Low temperature synthesis and performance investigation of co-doped (Cr, Co)–ZrSiO₄ ceramic pigments

Peng Li¹, Qiuhong Yang², Shaobo Zhang³

School of Materials Science and Engineering, Shanghai University, Shanghai, China

¹Corresponding author e-mail: yangqiuhong@shu.edu.cn, lipengshu26@163.com, zhangshaobo_1223@163.com

Abstract. In this paper, a green (Cr, Co)-codoped ZrSiO₄ pigment was successfully prepared with Li₂CO₃ as mineralizer via solid-state reaction method at low temperature. The samples were characterized by X-ray diffraction, thermogravimetry and differential scanning calorimeter analysis, respectively. The XRD results reveal that the Li₂CO₃ as mineralizer can promote the formation of ZrSiO₄ and decrease the synthesis temperature to 1000 °C that is 400–500 °C lower than the without mineralizer. The TG-DSC curve doped with Li₂CO₃ shows that zirconia and silica react to form zircon at 1000 °C. It is indicated that the Li₂CO₃ can reduce reaction activation energy and Si-O bond degree to promote zircon formation. After calcining at 1000 °C for 2h, the intensity of the colour in the samples varies from light green to dark green, depending on the co-doping content. The sample with 8mol% (Co, Cr) particles exhibit brilliant green ($a^* = -19.33$), the value of $a^*$ is almost as good as commercial pigments, which indicates it is a potential candidate for ceramic pigments application. More importantly, the preparation method has the advantages such as reduce color ion doping, simplicity of process, and can also be used for preparing other zircon-based high-temperature colorants.

1. Introduction

Zirconium silicate (ZrSiO₄), commonly called zircon, has attracted considerable interest from researchers due to its excellent chemical and thermal stability, high anti-corrosion, high tinctorial strength [1-3], which give a role in the applications of refractories, enamels and glazes [4-6]. The metal ions can be incorporated into zircon structures to synthesize colored materials, which are used as ceramic pigments [7]. Especially, in recent decades, the zircon-based ceramic pigments such as iron zircon(Fe₂O₃@ZrSiO₄) pink coral pigments [7], CdS₆Se₄-x@ZrSiO₄ red pigments [8], praseodymium zircon (Pr-ZrSiO₄) yellow pigments [9], vanadium zircon(V-ZrSiO₄) blue pigments [10], which have been widely investigated.

However, using zirconia and silica as raw materials, the synthesis temperature of ZrO₂ + SiO₂ → ZrSiO₄ is above 1500 °C which is too high to realize industrial production [11]. Therefore, it is especially important to reduce the synthesis temperature of ZrSiO₄. In fact, the various synthesis methods have been reported in the literature to prepare zircon in low temperature, such as hot press sintering [12], sol–gel method [13] and precipitation method [14] and so on. Nevertheless, the above methods are difficult to industrialize. These methods often use acids, or alkaline fluoride as...
mineralizer to reduce temperature of synthesis. Unfortunately, the toxic and harmful by-products are often produced during the actual preparation process, such as SO\(_2\), NO\(_x\) and SiF\(_4\) (SiO\(_2\)+4NaF→SiF\(_4\)+2Na\(_2\)O), which are harmful to the environment [15]. In addition, the by-product processing requires complicated operations and expensive equipment that is difficult to apply to industrial production. In contrast to this, the solid-state reaction method is a traditional ceramic preparation method with advantages in terms of easily available raw materials, convenient operation of production. According to the literature, Li\(_2\)CO\(_3\) is easily liquefied and can reduce the activation energy of the reaction. Thus, we choose Li\(_2\)CO\(_3\) as a mineralizer. Besides, in order to obtain a strong green color, the chromium content is up to 18%[16-18], which are difficult for industrial applications due to the high doping content. For our knowledge, there have been few reports that a small amount of (Cr, Co)-codoped particles to produce green pigments, indicating that reducing the amount of chromium to synthesize bright color is a very meaningful research direction.

In this work, the purpose was to synthesize ZrSiO\(_4\) at low temperature and explore the possible of mineralizer Li\(_2\)CO\(_3\) to reduce temperature. Besides, the phase structure transition in the synthesis of ZrSiO\(_4\) was analyzed. More importantly, the effects of co-doping (Cr, Co) content on the coloration of the pigments were systematically investigated.

2. Experimental procedure

2.1. Sample preparation

The samples were prepared via solid state reaction using nanopowders baddeleyite (m-ZrO\(_2\), 99 wt %), amorphous silica (SiO\(_2\), 99.5 wt%) (Shanghai Macklin Biochemical Co., Ltd., China), cobalt oxide (Co\(_2\)O\(_3\), 99 wt %), chrome oxide (Cr\(_2\)O\(_3\), 99 wt %) as raw materials, Li\(_2\)CO\(_3\) (98.5 wt %) was selected as mineralizer. The equimolar mixture of ZrO\(_2\)-SiO\(_2\) nanopowders doped with 0.5 wt% Li\(_2\)CO\(_3\) were milled in deionized water using planetary mill for 2 h, and dried at 110 °C in air. A series of different components with x mol% (Co, Cr) (x=0.5, 1, 2, 4, 8) powder were fully grinded evenly. Subsequently, the samples were sintered at 800-1100 °C for 2 h in air, respectively. The temperature increase rates were about 5 °C per minute.

