

Synthesis of a Zircon–Cadmium Sulfo Selenide Pigment by a Sol–Gel Technique

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Preparation of fire red cadmium sulfo- selenide pigments based on zircon via solid-state reactions encountered with some difficulties. Undesirable reactivity and inadequate homogeneity of components are two important problems, which counteracted on completely covering of color agents by zirconium silicate and so stable production of these materials. It has shown that by using a sol–gel method the above-mentioned problem will be eliminated and a desirable color shade can be obtained. In the sol–gel process, at first a precipitant was prepared by mixing of Se (dissolved in sodium sulfide solution) and a cadmium sulfate-zirconium acetate solution. Gelation was occurred by adding a diluted sodium silicate solution into the washed and dried precipitant. The mineralizer was lithium fluoride, which was added to the washed/dried gel. Calcinations of the later compound were done at about 950°C. The experiments showed that the relative volume of zircon to cadmium sulfo selenide has an important role on a complete encapsulation of colorants and so on quality of pigment. According to our experiment, the optimum relative volume of colorant agent to zircon was determined as about 40/60.

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1. Introduction

Fire-red pigments are synthesized by heating mixtures of cadmium and selenium precursors as low as 500–700°C.^{1)–3)} However, as these pigments are not enough stable during the gloss firing temperatures employed in the white ware ceramic industries, they can only be used as low firing temperature pigments in a third firing procedure.^{4)–7)} A known method for improving the stability of fire-red pigments at high temperature is encapsulating of its particles into a transparent zirconium silicate layer.⁸⁾ In the traditional method, the pigment ingredients, i.e. coloring agent, zirconia, silica, and mineralizer are mixed thoroughly and then are fired at 950–1100°C, followed by grinding and chemically removal of its by-products.^{9),10)} Pigments that produced by this way are not able to induce fully saturated colors in fired glazes.^{9),10)} It is believed that this is due to a low level of cadmium sulfo-selenide inclusions enclosed in the zirconium silicate crystals, and the residual un-reacted materials, i.e. silica, zirconia, unpigmented and poorly pigmented zirconium silicate crystals.

It is known that amorphous materials are more reactive than their crystalline ones. This comes from the fact that these materials have located at higher energetic state. Moreover, a part of incomplete reactions in the traditional method for synthesizing of pigments seems to be due to the lack of homogeneity of mixture. The product of chemical reaction routes is also relatively free from this problem. Therefore, it seems that the use of a more reactive material is necessary to overcome the solid-state reaction disadvantages and the sol–gel processing is the preferred route in this regard. This technique allows to produce a high purity, ultra fine particles and potentially more homogeneous powder, which interact at lower temperatures.^{2),3)} These benefits caused that the sol–gel processing became recently one of the main route for synthesizing of new inorganic pigments. According to the Badenes et al., sol–gel methods decrease 300°C the pigment formation temperature in relation to that of the ceramic route.¹¹⁾ Ricceri and co-workers have been prepared a blue pigment by doping Fe and Ti ions into the corundum lattice

through the sol–gel method.¹²⁾ Alarcon claimed that a high purity and non-agglomerated powders with controlled particle size of either undoped zircon or vanadium-containing zircon solid solution were observed to form by using the sol–gel procedure¹³⁾ and Estrada and his co-workers have synthesized a new vanadium cordierite pigment by this method.¹⁴⁾

2. Experimental

Table 1 shows the chemical compositions which were used in this work. The initial chemical composition which was used in this study was R₁. The materials which used were zirconium acetate (Yixing Xinxing Zirconium), a commercial grades of cadmium sulfate and selenium, sodium sulfide (Iran Sulfur), a sodium silicate solution (Merck 335513921) and a commercial grade lithium fluoride as mineralizer.

Figure 1 depicts the initial procedure, which adopted for synthesizing of zircon based cadmium sulfo-selenide pigment. Heat-treatment of the mixtures was done in an electric kiln, at a reducing atmosphere, prepared by burying of materials under a thin carbon powder layer, in a closed mouth crucible. The heating rate and soaking time at maximum temperature were 15°C/min and 30 min, respectively. The product was washed with a mixture of 50 vol% sulfuric acid and 50 vol% nitric acid solutions, followed by washing with water, 5 mol/l sodium hydroxide and finally rinsing with distilled water.

