

Synthesis and Characterization of Red, Green and Blue Pigments for High Temperature Resistant

Yamin Ma

Pingdingshan University, Pingdingshan, Henan 467000, China
mayami_pdsu@126.com

Pigment is a kind of very important chemical raw material, non-toxic, stability of the pigment is a problem to be solved. This paper studied the synthesis and properties of red green and blue light non-toxic heat-resistant paint. In this paper we selected three systems were drilled blue (CoAl_2O_4) pigment, half red sulfide decorated $\gamma\text{-Ce}_2\text{S}_3$ and green ZnO-CoO pigment, these three kinds of high temperature resistant pigments can be used not only in the color fluorescent powder coloring, and all of them have very wide application fields for example, the potential applications are printing ink, rubber, ceramics, glass, art and other fields. At present, our country uses the upscale high temperature resistant pigment, for example uses in the phosphor powder screen uses the high temperature blue color pigment blue, basically depends on the import. We hope to be able to produce better quality and lower cost of blue pigment to replace imported products to achieve the localization of the production of the pigment, thereby further reducing economic costs and improve economic efficiency.

1. Introduction

There are many types of colors can be classified into red, orange, yellow, green, green, blue, purple, gray, white, black and other colors. They are not isolated, there exists a certain relationship between all kinds of color, a color can be made by three parameters, namely the hue, saturation and brightness. Microwave heating usually transforms the electromagnetic energy into heat energy by microwave dielectric effect (Ruan et al., 2004). Due to the fact that the dielectric materials are composed of polar molecules and nonpolar molecules, these polar molecules are shifted from the original random state to the polar orientation of the electric field under the action of electromagnetic field (Liu et al., 2016; Tong et al., 2016). Color hue is the difference between the characteristics, tone object determines the light spectral composition and surface reflection (or transmission) radiation at different wavelength ratio of human feeling, color reflects the relationship between color in terms of quality. Under the action of high frequency electromagnetic field, these orientations change according to the change of alternating electromagnetic field. At this time, the electromagnetic field energy can be transformed into the heat energy of the medium, so that the temperature of the medium is increased, which is the basic principle of microwave heating (Ma et al., 2013).

The big red pigment $\gamma\text{-Ce}_2\text{S}_3$ brightness is not enough, is also the pigment L^* value is not high enough, in the hope that the other performance of the same or increase the brightness of the pigment is approximately equal to the situation, make it more popular (Fouda et al., 2012). According to reports, the pigment in the air temperature resistance of only 350°C , this study hopes to further improve the thermal stability of the pigment in the air, broaden the scope of application of the pigment (wang et al., 2012). Green high temperature pigment ZnO-CoO synthesis, hope to use different methods to synthesize the green pigment. The synthetic pigment is more green and brighter than the ordinary synthetic pigment, which makes the color of the pigment more vivid and more popular (Maat, 2016; Xu et al., 2013; Sakhmetova et al., 2016).

Blue pigment blue high temperature drilling development the first problem to be solved is to develop drilling blue pigment synthesis method, a simple and only in this way, it is possible to achieve the industrial production of the pigment in the case of low cost (Fouad et al., 2012). The second is to solve the problem that the pigment raw material cost, and the cost of raw material is mainly caused by drilling, and drilling elements are widely believed to have certain harm to the environment, so how to reduce the pigment content in drilling elements into second problems to be solved. Once again, it is necessary to solve the problem of optical

properties, particle size and distribution of the pigment, and hope to be more excellent than the optical properties of the blue pigment imported from abroad (Huang et al, 2014; Giustetto et al, 2012; Liventsova et al, 2016).

2. Effect of boric acid on the synthesis of γ - Ce_2S_3 red pigment

2.1 Experimental process

Experimental reagent: $Ce(SO_4)_2$, CS_2 , H_3BO_3 , Na_2CO_3

Experimental procedure:

1) Accurately called $Ce(SO_4)_2$, Na_2CO_3 and boric acid. Mixing and grinding evenly in agate bowl. Specific formulas are listed in Table 1.

2) The raw material mixture into the porcelain boat, placed in a closed tube furnace.

3) Nitrogen into the reaction system of furnace tube out of the air, and then began to rise.

4) Warm up to 380 °C, convert N_2 atmosphere to $N_2 + CS_2$ atmosphere until the reaction is over.

Which V_{CS_2}/V_{N_2} is 0.1, the flow rate of 0.18 L/min, heating rate of 1.2 °C/min, heating up to 900 °C insulation 3h. Cool to room temperature.

5) After grinding, washing, filtering and drying, the product is A1 to A8.