2.2. Characterization

The phase structures of the samples were characterized by the model D/Max-2200 X-ray diffractometer (XRD, Rigaku Co., Ltd. Japan). The thermogravimetry and differential scanning calorimeter (TG-DSC) analysis of the samples were carried out by a NetzschSTA449/C differential scanning calorimeter (Netzsch Instruments Ltd., Germany) in air with a temperature increasing rate of 10 K/min. The reflectance curves were measured in the wavelength range of 400-780nm, and L*, a*, b* parameters (CIELab) of the samples were obtained from a model UH4150 UV/VIS/NIR spectrophotometer (Hitachi High-tech Science Co. Ltd., Japan). In this system, L* is the color lightness (from black L*=0 to white L*=100), a* is the green (-a*)/red (+a*) axis, and b* is the blue (-b*)/yellow (+b*) axis, respectively.

3. Results and discussion

3.1. TG-DSC curve analysis

In order to understand the mineralizer influence of Li\(_2\)CO\(_3\) on the ZrSiO\(_4\) synthesis, the TG–DSC curves of equimolar ZrO\(_2\)-SiO\(_2\) nanopowders mixture adding 0.5wt% Li\(_2\)CO\(_3\) were measured from room temperature to 1000 °C. As shown in Fig.1, the TG curve shows two stages of weight loss. The first one of 2.1% weight loss is from room temperature to 194 °C, which is attributed to the evaporation of water from raw materials and accordance with the endothermic peaks at 194 °C in DSC curve. The second stage from 194 °C to 1000 °C is associated with the synthesis of ZrSiO\(_4\) [19]. At 416 °C and 468.8 °C, the DSC curve shows exothermic peaks attributed to the crystallization of amorphous silica [20]. The Fenner has used crystalline phase diagrams to demonstrate the
The weakly endothermic peaks at 560 °C can be attributed to the structural changes of SiO₂, which illustrates the trend of reduce the bonding degree of the Si-O bond requires absorption of heat [22]. Since the m-ZrO₂ is converted to the t-ZrO₂, it exhibits an endothermic peak at 783 °C. The thermal reaction proves ZrO₂ + SiO₂ → ZrSiO₄ at 950 °C. In addition, according to compare with the DSC curve of ZrO₂-SiO₂ nanopowder mixtures in our previous work [23], adding mineralizer Li₂CO₃ can effectively accelerate the movement and break of Si-O bonds, which can further facilitate the synthesis of zircon.

**Fig. 1.** TG–DSC curves of ZrO₂-SiO₂ nanopowder mixtures with 0.5wt% Li₂CO₃.

### 3.2. X-Ray difraction characterization

**Fig. 2.** XRD patterns of ZrO₂–SiO₂ nanopowders (a) undoped mineralizer, (b) doped with 0.5wt% Li₂CO₃ sintered at different temperatures for 2 h.

Fig. 2 reports the comparison between the X-ray patterns of (a) undoped mineralizer, (b) doped with 0.5wt% Li₂CO₃. As shown in Fig. 2(a), at 1200 °C the sample is mainly m-ZrO₂ and small amount of t-ZrO₂, it is indicated that the m-ZrO₂ phase starts to react to t-ZrO₂. As the sintering temperature increases to 1300 °C, a trace of SiO₂ can be found, which indicates that amorphous silica is transformed into crystalline phase. Especially, the peak intensity of t-ZrO₂ is weakened compared with 1200 °C, which is due to the formation of ZrSiO₄ can be accelerated by the reconstructive phase
transition m-ZrO₂→t-ZrO₂ owing to Hedvall effect [24, 25]. It could be seen that ZrSiO₄ is near completely synthesized until the sintering temperature reaches 1400-1500 °C, which shows a high degree of crystallinity. However, the ZrSiO₄ is formed at high temperature of 1400-1500 °C, which increases the cost of preparation and was not conducive to industrial production and application. Therefore, it is critically important to synthesize ZrSiO₄ at a lower temperature.

