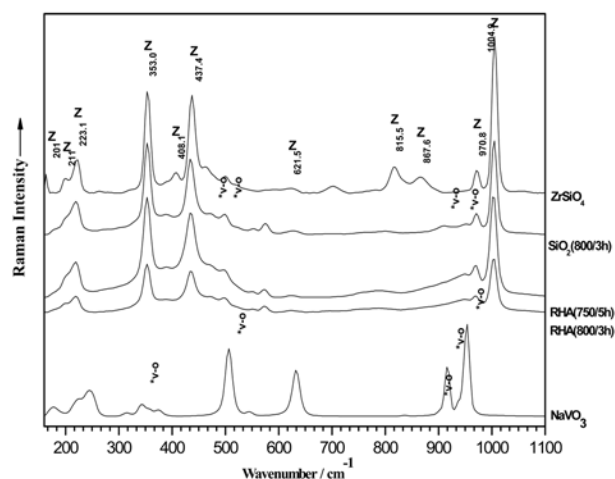


Fig. 10. Raman spectra of vanadium 0.2 mol% doped zircon blue pigments using SiO₂ and RHA at different temperatures. Z : Zircon.

pigments synthesized in this research.

Fig. 10 shows the Raman spectra of the V-ZrSiO₄ pigment synthesized using rice husk ash and SiO₂. Table 4 shows the symmetry species mode assignment for each frequency. When rice husk ash was used to synthesize pigments the optimum condition was 750 °C for 5 hours and zircon was produced at lower temperatures than when SiO₂ was used. As shown by the comparison in Table 4 the majority of the bands presented in Fig. 10 are the characteristic bands of ZrSiO₄. In the case of the pigment synthesized using rice husk ash at 750 °C, the characteristic zircon bands including the most intensive zircon B_{1g} mode showed almost the same peak intensity as in the case of the pigment synthesized using SiO₂ at 800 °C. This is due to the higher reaction rate of amorphous rice husk ash. The result of the Raman analysis on commercial ZrSiO₄ powder and the zircon powder synthesized by Syme *et al.* [22] showed almost the same pure zircon assignment at E_g, A_{1g} and B_{1g}. In the case of the vanadium-doped pigments, unique vibrational modes are shown although weak at

Table 3. Raman band wavenumber(ν) observed for the V-doped pigment using RHA(750/5 h), SiO₂(800/3 h) and single crystal (Wall *et al.*[11]) compared with those observed for commercial zircon powder, together with assignments from pure zircon by Syme *et al.*[22]

V-ZrSiO ₄ single crystal (Wall <i>et al.</i> [11])	V-doped ZrSiO ₄ Pigment (RHA)	V-doped ZrSiO ₄ Pigment (SiO ₂)	Commercial ZrSiO ₄ Powder	ZrSiO ₄ (Syme <i>et al.</i> [22])	Assignment
ν/cm^{-1}	ν/cm^{-1}	ν/cm^{-1}	ν/cm^{-1}	ν/cm^{-1}	ν/cm^{-1}
1007	1003	1005	1005	1009	Zircon B _{1g}
974	971	971	971	975	Zircon A _{1g}
953	950	950			V-O ^a
925	-	-	923	925	Zircon E _g
918	912	910			V-O ^a
912	882	876			V-O ^a
852		851	867		-
	788	798	815		-
	625	625	640	641	Zircon B _{1g}
	571	615	621		-
	498	499			V-O ^a
	473	473			V-O ^a
	434	433	437	439	Zircon A _{1g}
	389	389	408	393	Zircon E _g
					V-O ^a
	353	353	353	357	Zircon E _g
	219	219	223	225	Zircon E _g
			211	214	Zircon B _{1g}
	201	201	201	202	Zircon E _g
	181	181			-

Table 4. Raman Internal vibrations and wavenumber($\tilde{\nu}/\text{cm}^{-1}$) of synthesized pigments are compared with other compounds in which vanadium has tetrahedral coordination.

