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Synthesis and study of a new class of red pigments based on perovskite $YAlO_3$ structure

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Abstract

A red pigment has been prepared by substituting chromium ions in aluminum ion sites in $YAlO_3$ perovskite structure. In a first step, effect of various mineralizers on $YAlO_3$ formation has been investigated, which resulted in decrease of formation temperature down to 1400 °C. In the next step, a red pigment corresponding to $YAl_{1-y}Cr_yO_3$ ($y = 0.05$), has been prepared by heating a mixture containing Y_2O_3, Al_2O_3 and Cr_2O_3 at 1500 °C for 6 h. Later, effect of the doped chromium amount on the pigment redness (a^*) has been studied. The highest redness has been obtained when y was $0.04(YAl_{1-y}Cr_yO_3)$. Application of the prepared red pigment in low and high temperature glazes, demonstrated its high chemical and thermal stability.

Keywords: Red pigment; Perovskite; Yttrium aluminate; Chromium(III) oxide

1. Introduction

The economic conditions of the last decade have dictated two main directions for pigment product development:

- Economization of existing pigment manufacture, with consideration price competition.
- Discovery and development of new inorganic pigments with higher performing characteristics.

Also a third development started earlier, driven by national laws and regulations in the ecological and toxicological area, about replacement of inorganic pigments, such as red lead, lead molybdate, and chrome orange, by ‘‘environmentally friendly’’ or less toxic substances [1]. Therefore the search for new ceramic pigments is now a high-priority field in the ceramics industry. In this sense, the obtaining of new red-shade ceramic pigments is necessity, because of the scarce variety of existing ones and the limitation imposed on their use by the current technological and environmental requirements [2].

One way to obtaining red hue is intensification of the crystal field of the chromium(III) ion when it substitutes for aluminum(III), in the corundum structure [3].

Red development in $YAlO_3$ structure with chromium(III) as dopants is similar to ruby, this similarity is due to the octahedral spaces of six oxygen ions in $YAlO_3$ structure, therefore this system is suitable to produce red pigment with low toxicity, a great thermal stability and chemical resistance [4–6].

On the other hand, solid state reactions between oxides (Al_2O_3 and Y_2O_3) take place with great difficulty and need to reach high temperatures (above 1800 °C), consequently it is necessary to add additives in small amounts for favoring the interdiffusion process, these additives are known as mineralizers [7].

In this paper, effects of different mineralizers and Cr^{3+} ions on synthesis of perovskite $YAlO_3$ and its solid solutions have been investigated.

2. Experimental

2.1. Starting materials and procedures

The starting materials used for the synthesis were yttrium oxide (Y_2O_3, 99.9% pure, Merck, Germany), aluminum oxide

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Table 1
Prepared compositions and their references

Composition	Reference
$YAlO_3$	P_1
$YAl_{0.97}Cr_{0.03}O_3$	P_2
$YAl_{0.96}Cr_{0.04}O_3$	P_3
$YAl_{0.95}Cr_{0.05}O_3$	P_4
$YAl_{0.94}Cr_{0.06}O_3$	P_5

(Al_2O_3, 99.9% pure, Merck, Germany) and chromium(III) oxide (Cr_2O_3, 99.9% pure, Merck, Germany). To prepare the samples stoichiometric mixture of the reactants homogenized in a planetary ball-mill (FRITSCH-Pulverisette 5, Germany), using agate vessels and acetone as dispersing media. The dried mixtures were homogenized with selected mineralizers in a planetary ball mill, and then heated in an electric furnace. The maximum temperature was 1300–1500 °C, reached with a heating rate of 10 °C/min. The maximum temperature was retained for 6 h, and the samples were left to cool freely in furnace. The calcined samples were ground up to an average size of about 8 μm.

The prepared nominal compositions and their references used in present study are shown in Table 1.

Another study was conducted on the effect of some mineralizers on formation of perovskite structure. The mineralizer systems used for the present study are presented in Table 2. These mineralizer systems were always added in a fixed quantity of 6 wt.%.

In the next step, effect of Cr_2O_3 content (as colorant agent) on redness of $YAl_{1-y}Cr_yO_3$ pigments was investigated by adding various amounts of Cr_2O_3 ($y = 0.03$, 0.04, 0.05 and 0.06).

