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Processing and characterisation of various mixed oxide and perovskite-based pigments for high temperature ceramic colouring application

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Abstract

The potential of using new mixed oxides based on perovskite and cerium oxide-based pigments, for high temperature (above 1000 °C) ceramic colouring applications is presented in this paper. The solid-state synthesis method was used to manufacture the various pigment precursor powders used in this study. In the case of Er_6MoO_{12}, orange–yellow colours were observed at calcination temperatures of 1200 °C and 1300 °C with different soaking times. Examination of the X-ray diffraction pattern generated after heat treatment at 1200 °C for 2 h revealed the single-phase nature of the compound. However, when applied to unleaded commercial transparent glaze, the pigment powder changed to a light pink colour indicating instability of the pigment in the glaze. Similarly mixed oxides such as $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ and $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ produced vivid blue and violet–blue colour powders, respectively when calcined between 950 °C and 1050 °C for different soaking times. X-ray diffraction patterns for $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ showed the presence of the phases which included (a) $BaCuSi_4O_{10}$ (b) $La_2Si_2O_7$ (c) SiO_2 and La_2O_3 (trace) whereas $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ confirmed the presence of the phases such as (a) $BaCuSi_4O_{10}$ and (b) $BaCuSi_2O_6$. These pigment powders were also not stable and light-green colours were observed when they were immersed in the unleaded commercial transparent glaze. Finally, $A_xB_{(2-x-y)}Cr_yO_3$ (A = rare earth and B = Al) perovskite-type compounds produced a variety of shades of red and yellow colour depending on the rare earth, the value of x and y, and the calcination temperature. An intense brownish-red colour was obtained when the rare earth Erbium was used with $x = 1$, $y = 0.06$. From the X-ray diffraction trace, Er (Al Cr)O_3 was found to be the only phase present. SEM micrographs indicated the presence of agglomerates as well as two different types of crystals in terms of morphology. EDX spectra confirmed that both types of crystals had the same composition. When applied in an unleaded transparent glaze, the brownish-red colour pigment powders turned into very pale yellow in the glaze, again indicating instability of the pigment powder in the commercial transparent glaze.

Keywords: Colour; Pigment; Ceramic pigment; Green; Blue; Yellow; Violet; Red; Brownish-red

1. Introduction

Inorganic pigments produced and marketed as fine powders are an integral part of many decorative and protective coatings and are used for the mass colouration of many materials including glazes and ceramic bodies [1]. Ceramic pigments are basically a white or coloured material, having high thermal stability and chemical resistance in order to be used at high temperature [2]. Recently the development of new ceramic materials has fostered the research and application of pigments stable to over 1200 °C. Ceramic pigments based on oxides, spinels, aluminates, etc., are prepared with blends of oxides as starting mixtures with the proper particle size distribution of powders, employing also additions of salt-like halides and borates that have a mineralising function [3,4]. The mixtures of these substances are subjected to a thermal treatment to obtain a reaction product with a well-defined crystal structure that can possess a colour, or that will become coloured by insertion of metallic chromophores. The substance must posses a high thermal and chemical stability under severe environments in commercial use. Research in the fields of ceramic pigments is oriented towards the enlargement of the chromatic set of colours together with an

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increased thermal and chemical stability. The pigments based on various mixed oxide structures and also pervoskite are less known and represent only a small but an important part of the range of inorganic pigments.

The classical red pigments used to date in the ceramic industry are of two types: iron oxide (Fe_2O_3 in zircon matrices) and lead oxide (Pb_3O_4 in tin oxide matrices). The higher quality red colours are produced using cadmium sulfoselenide, which unfortunately is poisonous and unstable above 900 °C.

With a few exceptions, the majority of the ceramic pigments are based on inorganic oxides. Such oxides are the only coloured materials capable of withstanding the severe conditions encountered during decorating, i.e., the high temperature and the corrosive action of the vitrified liquid. The severity of these conditions has restricted the palette of colours available for ceramic applications. Many attempts have been made to extend the range of ceramic pigments. Extensive investigations have already been made into the spinel, sphene, garnet, pyrochlore, etc., structures as pigments for high temperature ceramic applications [5–7]. The structure, which is not commonly encountered as a commercial pigment, is the perovskite structure. The term "perovskite" is applied to the structure of those materials, which crystallize with symmetry closely related to that of the mineral perovskite, $CaTiO_3$ [8–11]. Many of these materials have important technological applications and interesting physical properties. Most of the compounds with the general formula ABO_3 have this perovskite structure which may be described as a simple cubic unit cell with a large cation (A) on the corners, a smaller cation (B) in the body centre, and oxygen (O) in the centres of the cube faces (Fig. 1). The structure consists of a network of corner linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral holes. In the perovskite structure, the A cation is co-ordinated with 12 oxygen ions and the B cation with six. Thus the A cation is normally found to be somewhat larger than the B cation. In order to have contact with the two cations A, B and O (oxygen) ion, (R_A+R_O) should be equal to $\sqrt{2}(R_B+R_O)$, where R_A, R_B and R_O are the ionic radii of the species. The cubic perovskite structure is stable only if the tolerance factor, t, has an approximate range $0.8<t<0.9$ and a somewhat larger range for a distorted perovskite structure. The tolerance factor t is defined as

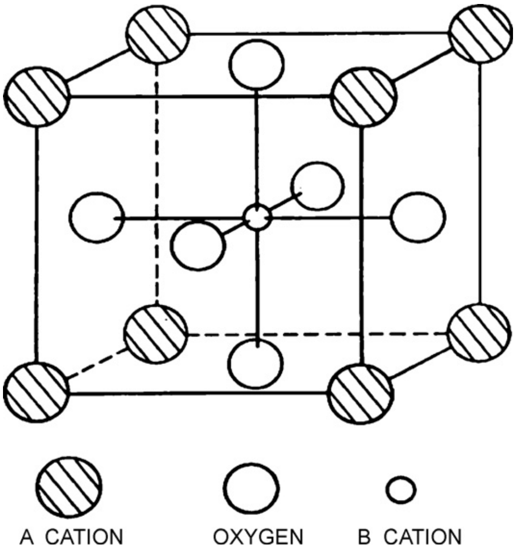


Fig. 1. Perovskite structure, ABO_3.

$$t=\frac{R_A+R_O}{\sqrt{2}(R_B+R_O)}$$

It is important to note that in the perovskite structure, the sum of the valancies of A and B has to equal 6.