Table 1. Component of mixture

No.	A1	A2	A3	A4	A5	A6	A7	A8
$Ce(SO_4)_2/g$	6.58	6.58	6.58	6.58	6.58	6.58	6.58	6.58
Na_2CO_3/g	0.112	0.112	0.112	0.112	0.112	0.112	0.112	0.112
H_3BO_3/g	0	0.11	0.21	0.31	0.41	0.51	0.61	0.71

2.2 Results and discussion

Using METTLER TOLEDO TGA thermal gravimetric and differential determination of reactant and product scanning calorimetry TG-DSC curve; by Rigaku D/max2500 X ray diffraction analyses were conducted on samples of phase and structure, test conditions: $20^\circ < 2\theta < 80^\circ$, CuK α radiation, pressure is 40kV, the current is 30mA; the size and morphology of Sirion type field scanning electron microscopy observation of particles, the voltage is 20kV; with South Korea DARSAPRO 5000 PSI reflectance measuring the reflectivity of the sample and color coordinates, determination wavelength is 380~780nm.

It can be seen from figure 1 that when the addition of boric acid is zero, there is a certain α - Ce_2S_3 . When the addition of 0.1 g of boric acid, the α - Ce_2S_3 in the sample disappeared, which was γ - Ce_2S_3 . It can be seen that boric acid and sodium carbonate can reduce the synthesis temperature of γ - Ce_2S_3 . When the amount of boric acid was increased to 0.4 g, a new phase $CeBO_3$ was formed, and finally, when the amount of boric acid was added to, it was not only $CeBO_3$, but also a new substance B_2S_3 .

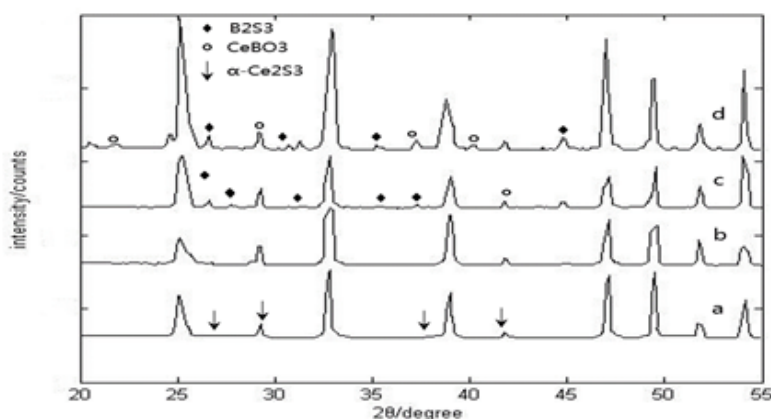


Figure 1: XRD patterns of samples

The samples of SEM images that changes with the addition of boric acid, the particle size of the sample size and morphology are essentially the same, showing irregular shaped or spherical structure, but with uniform particle size distribution, distribution range is about 0.5~2 μ m, the average particle size is about 1 μ m

3. Synthesis and characterization of green high temperature pigment ZnO–CoO

3.1 Experimental process

Based on the green pigment $Zn_{1-x}Co_xO$ formula, the precursor was prepared by co precipitation method, and the pigment was prepared by resistance heating and microwave heating. This paper mainly discusses the influence of the precipitating agent and heating method on the $Zn_{1-x}Co_xO$, the reflection properties and the color coordinates of $Zn_{1-x}Co_xO$.

Under the condition of 25 °C in NaOH, NH_3H_2O and $C_2H_2O_4$ the mixed precipitant solution is slowly added into $Co(NO_3)_6H_2O$ and $Zn(NO_3)_6H_2O$, NaOH and NH_3H_2O titration end point pH value of 8 to 8.5 HZeZo; titration end point pH value is 6, the precipitation in the vacuum filter. The filtrate drops of NaOH solution with 2mol/L, no precipitate, Co^{2+} ten and Zn^{2+} have been precipitated completely. The resulting precipitate was dried for 2 hours under the condition of 110 DEG C, and the precursor of the sample was obtained after the precipitation was completely dried. The precursor after grinding in a high-temperature furnace in 110 °C calcined at 1.5 hours, the samples obtained were recorded as A1~A6. The oxalic acid as precipitant samples were divided into two, one in a high-temperature furnace at the temperature of 1100 °C to 1.5 hours, another by microwave heating to 1100 °C, heat for 10 minutes, the samples were designated as B1~B6, as shown in table 2.