Finally, to evaluate stability of the synthesized pigments, 5 wt.% of them were introduced in two industrial glazes: one transparent glaze for wall tiles at 1050 °C and another transparent one for sanitary ware at 1170 °C. The mixtures were milled in distilled water media for 30 min and applied on the surface of the ceramic supports using an air brusher (an instrument to spray glaze on the surface of tiles).

2.2. Characterization techniques

For the structural characterization of the synthesized materials, an X-ray diffractometer Philips Xpert MPD, equipped with a copper cathode was used. The measurements were performed in 2θ interval of 20–60° with measuring step of 0.02° and detecting time constant of 1s in each step.

Table 2
Mineralizer systems with their references

Mineralizer system/weight portion	Reference
NaF	M_1
MgF_2	M_2
NaF:MgF_2 (3.2:2)	M_3
NaF:MgF_2:Li_2CO_3 (3:2:1)	M_4

Optical absorption spectra in the visible range were obtained by an UV–vis spectrophotometer (EYE 7000A, Gretamacbeth) using D_{65} illuminant. The CIE Lab chromatic coordinates were calculated from the reflectance spectra.

Synthesized materials were characterized microstructurally using a scanning electron microscopy (LEO 1455 VP) coupled with an energy dispersive X-ray spectrometer (SEM-EDAX).

Thermogravimetric analysis (TG), were carried out using a STA-1640 (Polymer Laboratories, England) in air with powdered alumina as reference and heating at 10 °C/min.

3. Results and discussion

3.1. Study of the mineralizer system on perovskite ($YAlO_3$) phase development

XRD pattern of the calcined samples without mineralizer at 1500 °C for 6 h in Fig. 1, demonstrates remaining of large quantities of unreacted yttrium oxide and formation of undesirable phases ($Al_5Y_3O_{12}$"cubic" and $Y_3AL_5O_{12}$"tetragonal"). Therefore it is necessary to use mineralizer. The mineralizer acts as a flux; it increases the transport rates, reduces the calcination temperature, and promotes crystal growth. Alkali halides-specially fluorides or chlorides are common mineralizers, but fluorine is preffered over chlorine in the Cr^{+3}: Al_2O_3 process, the preference is due to the lesser electron affinity of fluorine [8].

As Fig. 2 shows, although addition of M_1, M_2 and M_3 mineralizer systems were resulted in formation of small quantity of the perovskite phase, undesirable phases ($Y_3Al_5O_{12}$ and $Al_5Y_3O_{12}$) were still dominant.

As TG results in Fig. 3 shows, in the case of NaF addition, although it has low melting point (990 °C), it easily evaporates and escapes from the system. On the contrary, MgF_2 evaporates slowly, but melts at higher temperature (1270 °C). On the other hand although M_3 mineralizer system, corresponding to the

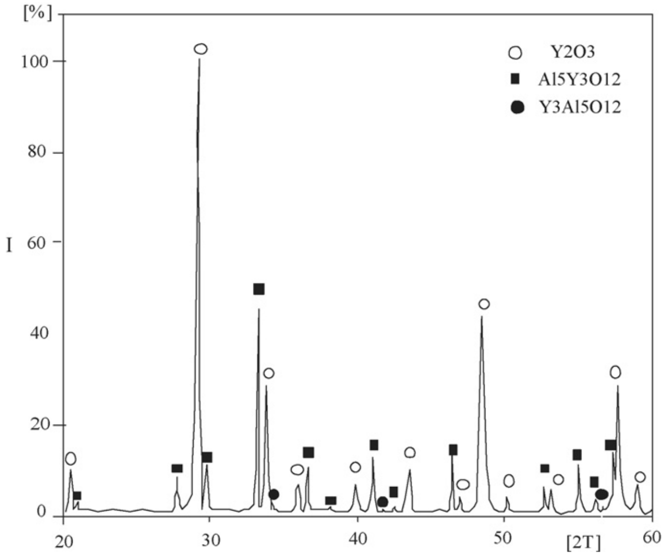

Fig. 1. XRD pattern of the sample referenced as P_4 without mineralizer at 1500 °C/6 h.

