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Short communication

Synthesis of $Y(Al,Cr)O_3$ red pigments by co-precipitation method and their interactions with glazes

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Abstract

New red pigment based on the system $YAl_{1-y}Cr_yO_3$ ($y = 0.01$–0.1) was synthesized by co-precipitation method. The precipitant was attained by mixing solutions of yttrium, aluminum and chromium nitrates, respectively, and addition of ammonia as the precipitator. The effects of chromium as dopant and glaze composition on the color shade of resulting pigments were studied. EDX analysis of the prepared pigment particles, which was embedded in glaze, showed the occurrence of reactions between some glaze constituents and pigment particles. Accordingly, a glaze which was enriched in Al_2O_3 and poor in ZnO was more suitable in point of achieving a reddish shade. The resulting pigments were characterized by using X-ray diffraction (XRD), SEM and UV–vis spectrophotometer.

Keywords: Perovskite; Ceramic pigment; Yttrium aluminate; Co-precipitation

1. Introduction

Nowadays there is an interest for developing more stable red pigments in the ceramic industry. Therefore, new host structure and new synthesizing methods, involving less toxic materials, can be profitable in this regard. The perovskite structure, which exhibits great thermal stability and chemical resistance [1–4] can be considered for this purpose. In a perovskite structure like $YAlO_3$, substitution of Al^{3+} by some Cr^{3+} ions can change the initial colorless structure to a red color one, depending on the extent of substitution [1,2].

On the other hand, it is well recognized that wet-chemical processing of a multi-cation system provides advantages like more chemical homogeneity and reactivity of the product. Various wet-chemical methods have been developed and successfully used in these years for low temperature production of pure powders. These methods include sol–gel processing, hydroxide co-precipitation, glycothermal treatment, spray pyrolysis and combustion synthesis. Among them, co-precipitation seems to be relatively easy and economical route [5–8]. Therefore, a reddish chromium doped $YAlO_3$-based pigment was synthesized by the co-precipitation method. In this way, the effect of the chromium amount on the pigment redness (a^*) and the interaction between pigment particles and glaze composition during glaze firing were investigated.

2. Experimental

2.1. Starting materials and methods

The materials, which were used were reagent grade chemicals consisted of yttrium oxide (Y_2O_3, 99.99% pure), aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$, 99.9% pure), chromium nitrate ($Cr(NO_3)_3{\cdot}9H_2O$, 99.9%), NaF, $MgF_2$and Li_2CO_3. The three later materials were used as mineralizer [1,2,9,10], with a weight ratio of 3NaF, $2MgF_2$, $1Li_2CO_3$.

The pigments were prepared according to a $YAl_{1-y}Cr_yO_3$ stoichiometry, in which y was changed between 0.01 and 0.1. At first, a solution of $Y(NO_3)_3$ was prepared by dissolving Y_2O_3 in hot diluted nitric acid. In order to prepare a homogeneous solution of pigment ingredients, the resulted solution was then mixed with appropriate amounts of aqueous solutions of aluminum and chromium nitrates. Gradually addition of a 25% ammonia to the resulting solution led to its instability at pH of

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9. Aging of the instable solution was done by stirring for 24 h. The product was then filtered and rinsed with distilled water. The resulted material was dried at 100 °C for 24 h.

The samples were prepared by mixing of above-mentioned derived powder with the selected mineralizers, in an agate mortar. Heat treatment was done in an electric furnace at 1400 °C for 4 h. The heating rate was 10 °C/min and the samples were left to cool freely in the furnace. The stability and chemical resistance of the resulting samples were investigated by addition of 5 wt% pigments to different transparent glazes. The resulted glazes were then applied on suitable ceramic bodies and were fired at 1080 °C and 1200 °C, according to fast-firing schedules.

2.2. Characterization techniques

The crystallinity of the fired samples was determined by an X-ray diffractometer (Simense, D500) equipped with a copper cathode. The measurements were performed in a 2θ interval of 20–45° with scanning step of 0.02° and detecting time constant of 1 s in each step. The colorimetry spectra of the fired glazes were obtained by a UV–vis spectrophotometer (EYE 7000A, Gretamacbeth) using D_{65} illuminant. The CIE Lab chromatic coordinates were calculated from reflectance spectra. The morphology of synthesized pigments and their chemical resistance in the glaze matrix were characterized using a scanning electron microscope (Stereoscan S360), coupled with an energy dispersive X-ray spectrometer.