V-O tetrahedral ¹¹⁾	Site group ¹¹⁾	Factor group ¹¹⁾	ZrSiO ₄ : V Powder ¹¹⁾	ZrSiO ₄ : V Powder (RHA)	NaVO ₃ synthesized	V ₂ O ₅ commercial
T _d	D _{2d}	D _{4h}	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$
V ₁ (A ₁) Symmetric stretching	A ₁	A _{1g}	950	950	953	991
V ₂ (E) Bending	A ₁	A _{1g}	378	-	342	301
V ₃ (F ₂) Asymmetric stretching	B ₂	B _{1g}	917	912	915	699
	E	E _g	908	882	-	-
V ₄ (F ₂) Bending	B ₂	B _{1g}	503	498	506	481
	E	E _g	473	473	-	-

950, 912, 882, 498 and 473 cm⁻¹. The low intensity bands presented in Fig. 10 were not observed in the pure zircon powder. That is, they are the bands that are presumed to be the V-O vibration modes of the vanadium in the tetrahedral VO₄ coordination in the zircon structure. As shown in Table 4, these bands were also found in other compounds with a tetrahedral coordination (the α -NaVO₃ synthesized in the present research as well as commercial V₂O₅. De Waal *et al.* [11] reported that the new internal modes not observed with a pure zircon powder were caused by the presence of the vanadium located at the silicon site

of the D_{2d} site in the zircon lattice. That is, as shown in Table 4 the peaks at 950, 912, 882, 498, 473 cm⁻¹ observed with the V-ZrSiO₄ pigment synthesized using rice husk ash were confirmed to be the V-O vibration modes (V₁ (A₁) stretching, V₃ (F₂) asymmetric stretching, and V₄ (F₂) bending) that are related to Raman active modes at each factor group (A_{1g}, A_{1g}, B_{1g}, E_g, B_{1g} and E_g). Therefore the vanadium ions of the zircon pigment synthesized using rice husk ash which are responsible for the blue coloring, are considered to be located at the Si⁴⁺ sites of D_{2d} symmetry in the tetravalent state.

Formation process of V-Zircon pigments

When pigment was synthesized in an alumina crucible the synthesized pigment formed 2-3 layers as shown in Fig. 11. The result of the XRD analysis on the individual layers is shown in Table 5 and the results of the Raman analysis in Fig. 12. As shown in Table 5, 2 layers of brown and yellow colors were observed in the pigments synthesized at 600 °C and 650 °C whereas 3 layers of yellow, brown and blue colors were observed in the pigment synthesized at 700 °C. According to the result of the XRD analysis on the pigments synthesized at 600 °C and 650 °C, in all the layers formed there was a detection of unreacted M-ZrO₂, quartz, cristobalite and NaVO₃ with a similar intensity. In the Raman spectra however, there was a distinct difference in the intensity. This is because the Raman frequency allows the detection as peaks of the vibration modes for inter-molecular interactions, even if the degree of crystallization is low. In the case of the pigment synthesized at 600 °C for 3 hours, the yellow layer which was formed above the brown layer, showed a higher Raman intensity of the main phase M-ZrO₂ as shown in Fig. 12. The yellow layer

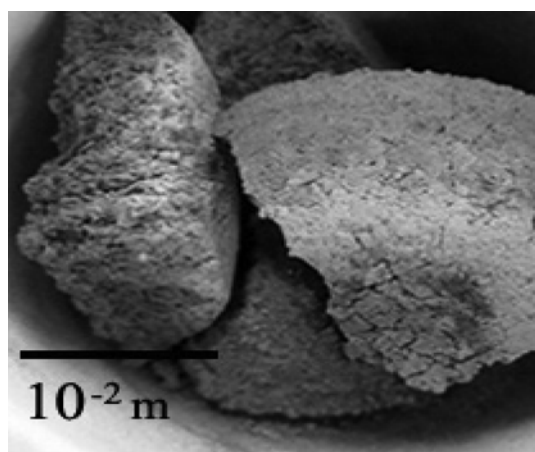


Fig. 11. Layers of pigment synthesized at 700 °C for 3 h.

Table 5. XRD phase study according to each layers of V-doped zircon pigments using RHA at different temperature and holding time.