The morphology and chemical composition of the synthesized samples were evaluated by scanning electron microscopy (LEO 440I). X-ray diffractometry (Seifert-3003 PTS), with a scan rate of 0.05°/s was also utilized for determination of crystalline phases formed before and after calcinations. Simultaneous Thermal Analyzer instrument (Polymer Laboratories, STA-1640) at a heating rate of 17°C/min and under nitrogen atmosphere was used to evaluate the reaction temperatures, which probably occurred between pigment constituents. For determination of the hue of synthesized pigments, the UV Spectroscopy (VARIAN–Cary 500) was used. The mean particle size of precipitated powder was determined by a particle size analyzer (Malvern Instruments–300 HAS).

3. Results

Figure 2 shows the X-Ray Diffraction (XRD) analysis of

Table 1. Chemical Analysis of the Two Compositions (mass%)

	SiO ₂	ZrO ₂	Cd	S	Se
R1	23	10.85	33.6	24.6	7.7
R2	34.5	16.2	25	18.4	5.8

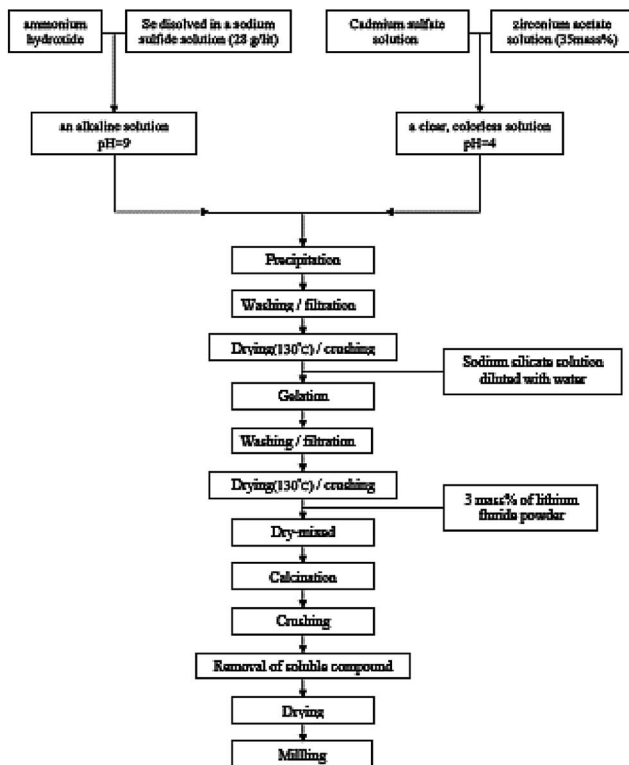


Fig. 1. Flow chart of synthesizing procedure for zircon-cadmium sulfo-selenide pigment.