3. Results and discussion

3.1. Effect of mineralizers on developing of perovskite ($YAlO_3$) structure

Fig. 1 shows the XRD patterns of mineralizers bearing and mineralizers-free $YAlO_3$ samples, after firing at 1400 °C for 2 h. Accordingly, in spite of the mineralizer bearing sample, which shows only perovskite, the other sample demonstrates an undesirable tetragonal phase ($Y_3Al_5O_{12}$). It seems the mineralizers provide a liquid phase (2) which enhances the diffusion rates of pigment ingredients during initial steps of heating procedure, hereby promotes crystal growth of the desirable $YAlO_3$ crystals.

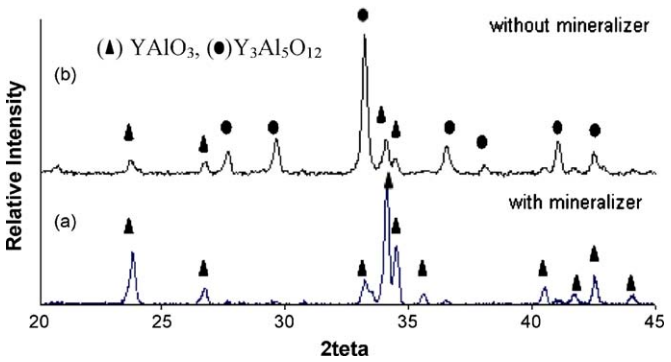

Fig. 1. XRD pattern of $YAlO_3$ sample (a) mineralizer containing and (b) mineralizer-free, after firing at 1400 °C for 2 h.

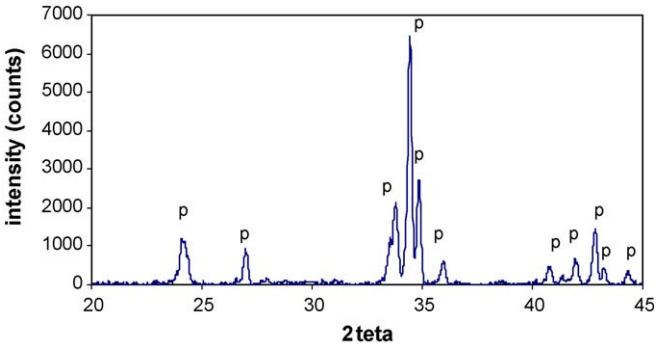

Fig. 2. XRD pattern of sample $YAl_{0.97}Cr_{0.03}O_3$ with mineralizer after firing at 1400 °C for 4 h.

3.2. Effect of chromium on developing of perovskite based red pigment

Fig. 2 depicts the XRD pattern of a fired composition based on $YAl_{0.97}Cr_{0.03}O_3$ and the added mineralizers. According to this figure, perovskite was again the sole crystalline phase which was formed in the sample. This means that the selected compound has been suitable for formation of a perovskite based structure.

Fig. 3a and b shows the morphology and EDX analysis of this pigment, respectively. The latter result confirms relatively the solution of Cr ion into the perovskite structure.