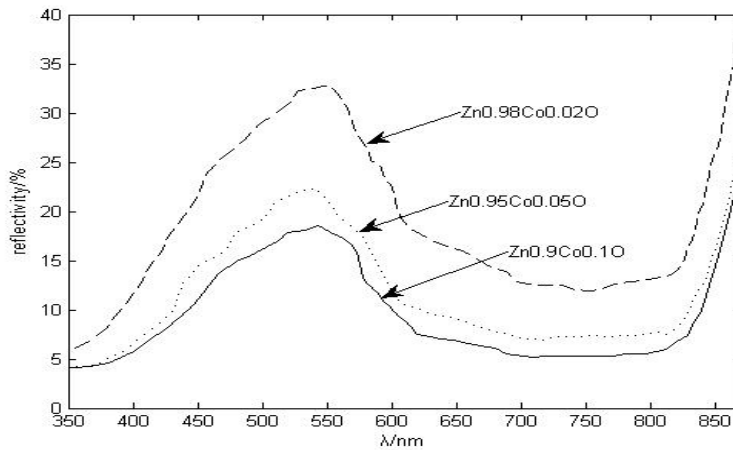
Table 2. Experiment design

Sample number	x/mol%CoO	Precipitating agent	Heating mode
A1	0.09	NaOH	Traditional heating
A2	0.04	NaOH	Traditional heating
A3	0.18	NaOH	Traditional heating
A4	0.09	NH_3H_2O	Traditional heating
A5	0.04	NH_3H_2O	Traditional heating
A6	0.02	NH_3H_2O	Traditional heating
B1	0.12	$H_2C_2O_2$	Traditional heating
B2	0.04	$H_2C_2O_2$	Traditional heating
B3	0.01	$H_2C_2O_2$	Traditional heating
B4	0.09	$H_2C_2O_2$	Traditional heating
B5	0.04	$H_2C_2O_2$	Traditional heating
B6	0.18	$H_2C_2O_2$	Traditional heating

3.2 Results and discussion

It can be seen from figure 2, along with the increase of Co^{2+} concentration, the diffraction peak position than pure ZnO to small angle Co^{2+} is only visible to the ZnO solid solution in the lattice, and the crystal lattice increases, but does not change the basic structure. The pigment completely keeps the basic configuration of ZnO crystal.

According to the reflectance spectra of the samples (Fig. 2), we can clearly see that with the increase of Co^{2+} concentration, the reflectance of green light and the red reflectance of 600 nm at the green 515 nm are gradually decreased. The sample L has the highest reflectivity at 515 nm, which is up to 51.32%, but the red reflectivity of the sample is too high and the color purity is only about 2.21, which is the lowest in the sample. The sample K has a high reflectivity at 44.12% 515 nm, but the color purity of the sample is not high, only about 2.61. However, the L^*a^*b value of the sample was 60, -32 and 8, the brightness of L' was about 55.21, and the a' value was a little brighter and more green than that of -32.54. The sample J is the most green in all samples, the a* value is 33.1, and the pigment has good color purity and brightness. Using oxalic acid as precipitant for the synthesis of pigment brightness and color purity is obviously better than sodium hydroxide and ammonia as precipitant of synthesized samples, so the oxalic acid is the best precipitant for preparing the pigment precursor. Compared with the traditional heating method, the microwave synthesis can obviously make the pigment brighter and greener.