Fig. 2(b) shows the XRD patterns of the doped with 0.5wt% Li₂CO₃ calcined at 800, 900, 1000 and 1100°C for 2 h, respectively. At 800°C, the sample was single phase m-ZrO₂ without any secondary phase can be detected, indicating that the reaction has not begun. When sintered at 900 °C, the new phase SiO₂ was observed which verified the reaction between ZrO₂ and SiO₂ around 900 °C in Fig. 1. At 1000 °C, ZrSiO₄ has been almost completely synthesized. The temperature rises to 1100 °C, and XRD has almost no change compared with 1000 °C, indicating that was complete synthesis of ZrSiO₄ at 1000 °C, which is 400–500 °C lower than the without mineralizer. The intensity of ZrSiO₄ diffraction peaks is enhanced relatively in the range of 800-1000 °C, which is in good agreement with the TG-DSC analysis in Fig. 1. As a result, after adding 0.5wt% Li₂CO₃, the synthesis temperature of ZrSiO₄ can be significantly decreased to 1000 °C, indicating that Li₂CO₃ is a useful mineralizer to prepare zircon at low temperature. Besides, the method used in this work is convenient, safe and free of byproducts.

3.3. Colour properties analysis of ceramic pigments

Fig. 3. Photographs (down) and their CIELab color (up) for different (Co, Cr)-doped concentration at 1000 °C.

Fig. 4. Reflectance spectra of (Co, Cr)-doped ZrSiO₄ ceramic pigment with x mol% (x=0.5, 1, 2, 4, 8) at 1000 °C.
Table 1. L*, a* and b* parameters of (Co, Cr)-doped ZrSiO4 ceramic pigment with x mol% (x=0.5, 1, 2, 4, 8) at 1000 °C.

| Samples          | L*   | a*   | b*   | Reference  |
|------------------|------|------|------|------------|
| 0.5mol%          | 87.63| -3.21| 0.86 |            |
| 1mol%            | 85.01| -4.82| -1.03|            |
| 2mol%            | 71.54| -6.56| -1.42| This paper |
| 4mol%            | 67.03| -10.18| -3.64|            |
| 8mol%            | 48.61| -19.28| -3.93|            |
| literature       | 50.80| -18.71| 20.23| [26]       |
| commercial       | 51.06| -17.28| 18.92|            |

According to the Cr/Co molar ratio of 3:1, a series of (Co, Cr)-doped ZrSiO4 ceramic pigments with different contents were studied. The photographs (down) of the prepared (Co, Cr)-doped ZrSiO4 with different concentration are shown in Fig. 3, together with their diffuse reflectance demonstrated in Fig. 4. In Fig. 3, the coloring of pigments became deeper as the increasing amount of co-doping content, the color changed from yellow-green to bottle green and a series of different color ceramic pigments are synthesized. Thus, any colour in the range from light yellow-green to dark green can be tailored by proper adjustment of the co-doping content. As shown in Fig. 4, with increasing co-doping content, the proportional decline in reflectivity, which can be ascribed to the increasing absorption of light caused by the higher amount of ceramic chromophores, presenting a progressively deeper color in samples.

In Table 1, the CIElab values of the calcined ceramics pigment are reported. In particular, a* parameter, which indicates the predominance of the green colour (negative values) on the red colour (positive values), is the most representative value of this pigment. The table shows that a* parameter decreases as the increase of the co-doping content. For the sake of comparison, Table 1 also reports the L*, a* and b* parameters of commercial green pigments and the literature pigments [26]. As can be seen from these data, it can be obviously observed the value of a* in 8mol% is almost as good as commercial and literature pigments, indicating that the pigments is successfully prepared a new green (Co, Cr)-doped ZrSiO4 ceramic pigment at low temperature via solid-state reaction method. It's especially important to mention that commercial and literature pigments require complex equipment and more doping content. The method used in this work exhibits many advantages that being free of volatile phases, simplicity of process, reduce color ion doping, indicating a more meaningful method to synthesize ZrSiO4-based ceramic pigment.

4. Conclusion
In this paper, a green (Co, Cr)-doped ZrSiO4 ceramic pigment with Li2CO3 as mineralizer was prepared via solid-state reaction method at low temperature. The XRD and TG-DSC results indicate that the Li2CO3 is an efficient mineralizer in reducing the crystallization temperature, destroying the Si-O bond binding energy, and accelerating the progress of the synthesis of zircon. The synthesis temperature of ZrSiO4 has been decreased to 1000 °C that is lower than 1400–1500 °C in literatures. The successful synthesis of ZrSiO4 by solid phase at 1000 °C is difficult and has not been found in other literature, indicating that this work is a significant innovation. The photographs, CIELab L*, a*, b* value and reflectance spectra of (Co, Cr)-ZrSiO4 pigments display the color changing from light yellow-green to dark green by adjustment of the co-doping content. After calcining at 1000 °C in air, a brilliant green (Co, Cr)-doped ZrSiO4 ceramic pigment is obtained at x=8mol% and its CIE coordination is a*-19.33. What's more, the value of a* is almost as good as commercial pigments, but with fewer coloring particles, which indicates that it is a potential decorating material for practical enamels and ceramic pigment applications. Besides, the preparation method is rapid, simplicity of process and is expected to be in large-scale industrial production.
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