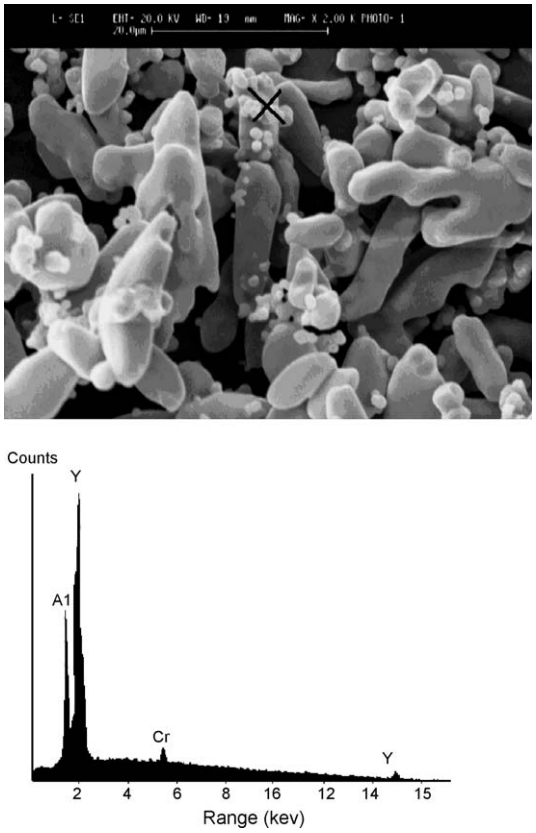

Fig. 3. (a) SEM micrograph and (b) the EDX analysis of the sample $YAl_{0.97}Cr_{0.03}O_3$ after firing at 1400 °C for 4 h.

Table 1
The composition of glazes, their firing temperature and the color shade of resulting glazes.

Composition (wt%)	SiO_2	Al_2O_3	ZnO	CaO	Na_2O	K_2O	PbO	B_2O_3	ZrO_2	Firing temp. (°C)	Resulting color shade
A	57	3	15	16	1	3	5	–	–	1080	Pink
B	55	12	2	6	7	8	2	7	1	1080	Red
C	57	15	1	6	6	8	-	6	1	1200	Red

3.3. Interactions between pigment particles and the transparent glazes

In order to find out the probable interactions between pigment particles and the glazes, 5 wt% of the above-mentioned pigment was introduced in three different glazes. The composition of glazes, their firing temperature and the resulted color shade have been shown in Table 1.

It can be seen that the glaze composition affect the color shade of the synthesized pigment. Fig. 4a and b shows an embedded pigment particle in the glaze A and its line scan analysis based on the Y, Al, Cr, Si, Zn and Ca elements, respectively. According to the line scan profiles, while the concentration of Y, Al, Cr and Si change predictably along the particle length, that of Zn and Ca show different unexpected profiles. The two later profiles indicate that probably some reactions have been occurred between glassy matrix and the pigment particle at their interfaces. This event led likely to undesirable compounds like $ZnAl_2O_4$ and/or $CaAl_2O_4$ and increasing of Zn and Ca amounts in pigment particle and especially glass-particle interfaces. These events can consume some of pigment components and so change the color shade of the resulted glaze. Using of the pigment in the glazes B and C was confirmed the above-mentioned explanation (Table 1). It can be concluded that the mentioned reactions were canceled with reducing of ZnO and CaO and enhancement of Al_2O_3 in the glaze, even when the firing temperature of glaze was increased to 1200 °C (glaze C). These observations are compatible with the fact that the solubility of a solid into a corrosive glassy phase is a function of differences in concentration of their components. The tendency of glaze for solving of pigment will be lower if these differences become lower.