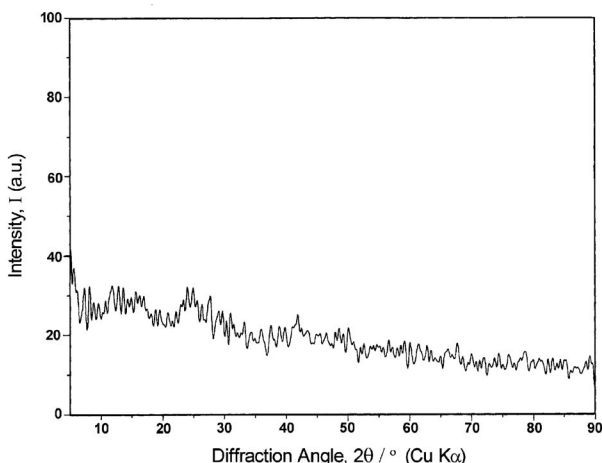
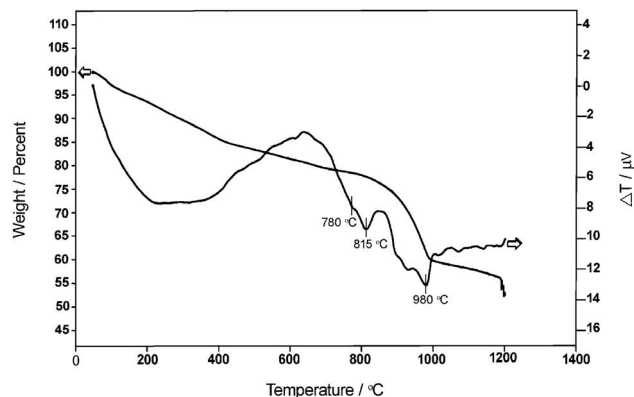
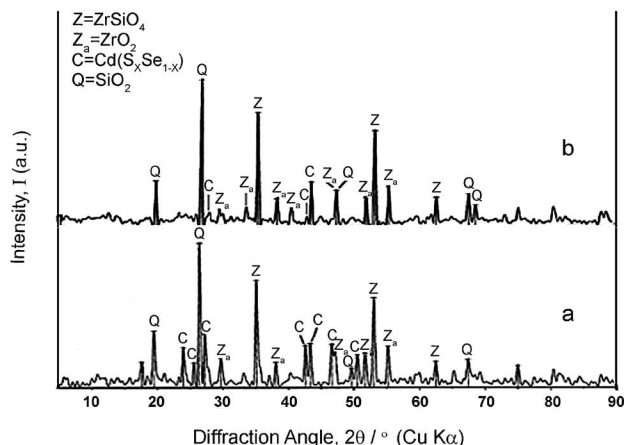
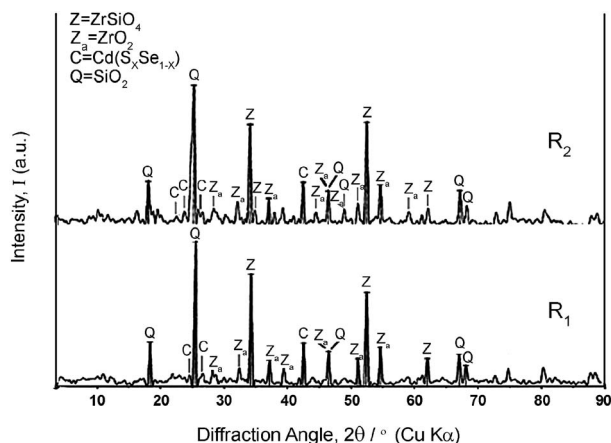
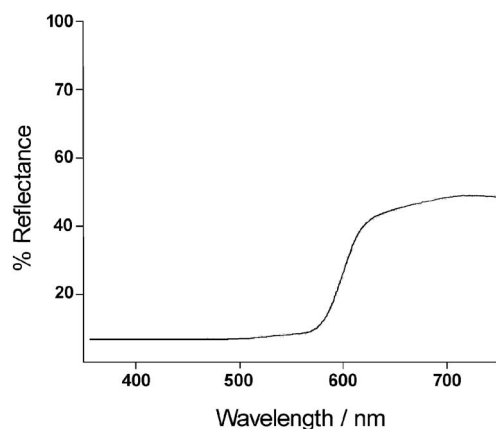
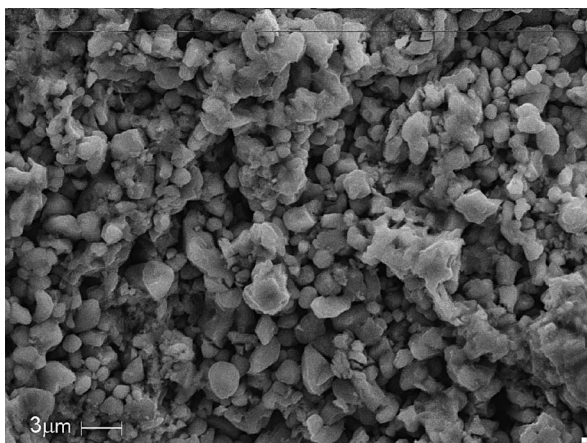


Fig. 2. X-ray diffraction of the amorphous powder obtained by a sol-gel technique.

the as received powder obtained by the above-mentioned procedure. As it can be seen, the powder is completely amorphous in point of XRD view. According to particle size analysis, the mean particle size of this powder was about 0.4 μm. It seems that the powder has been agglomerated during drying