Powder color of layers / Phase present						
Temp.(°C)		600 (3 h) 650 (3 h)		700 (3 h) 700 (5 h) 700 (7 h)		
		700(10 h)				
				Blue layer	Z(vs) M(w)	Z(vs) M(t)
Yellow layer	M(vs), C(m), Q(w), N(t)	M(vs), C(m), Q(w), N(t)	Brown layer	M(vs) C(m) Q(w) N(t)	M(vs) C(m) Q(w) N(t)	M(vs) C(m) Q(w) N(t)
Brown layer	M(vs), C(m), Q(w), N(t)	M(vs), C(m), Q(w), N(t)	Yellow layer	M(vs) C(m) Q(w) N(t)	M(vs) C(m) Q(w) N(t)	

*Z : Zircon, M : m-zro2, Q : quartz, C : cristobalite, N : NaVO₃

*vs : very strong, m : medium, w : weak, t : trace

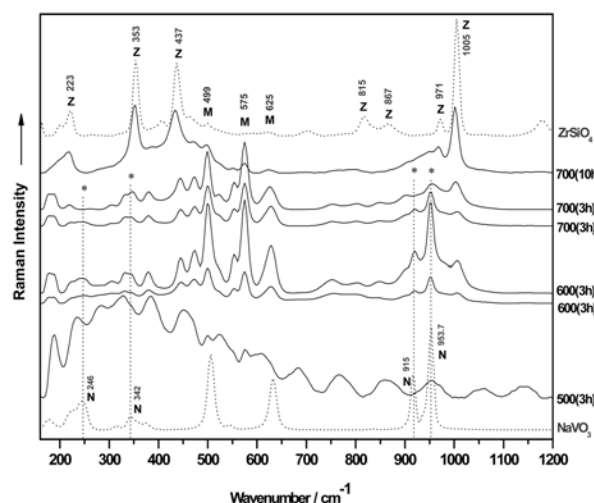


Fig. 12. Raman spectra of vanadium 0.2 mol% doped zircon blue pigments using RHA at different temperatures and times. Z : Zircon, M : Monoclinic ZrO₂, N : NaVO₃.

also showed a remarkable increase in the Raman intensity of NaVO₃ compared to the brown layer.

Where the calcination temperature was 700 °C, the result of the XRD analysis showed the detection of almost the same phase regardless of the holding time. In this case, the main phase of the blue layer was zircon while a trace of zircon was detected in the brown layer. In the yellow layer, there was an observation of M-ZrO₂, quartz, cristobalite and NaVO₃ which were undergoing a reaction. According to the result of the Raman analysis in Fig. 12, the yellow layer of the pigment synthesized at 700 °C shows a remarkable decrease in the Raman intensity of NaVO₃ compared to the yellow layer of the pigment synthesized at 600 °C. This is due to the movement of vanadium ions into the zircon lattice as zircon begins to be formed. In the case of the pigment synthesized under the calcination conditions of 700 °C for 7 hours, the yellow layer at the bottom disappeared as the blue layer broadened thus forming 2 layers but there was no big change in the crystalline phase formed. This means that the synthetic reaction of the pigment has a tendency of spreading downwards that is, in the vertical direction. The pigment synthesized under the calcination condition of 700 °C for 10 hours formed only one layer of a V-ZrSiO₄ blue pigment which was found to be the single phase of zircon.

The formation process of V-ZrSiO₄ blue pigment using rice husk ash was determined by XRD and Raman analyses. And based on the results, a schematic model of the reaction process is shown in Fig. 13. It was confirmed that V₂O₅ which is responsible for the pigment coloring, first reacts with the mineralizer NaF at 600 °C to produce the intermediate phase NaVO₃ which is a eutectic and that in this way vanadium exists in the state of V⁵⁺. In this case, SiO₂ is converted to the vapor phase of SiF₄ [8]. SiO₂ diffuses as a form of SiF₄ into the M-ZrO₂ lattice to synthesize zircon until the temperature reaches 750 °C at which point the reaction is completed. It was determined that vanadium