(a) NaOH

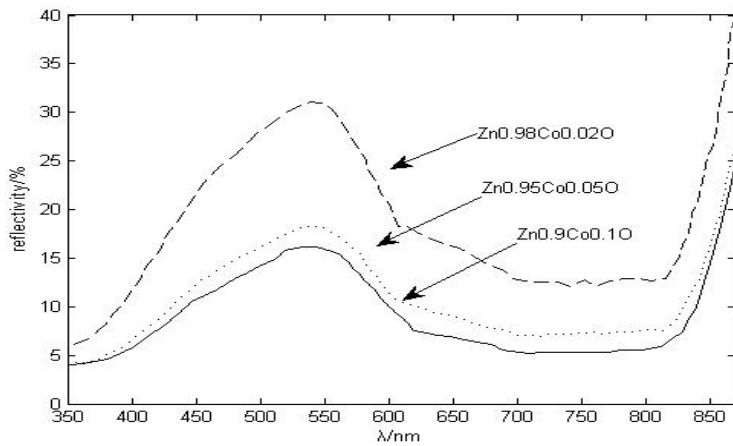
(b) $H_2C_2O_2$

Figure 2: Preparation of sample reflectance spectra

4. Synthesis and characterization of blue pigment blue

4.1 Experimental process

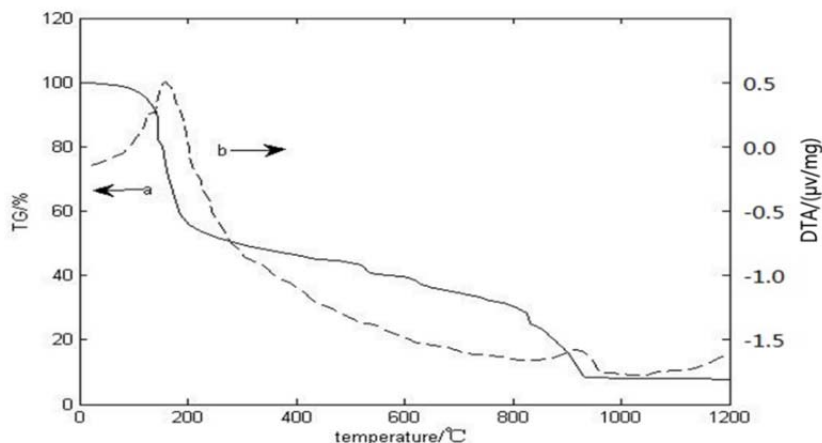
How to reduce the content of the elements in the pigment to make the pigment more economical and environmentally friendly become a trend in the development of blue pigment. However, for the requirements of application in reducing drilling elements must also improve the optical properties of pigment and color purity. Therefore, we hope to be able to prepare a composite reflective excellent blue pigment content of lower drill drill.

$Co(NO_3)_2 \cdot (6H_2O)$, $Al_2(SO_4)_3 \cdot 18H_2O$ and $MgSO_4 \cdot 7H_2O$, citric acid was added to the quality of the mixture of 4%, the use of anhydrous ethanol as grinding aids, mixing in the agate bowl grinding. The resulting mixture was dried at 115 °C for 1 hours, until completely dry samples after a high-temperature furnace 850 degrees burn 10 to 15 minutes, and then heated to 1100 DEG C to 100 minutes. The obtained products were obtained by grinding, washing, filtering and drying. The spinel blue powder was recorded as CA. In addition, the mixture of 1050°C, 1000°C and 950°C respectively under the condition of microwave radiation to 10 minutes, the heating time were 80 minutes, 72 minutes and 60 minutes, the microwave power is 200~1000W (with silicon carbide as microwave absorbent, alumina insulation materials), the samples were recorded as CB.

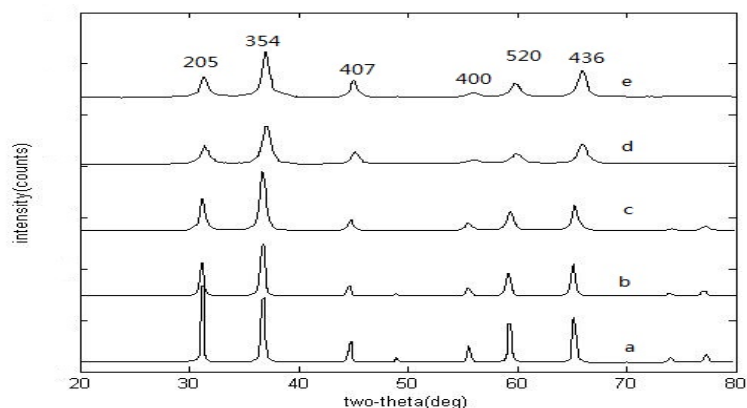
4.2 Results and discussion

The mixture has 3 distinct stages of weightlessness. From 10 °C to 250 °C, weight loss of about 40%, which is the main part of the mixture decomposition loss of crystal water and citric acid and nitrate; From 250 °C to 700 °C is lost $Al_2(SO_4)_3 \cdot 18H_2O$ in another part of the water of crystallization and decomposition of citric acid.

It is the decomposition of $\text{Al}_2(\text{SO}_4)_3$ from 700 °C to 820 °C. After 820 °C, there is almost no change in quality for the formation of blue diamond. Figure 3 showed that: 10 °C~250 °C for endothermic periods of intense, the only stage of citric acid combustion is an exothermic process, other reactions such as decomposition of the mixture and a part of crystal water nitrate is an endothermic process, because the quantity of citric acid is less, so the main performance for endothermic process. The stage of decomposition of aluminum, which is also endothermic process. After 820 °C, a stable exothermic peak appears in the process of the formation of the crystal and the phase transformation of the crystal.