Fig. 3. Simultaneous thermal analysis of sample R₁ in a nitrogen atmosphere.Fig. 4. X-ray diffraction of the pigment R₁, (a) before and (b) after washing.

procedure; however is yet finer than the product of normal milling procedures. **Figure 3** depicts the simultaneous thermal analysis of the amorphous powder. There are two main endothermic peaks at the Differential Thermal Analysis (DTA) and an abrupt mass reduction at about 900°C at the Thermo-Gravimetry (TG) graphs. **Figures 4** and **5** show the XRD patterns of powder R₁ and R₂ after firing at 1030°C for 30 min. Here the Fig. 4(a) and (b) letters indicate the washed and as-fired powders, respectively. According to these figures, in spite of different in intensity, the same kinds of crystalline phases of ZrO₂, quartz, zircon and Cd(S_xSe_{1-x}) have been precipitated in the two samples during firing. **Figure 6** shows the reflectance spectrum of the glaze surface containing 10 mass% of pigment R₂, fired at 1020°C in a fast firing schedule in an electric kiln. The heating rate up to maximum temperature was 34°C/min and the soaking time was 5 min. **Figures 7** and **8** depict the scanning electron microscope (SEM) micrographs of the synthesized compacted pigment powder R₂ and

Fig. 5. X-ray diffraction of the pigments R_1 and R_2 .Fig. 6. Reflectance spectra for glaze containing pigment R_2 .Fig. 7. Scanning electron photomicrographs of pigment R_2 .

microstructure of the matured wall tile glaze containing 10 mass% of it, respectively. **Figure 9** depicts the Energy Dispersive X-ray analysis (EDX) of a cluster of pigment constituents, which has been marked in the glaze (Fig. 8(b)).

4. Discussion

It is said that cadmium sulfo selenide forms at an interval

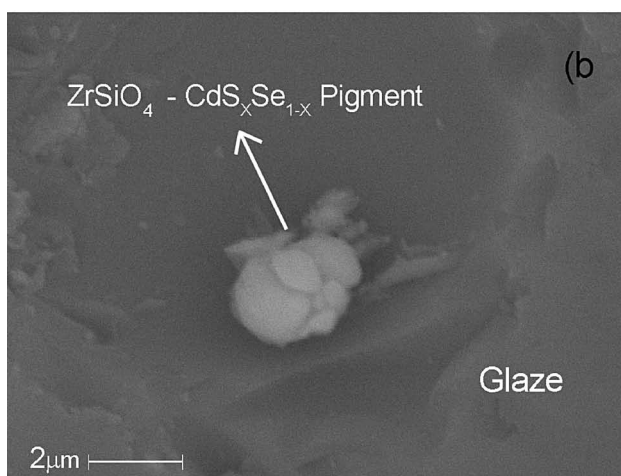
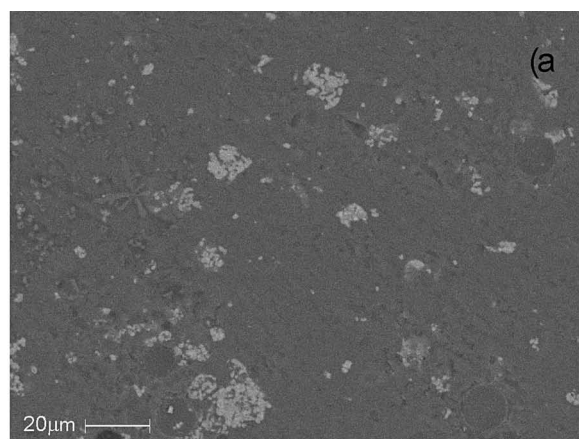
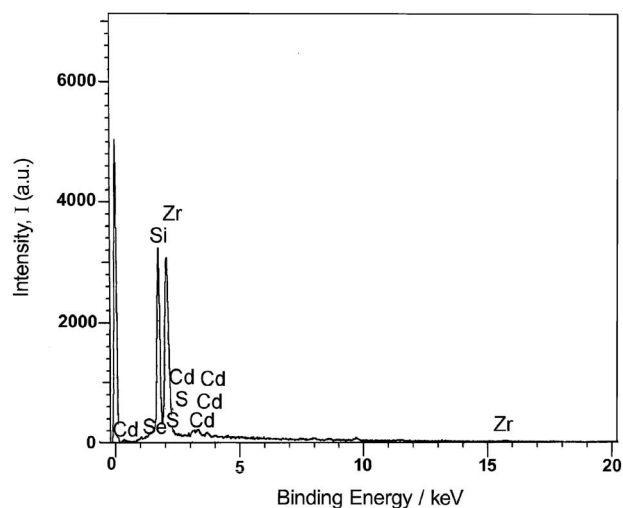
Fig. 8. Microstructure of the matured wall tile glaze containing 10 mass% of R_2 with two different magnifications, (a) $500\times$ and (b) $8000\times$.