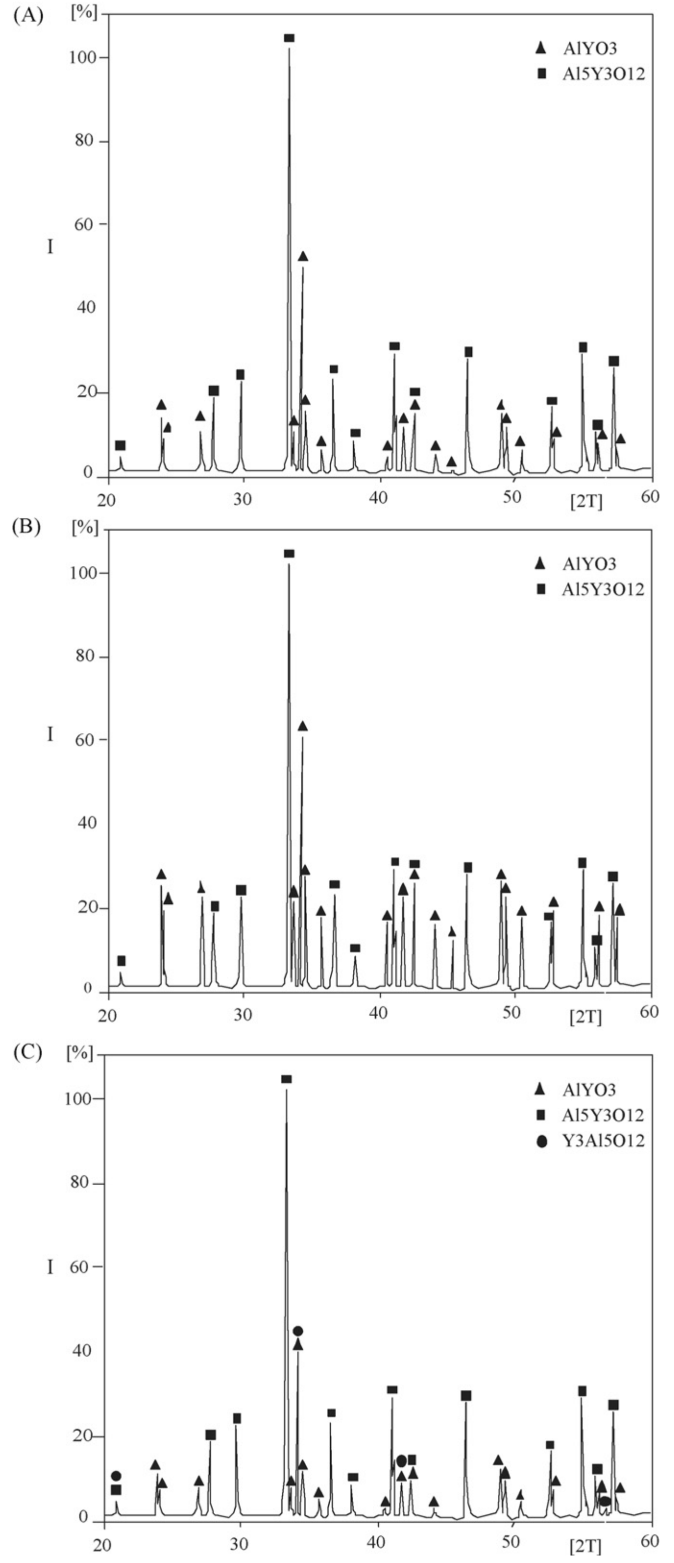

Fig. 2. XRD pattern of the sample referenced as P_4 with M_1(NaF) mineralizer (A), M_2 (MgF_2) mineralizer (B), and M_3(NaF:MgF_2) mineralizer (C).

eutectic point of NaF–MgF_2 diagram [9], has low melting point around 835 °C and evaporates slowly, it was not effective mineralizer due to its high viscosity.