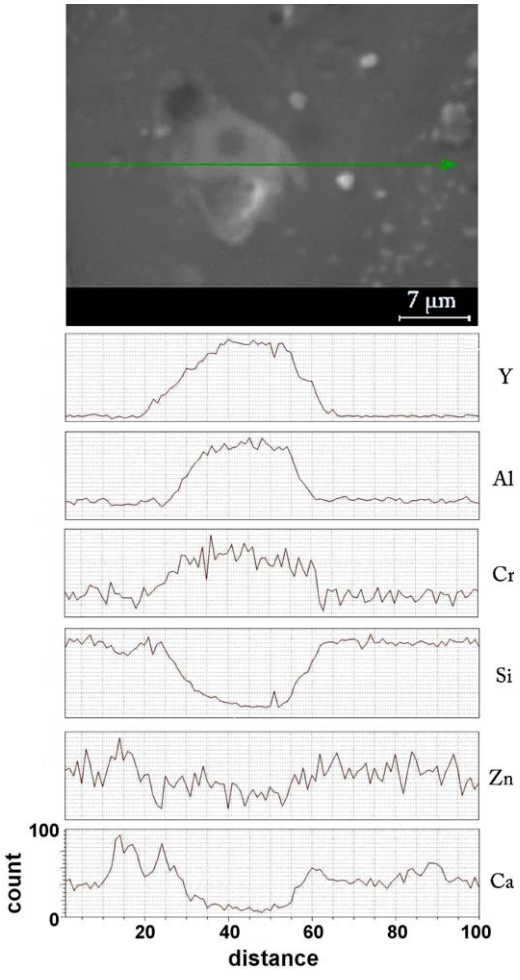

Fig. 4. Back scattered SEM image and line scan analysis of elements in the pigment crystals embedded in the glaze A after fast firing at 1080 °C.

3.4. Colorimetry

The effect of Cr content on the thermal stability and colorimetry, i.e. L^*, a^*, b^* values, of synthesized pigment was evaluated by addition 5 wt% of pigments (with different chromium content of 0.01–0.1) in frit B. The results have been tabulated according to Table 2.

As it can be seen the highest red component, i.e. a^*, belongs to $YAl_{0.97}Cr_{0.03}O_3$ sample.

Fig. 5 depicts the absorption spectra of the mentioned glazes.

As can be observed, the absorption values are smaller considerably at the wavelength lower than 580 nm. Furthermore, the results show that when y is equal to 0.03 the highest red shade obtained.

Table 2
The effect of Cr content on the color properties of $YAl_{1-y}Cr_yO_3$ pigments, when added in glaze B and fast fired at 1080 °C.

Formula	Pigments applied in frit B		
	L^*	a^*	b^*
$YAl_{0.99}Cr_{0.01}O_3$	57.175	27.583	26.463
$YAl_{0.97}Cr_{0.03}O_3$	40.669	30.024	23.928
$YAl_{0.95}Cr_{0.05}O_3$	40.601	23.278	20.292
$YAl_{0.94}Cr_{0.06}O_3$	41.287	27.259	18.394
$YAl_{0.9}Cr_{0.1}O_3$	50.971	21.229	21.576

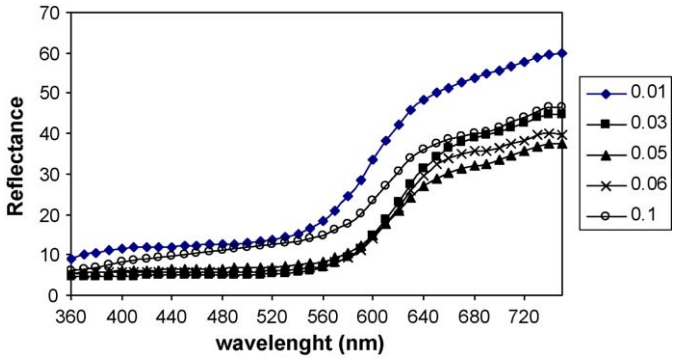

Fig. 5. Absorption spectra of the glaze B containing 5 wt% of various pigments, after fast firing at 1080 °C.

Table 3
CIE Lab chromatic coordinates of $YAl_{0.97}Cr_{0.03}O_3$ pigment used in glaze C and fast fired at 1080 °C.

Formula	L^*	a^*	b^*
$YAl_{0.097}Cr_{0.03}O_3$	35.968	25.113	16.26

By using of $YAl_{0.97}Cr_{0.03}O_3$ in the high temperature glaze C, the a^* value did not change, demonstrating it high thermal stability of the synthesized pigment (Table 3).

4. Conclusions

A red pigment based on $Y(Al,Cr)O_3$ perovskite structure was synthesized. The results showed that the presence of a mixture of mineralizers containing 3NaF, $2MgF_2$ and $1Li_2CO_3$ was necessary for preparation of a desirable pigment. By using this mixture, perovskite was merely formed as at 1400 °C. The work also showed that the glaze composition had a significant effect on the color shade of pigment bearing glazes. Accordingly, higher amounts of Al_2O_3 and lower amounts of ZnO and CaO are suitable for obtaining a desirable color shade. A satisfactory redness value (a^*) was observed when chromium content (y) was 0.03.

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