Fig. 9. EDX analysis of a cluster of pigment particle in the fired glaze.

temperatures of $500\text{--}700^\circ\text{C}$.^{1),2)} Accordingly, it seems that the broad exothermic peak of the DTA traces, at the temperature interval of $400\text{--}780^\circ\text{C}$ which is associated with an obvious weight loss, is due to crystallization of a solid solution of Cd

(S_xSe_{1-x}) and also sublimation and dissociation of some of the ingredients. Ellison has measured the enthalpy of formation of zircon at 277 K.¹⁵⁾ According to him, the enthalpy of formation of zircon at this temperature is between 38.671–42.504 kJ/mol. As the endothermic peak at 815°C is not associated with an abruptly weight change, it is attributed to formation of zirconium silicate. The occurrence of other semi tooth-like endothermic peak at about 980°C should be due to melting of un-encapsulated pigment particles and/or perhaps formation of a glass phase by the later particles and residual silica, Na_2O , and F compounds, respectively. Melting is associated with increasing the rate of volatilization of the above-mentioned components, shows itself as a 29 mass% loss. According to these results, the firing temperature of the sol-gel yield should be kept lower than this temperature region and/or heat treatment should be done at least under a static atmospheric condition. Upon this, the synthesizing kept under a reduced and closed crucible that helped the firing temperature to be increased and ability to encapsulation of colorant to be improved. According to Fig. 4, a high amount of $Cd(S_xSe_{1-x})$ has removed away by washing the fired sample. This means that there had been remained a considerable amounts of unprotected cadmium sulfo-selenide after firing and the amounts of zirconium and silicon oxides would were lower than whatever was necessary for complete surrounding of $Cd(S_xSe_{1-x})$ inclusions. Therefore, increasing of zircon precursors, in comparison with cadmium sulfo-selenide constituents, was considered. This new composition has been shown as R_2 in Table 1.

Double fast firing wall tile glaze containing 10 mass% of this pigment, showed that R_2 bore a higher fire-red hue and more saturation than R_1 . According to our calculation, the volume part ratio of pigment inclusion to zircon in R_2 was about 41 to 59 while in R_1 it was completely inverse, i.e. 58 to 42, which means that in the former case there had been enough zircon particles to protect the colorants from decompose and/or oxidizing during firing. Figure 6 displayed that the maximum reflectance of the glaze surface happened at a wavelength of 625 nm, which is consistence with the red wavelength section of the spectrum.

According to Figs. 7 and 8, the particle sizes of the milled and dispersed particles in the matured glaze has been distributed between the order of sub microns up to several microns, means that the primary amorphous particles had been agglomerated and sintered during firing procedures. In spite of small dimension of the cluster, the EDX showed that a

substantial Cd, S, and Se have been encapsulated into zircon particles.

5. Conclusions

According to the results, the output of a sol-gel reaction of zircon based cadmium sulfo-selenide precursor was an amorphous powder. The optimum relative volume of colorant agent to zircon was determined as 41 to 59 that were more than whatever was predicted. Simultaneous thermal analysis of amorphous precipitated powder of pigment ingredients showed that the synthesizing of pigment should be done under a static condition to prevent from sublimation and volatilization of colorant agent from the system and to shift the synthesizing to higher temperature. This later parameter helps that encapsulation of colorant take places more suitably.

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