Finally, in order to decrease the viscosity Li_2CO_3 was added to the above mentioned binary mineralizer system. The obtained ternary mineralizer system ($NaF/MgF_2/Li_2CO_3$ (3 wt.%/2 wt.%/1 wt.%)) has dominant mineralizing effect resulting from its low melting point, suitable fluidity and low evaporation rate and therefore enhancing provskite phase formation by favoring the interdiffusion process between ions.

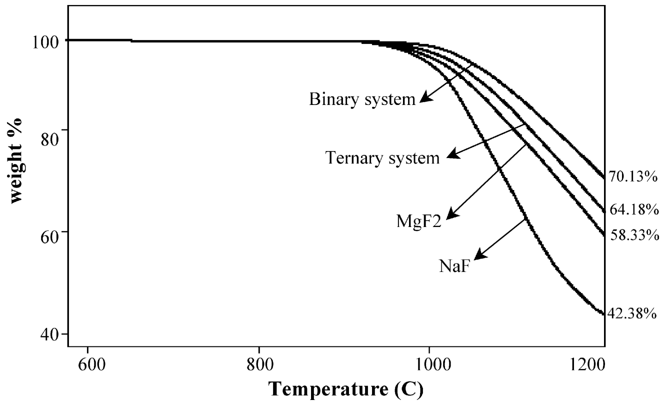

Fig. 3. TG curves of mineralizer systems.

XRD pattern in Fig. 4 demonstrates formation of single phase of perovskite ($YAlO_3$), when the ternary mineralizer system (M_4) was used.

As a result, the ternary system was selected as the most suitable mineralizer, for $YAlO_3$ formation.

3.2. Preparation of perovskite based red pigments

3.2.1. Effect of calcination temperature

According to XRD patterns in Fig. 5, calcination of the sample corresponding to stoichometric mixture, P_4 (containing 6 wt.% M_4 mineralizer system), results in formation of single perovskite phase only when the maximum calcination temperature is 1400 °C or above.

It must be pointed out that all synthesized samples showed shades of red color, but the highest red component (a^*) was

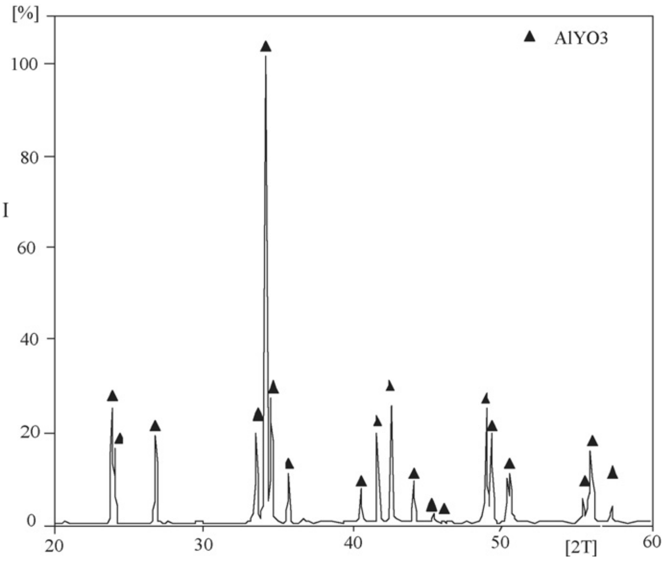

Fig. 4. XRD pattern of the sample referenced as P_4 prepared with M_4 (NaF:MgF_2:Li_2CO_3) mineralizer at 1500 °C/6 h.