(a) TG_DTA curves of sample CA-2



(b) XRD patterns of cobalt blue powders of series samples

Figure 3: TG_DTA curves of sample CA-2; XRD patterns of cobalt blue powders of series samples

5. Conclusion

This article mainly introduces the contents of the following 3 parts: effect of boric acid on the synthesis of $\gamma\text{-Ce}_2\text{S}_3$ red pigment and synthesis and characterization of green high temperature pigment as well as synthesis and characterization of blue pigment blue. The red pigment $\gamma\text{-Ce}_2\text{S}_3$ was synthesized by high temperature solid state reduction method with anhydrous sulfuric acid, sodium carbonate and boric acid as main raw materials in 800 °C CS_2+N_2 atmosphere. With different precipitants, using a series of green pigment $\text{Zn}_{1-x}\text{Co}_x\text{O}$ was synthesized by co precipitation method, which using oxalic acid as precipitant, the sample obtained by the color purity of the best, and the pigment particles are distributed evenly, the average particle size is about $20\mu\text{m}$. Although the blue pigment has a very low content of the drill, the reflectivity of red light is too high and the color purity is not ideal. In which the incorporation of a small amount of Mg^{2+} , which can reduce the reflection to red light and improve the color purity of the samples at 600nm, the samples in the color purity although less than the former, but because it has a lower content of drilling so as to make it more economical and environmental protection.

Reference

- Fouad O.A., Hassan A.M., El-Wahab H.A., 2012, ChemInform Abstract: Synthesis, Characterization and Application of Some Nanosized Mixed Metal Oxides as High Heat Resistant Pigments: Ca₂CuO₃, Ca₃Co₂O₆, and NiSb₂O₆, Journal of Alloys & Compounds, 537(41), 165-170. DOI: 10.1002/chin.201241013.
- Fouda M.F.R., Elkholy M.B., Moustafa S.A., 2012, Synthesis and Characterization of Nanosized Pigments. International Journal of Inorganic Chemistry. DOI: 10.1155/2012/989281.
- Giustetto R., Seenivasan K., Pellerej D., 2012, Spectroscopic characterization and photo/thermal resistance of a hybrid palygorskite/methyl red Mayan pigment, Microporous & Mesoporous Materials, 155(11), 167-176. DOI: 10.1016/j.micromeso.2012.01.024.
- Huang W., Feng L., Yan X., 2014, Characterization of a high-temperature resistant strain of *Pyropia yezoensis* and its pilot cultivation in mariculture farm, Journal of Fisheries of China. DOI: 10.1155/2012/989281.
- Liu S.G., Li Y.M., Wang Z.M., 2016, Enhanced high temperature oxidization resistance of silica coated γ -Ce₂S₃, red pigments. Applied Surface Science, 387, 1147-1153. DOI: 10.1016/j.apsusc.2016.07.046.
- Liventsova N.V., Egorova O.V., Liventsov S.N., Blank M.O., 2016, Present Chemical Production Simulator Model Validation Method, Chemical Engineering Transactions, 52, 229-234, DOI: 10.3303/CET1652039
- Ma K.C., Jiang Y.Q., Liu Y.J., 2013, Synthesis of methyl phenyl silicone resin and its application as high temperature resistant coatings, Xiandai Huagong/modern Chemical Industry, 33(4), 91-94+96. DOI: 10.1364/AO.56.002068.
- Maat C., 2016, Blanket for transfer of printing inks notably with nanometer-scale pigments, resistant to high temperatures, WO/2016/034811, DOI: 10.1038/nphoton.2016.157
- Ruan L.F., Yu Z.B., He W., 2004, Melanin pigment formation and increased UV resistance in *Bacillus thuringiensis* following high temperature induction, Systematic & Applied Microbiology, 27(3), 286-289. DOI: 10.1078/0723-2020-00265.
- Sakhmetova G., Brener A., Satayev M., Korabayeva K., 2016, On the Mesoscopic Model of Mass Transfer in Microporous Membranes, , Chemical Engineering Transactions, 53, 49-54, DOI: 10.3303/CET1653009
- Tong Y., Fu J., Chen Z. Synthesis, 2016, Characterization, and NIR Reflectance of Highly Dispersed NiTiO₃ and NiTiO₃/TiO₂ Composite Pigments, Journal of Nanomaterials, 2016(1-2), 1-6. DOI: 10.1155/2016/5464978.
- Wang H.Z., Yan X.H., Lin L.I., 2012, Selection and characterization of a high-temperature resistant strain of *porphyra yezoensis* ueda(BANGIALES,RHODOPHYTA), Oceanologia Et Limnologia Sinica, 43(2), 363-369. DOI: 10.1038/nphoton.2012.157
- Xu H., Yan Y., Qu L., 2013, Synthesis and characterization of blue-to-green electro phosphorescence emitter based on pyrazole iridium complexes, Dyes & Pigments, 99(1),67-73. DOI: 10.1016/j.dyepig.2013.04.022