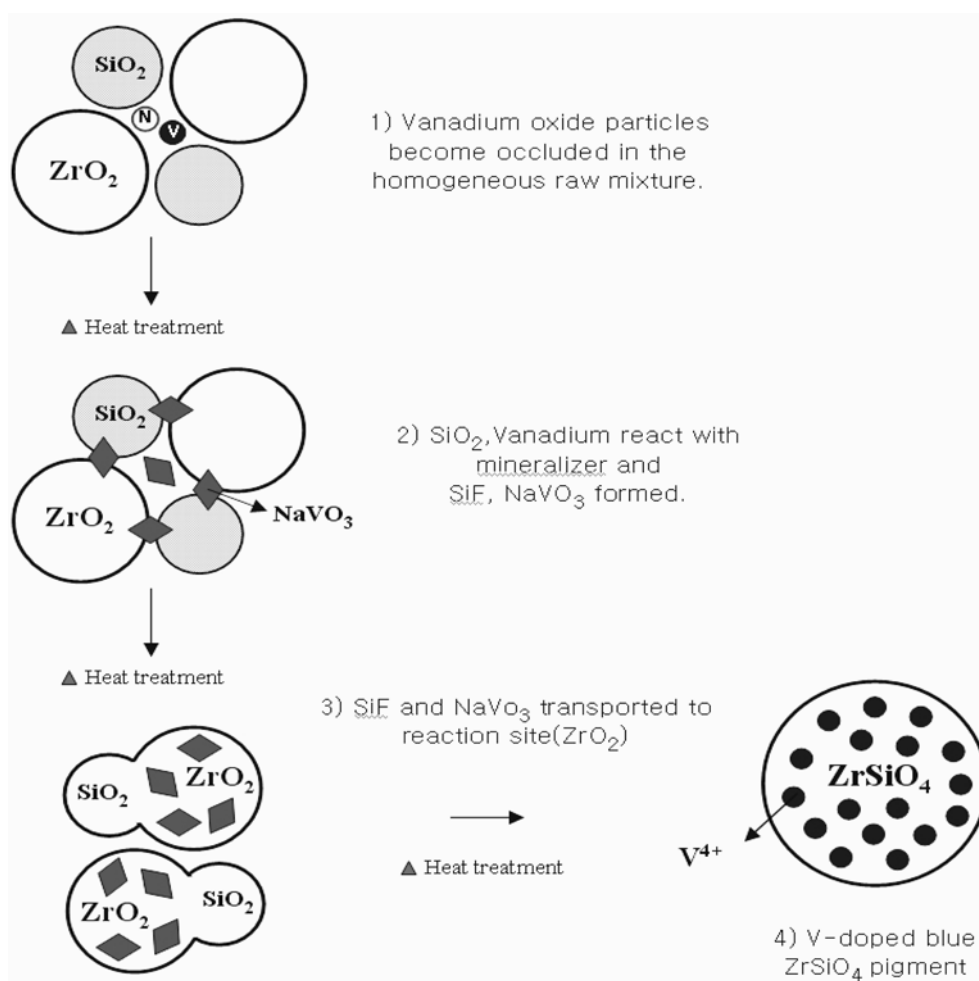
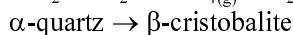
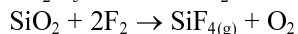
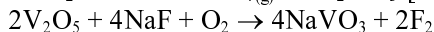
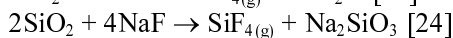


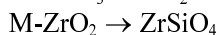
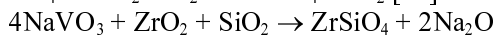
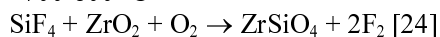
Fig. 13. Schematic model for formation of the vanadium zircon ceramic pigment.

ions are included into the zircon structure in the state of V^{4+} resulting in the blue coloring.

*500-700 °C



*700-800 °C



Conclusions

(1) In the case where rice husk ash was used to synthesize a V-ZrSiO₄ pigment, the best coloring was obtained when synthesis was carried out at 750 °C for 5 hours with the addition of 0.2 mol% of V₂O₅ and 0.5 mol% of NaF; the resulting color values were L^* 58.38, a^* -12.87 and b^* -10.63.

(2) The formation process of the pigment synthesis is as follows: From 500 °C to 700 °C, the temperature for an active reaction there is the initial step reaction caused by the phase transition of α -quartz \rightarrow β -cristobalite involving the reaction of V₂O₅ with NaF to produce the intermediate phase NaVO₃ and SiF₄. At the final step in the temperature range from 700 °C to 800 °C, zircon is synthesized as SiF₄ diffuses into the M-ZrO₂ lattice. As soon as it is produced, V^{4+} is incorporated into the mother crystal resulting in a turquoise blue coloring of the pigment.

(3) As for the valence of the vanadium ions in the synthesized pigment, the result of UV-Vis analysis showed the characteristic absorption bands of V^{4+} at 290 nm ($2B_1 \rightarrow 2A_1$) and 640 nm ($2B_1 \rightarrow 2E$).

(4) Based on the result of the Raman spectral analysis of the synthesized pigment, new assignments were made of the zircon internal modes at 1003, 971, 950, 625, 434, 389, 353, 219, 201 and 181 cm⁻¹ as well as the V-O vibration internal modes at 950, 912, 882, 498 and 473 cm⁻¹.

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