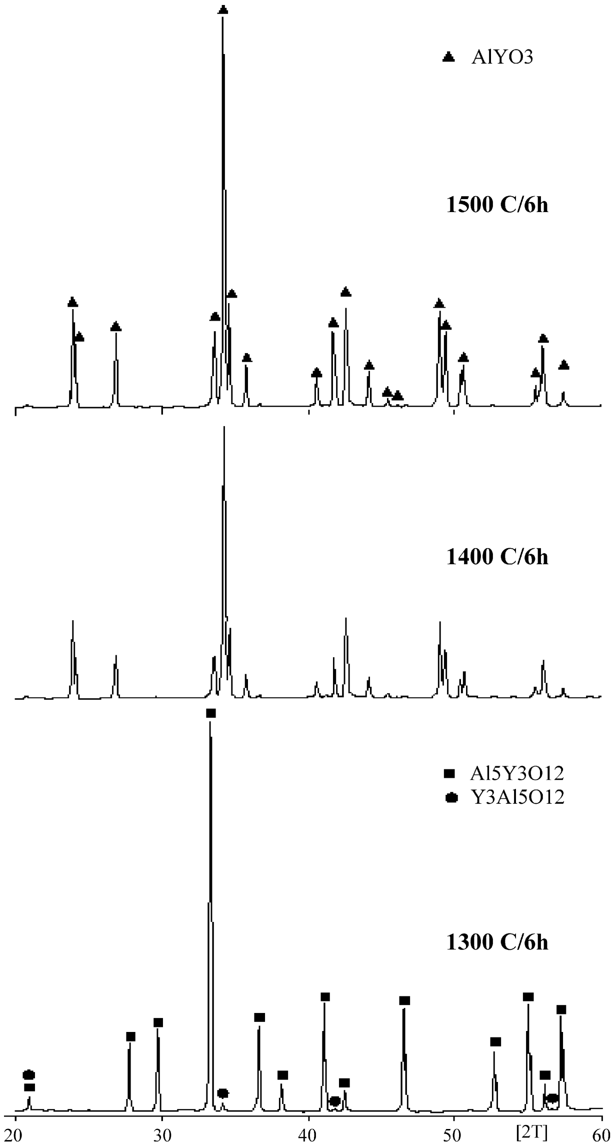

Fig. 5. XRD patterns of the sample referenced as P_4 prepared at 1500, 1400 and 1300 °C/6 h.

reached at 1500 °C, due to higher diffusion rate of Cr^{3+} in $YAlO_3$ structure.

3.2.2. *Pigment colors in relation to compositions and surrounding of chromium ions in the perovskite structure*

The ideal perovskite structure with $YAlO_3$ formula, has a cubic face-centered structure, the smaller Al^{3+} cation occupying octahedral sites and the larger Y^{3+} ions occupying the center of the unit cell (see Fig. 6) [6].

The electronic transition between d-electron orbitals in the chromium have relatively high energy, thus producing red tonality. The chromium(III) is in distorted octahedral configuration with the oxygen ions. The effect of the ligand field strength on the resulting energy levels, designated by spectroscopic terms $^4A_2$, $^4T_1$, $^4T_2$ and ^2E can be observed on the energy level diagram of the Cr^{3+} ion shown in Fig. 7 [5,6].

The theory of the ligand field, for an Cr^{3+} ion in an octahedral environment predicts the existence of three absorption bands. When white light passes through a crystal of ruby, portions of it with energies 2.2 and 3.0 eV corresponding to the energy differences between splitting levels of Cr^{3+} is absorbed. The absorption resulting from the first transition is in yellow–green part of the visible spectrum and the one from the second transition is in violet part. Thus the absorption in the red region, falls down to zero providing the red color of ruby [3–5].

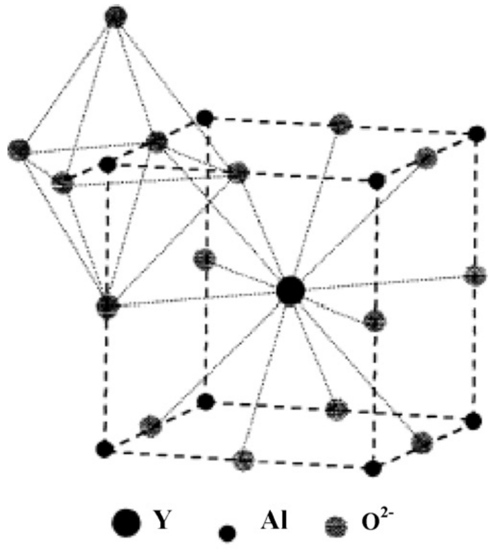

Fig. 6. Unit cell of the perovskite structure.

$YAl_{1-y}Cr_yO_3$ solid solutions were analyzed by UV–vis spectroscopy in order to study the surrounding of the Cr^{3+}. The absorption spectra corresponding to the synthesized samples are presented in Fig. 8.

As can be observed on the absorption spectra of the obtained solid solutions (Fig. 8), at wave length values smaller than 580 nm, there is a region of nearly constant absorption, probably owing to matrix effect and the distinction of the bands assigned to the allowed transition of the Cr^{3+} is impeded. It is also necessary to indicate that no absorption band appears in the visible spectrum between 580 and 700 nm (in the red region), contrary to the spectrum of green Cr_2O_3 where a wide absorption band can be appreciate in the same region.

The colorimetry results of the prepared pigment powders with various chromium contents is presented in Table 3 and illustrated in Fig. 9. As it seems the highest red component (the highest value of coordinates a^*) is reached in the pigment corresponding to the formula $YAl_{0.96}Cr_{0.04}O_3$ ($y = 0.04$).

Table 3
The effect of Cr content on the color properties of $YAl_{1-y}Cr_yO_3$ pigments

Formula	Powder pigments			Pigments applied in tile glazes (low temperature)		
	L^*	a^*	b^*	L^*	a^*	b^*
$YAl_{0.97}Cr_{0.03}O_3$	66.9	23.5	13.7	63.2	22.3	14.9
$YAl_{0.96}Cr_{0.04}O_3$	50.2	40.8	20.9	49.2	39.9	21.9
$YAl_{0.95}Cr_{0.05}O_3$	51.0	35.5	22.2	46.5	32.6	26.1
$YAl_{0.94}Cr_{0.06}O_3$	41.8	11.7	9.5	40.7	10.7	11.6

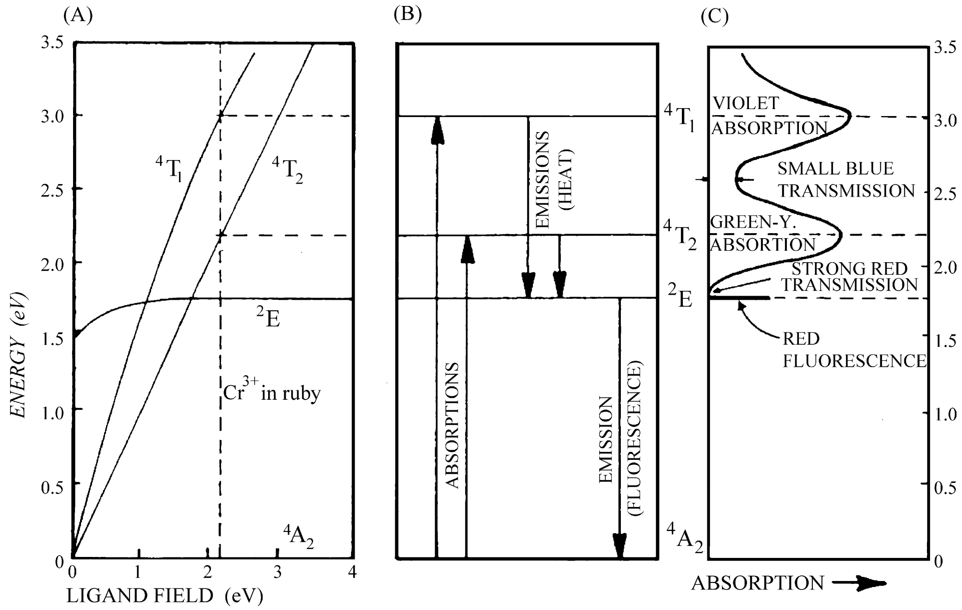

Fig. 7. The term diagram of Cr^{3+} in a distorted octahedral field (A), the energy levels and transitions in ruby (B), and the resulting absorption spectrum and fluorescence of ruby (C).

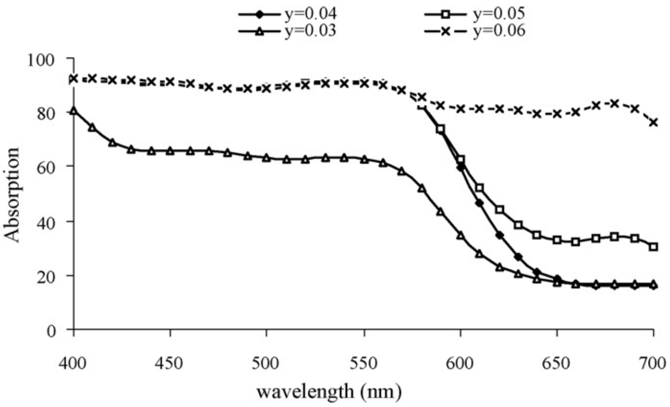

Fig. 8. UV–vis spectrum of the $YAl_{1-y}Cr_yO_3$ solid solutions.

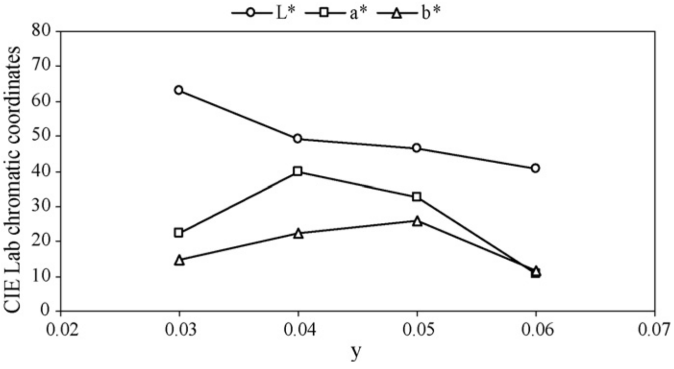

Fig. 9. The effect of y (chromium contents) on the CIE Lab parameters of the pigment powders.

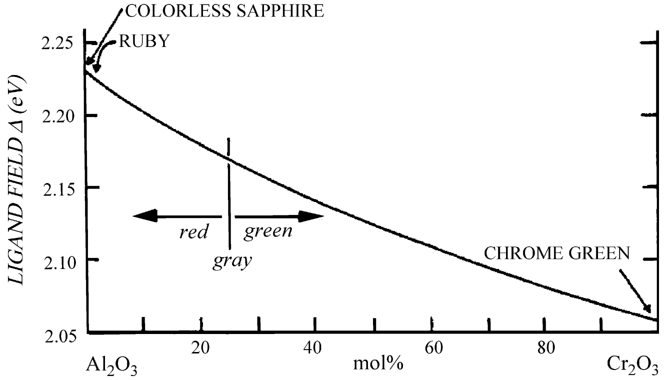

Fig. 10. The variation of the ligand field and color in the mixture system colorless sapphire and chrome green Cr_2O_3 [4].

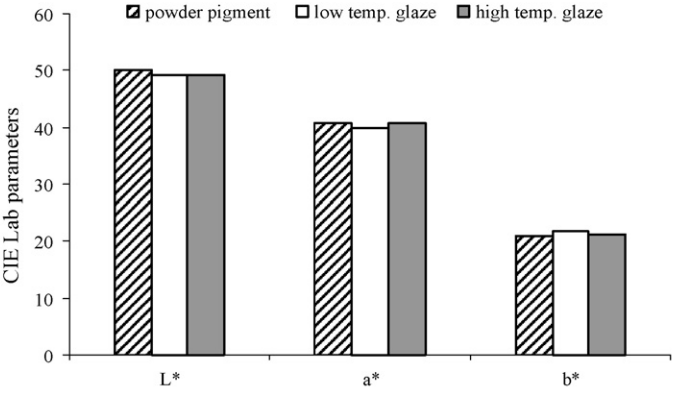

Fig. 11. CIE Lab parameters of low and high temperature colored glazes and powder pigment.

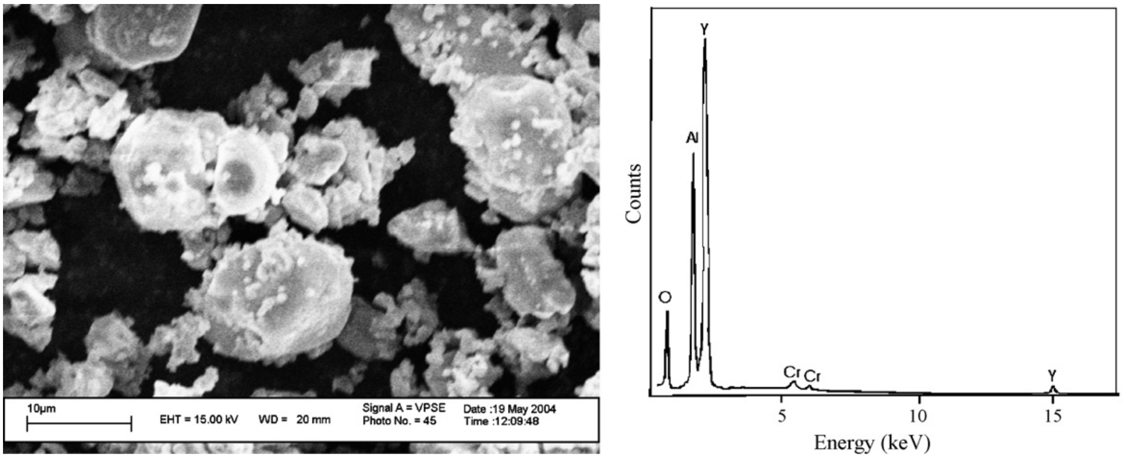

Fig. 12. SEM micrographs of the sample P_4 prepared together with spot chemical analysis.

The chromium concentration of ruby is increased, there is a change from red through gray to green as the ligand field becomes weaker as seen in Fig. 10. Concerning to similar way of red color development in Cr–$YAlO_3$ and Cr–Al_2O_3 crystals, the above results can be explained according to the changing of the ligand field by the amount of chromium in Al_2O_3.

As Fig. 8 shows, transmission in red area decreases when y (chromium content) increases. Concerning to similar way of red color development in Cr–$YAlO_3$ and Cr–Al_2O_3 crystals, the above results can be explained according to the weakening of the ligand field by the added chromium as seen in Fig. 7. As a result of the reduced field, the vertical dashed Cr^{3+} line, is shifted just a little to the left, the $^4T_1$ and $^4T_2$ levels is lowered, and these shifts, together with change in the shape of the band, results reducing in the red transmission.

However, when y value decreases down to 0.04 (for example $y = 0.03$), transmission in other visible zones also increases, resulting in decreasing of redness parameter (a^*).

3.2.3. Application of pigments in glazes

The colorimetry results of low temperature colored glaze are presented in Table 3. As it seems the CIE Lab parameters trend of colored glaze are similar to pigment powders.

Application of $YAl_{0.96}Cr_{0.04}O_3$ pigment in high temperature glaze indicated that the value of the co-ordinate a^*, was not decreased, demonstrating its high thermal stability (Table 4). Thermal stability of pigment refers to stabilized perovskite structure, that is related to high temperature synthesis process.

CIE Lab parameters of low and high temperature colored glazes and powder pigment are shown in Fig. 11 indicated little color changes and thermal and chemical stability of synthesized pigment.

Table 4
CIE Lab chromatic coordinates on glazed body colored at high temperature

Formula	$YAl_{0.95}Cr_{0.04}O_3$
L^*	49.3
a^*	40.7
b^*	21.1

3.2.4. SEM observations and spot chemical analysis of pigments

The SEM micrograph of the best synthesized pigment ($YAl_{0.96}Cr_{0.04}O_3$, $y = 0.04$) is illustrated in Fig. 12. The random spot chemical analysis (EDX) indicated almost the same chemical compositions as shown in Fig. 12.

4. Conclusions

- In this work, a red pigment based on $Y(Al,Cr)O_3$ perovskite structure was obtained.
- In order to decrease the perovskite structure formation temperature, various minerlizer systems were studied and the ternary system, 3 wt.% NaF:2 wt.% MgF_2:1 wt.% Li_2CO_3, was found as the most effective one.
- By using the selected mineralizer, perovskite formation temperature decreased from 1600 to 1400 °C.
- However, the most suitable temperature for diffusion of colorant and developing a red color in the perovskite structure, is 1500 °C.
- Effect of y value (chromium content) on colorimetry parameters was investigated, and the highest redness value (a^*) was obtained when y was 0.04.
- Applying the synthesized pigments in low and high temperature glazes, showed suitable red color that confirmed chemical and thermal stability of pigments in both glazes.

Acknowledgments

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