Recently attention has been focused on the crystal structure of perovskites and their possible use in ceramic applications. Kato and Takahashi have developed a reddish pink pigment by doping Cr with $NdAlO_3$–Al_2O_3 [12]. Pishch and Radion [13] have synthesized pigment based on the perovskite $CaTiO_3$ incorporating the colouring oxides (CoO and NiO) for possible use in high temperature applications. Similarly Marinova and Cordoncillo [14] have developed pigments in rare earth perovskite structures with the incorporation of small amount of chromium. Jansen and Letschert [15] have developed "environmentally friendly" yellow to red pigments on the perovskite structure (Ca, La) Ta (O, N) known as oxy-nitride compounds, which is an example of a semiconductor pigment. The use of rare earth aluminates having the perovskite structure has also been reported [16].

The synthesis and characterisation of these new inorganic ceramic pigments has been investigated in this paper and the stability of these pigments during application in both unleaded commercial transparent and lead-containing glaze has also been described.

2. Sample preparation

Several processing methods are available for the preparation of pigments. In the present research work, all the samples were prepared using the solid-state synthesis method. Raw powders were mixed according to the required composition and ball milled for 1 h using a high-density polyethylene plastic bottle containing zirconia-grinding media and distilled water as the liquid suspension. Subsequently, the milled powders were dried using an infrared lamp. The powders were placed in pure alumina crucibles and subjected to calcination at various temperatures and soaking times in order to generate colour.

3. Experimental techniques

3.1. X-ray diffraction (XRD)

XRD analysis of the samples was carried out on a Philips PW1730/00 diffractometer using monochromatic Cu Kα radiation, λ = 0.154060 nm. The objective of the XRD was to detect the various phases in the samples of calcined powder pigment.

3.2. Particle size

The average particle size of the samples was measured using a Malvern mastersizer X particle size analyzer.

3.3. *Spectrophotometry*

All colour measurements were performed using a Spectra Flash SF600 PLUS spectrophotometer supplied by Datacolor. The colour co-ordinates ($L^*a^*b^*$), which specify a colour in uniform colour space was measured with this instrument. Each colour in the uniform colour space can be denoted by three parameters $L^*a^*b^*$ in rectangular co-ordinates where:

- L^*: lightness axis, for white $L^* = 100$ and 0 for black.
- a^*: red–green axis, positive represents red and negative means green.
- b^*: yellow–blue axis, positive represents yellow and negative blue.

3.4. *Scanning electron microscopy (SEM)*

The SEM used was a JEOL JSM-6310 analytical scanning electron microscope, to determine the surface morphology and grain size of the calcined pigment powders.

3.5. *Application of the pigment powders to the glaze*

The stability of the pigment powders was tested in commercial transparent leadless glaze provided by the Ferro Corporation, Stoke on Trent, England. Lead-containing glaze was also used. Glazes were coloured by introducing 8 wt% of the pigments to the glaze. A homogeneous mixture of the pigment and glaze was obtained by milling the slip for half an hour in a high-density plastic container using zirconia/alumina-grinding media. The ground mixtures were then sieved and subsequently stained ceramic glazes were sprayed onto the standard test tiles using a spray gun. The mass of the glaze deposited in each tile was between 0.15 gm/cm^2 and 0.2 gm/cm^2.

Firing of the glazed samples was carried out in a Carbolite furnace using the conditions given below:

- Step 1: 100 °C/h to 120 °C, soaking time 2 h.
- Step 2: 100 °C/h to 600 °C soaking time 1 h.
- Step 3: 100 °C/h to 1070 °C soaking time 2 h.
- Step 4: furnace cooling.

4. Results

The following section describes the sample preparation and results for the new mixed oxides and perovskite-based pigments, namely:

(i) Er_6MoO_{12}.
(ii) $Ba_{0.5}La_{0.5}\ Na_{0.5}\ Cu_{0.5}Si_4O_{10}$.
(iii) $Ba_{0.5}La_{0.5}\ Na_{0.5}\ Cu_{0.5}Si_2O_6$.
(iv) $A_xB_{(2-x-y)}Cr_yO_3$.

4.1. *Er_6MoO_{12} pigment*

4.1.1. *Sample preparation*

The powders were mixed according to the equation below:

$$3Er_2O_3 + MoO_3 \rightarrow Er_6MoO_{12}$$

Powders were fired at temperatures 1100 °C, 1200 °C and 1300 °C, for 2 h and 4 h (Table 1). A ramp rate of 300 °C/h was used. No colour was obtained at 1100 °C for 2 h. However, an orange–yellow colour was observed at 1200 °C for 2 h and1300 °C for 2 h and 4 h, with slight variations in intensity.

Table 1
Sample name obtained after different calcination temperatures

Symbol	Formula	Calcination temperature (°C)	Soaking time (h)
Er	Er_6MoO_{12}	1100	2
Er1	Er_6MoO_{12}	1200	2
Er2	Er_6MoO_{12}	1300	2
Er3	Er_6MoO_{12}	1300	4

Table 2
L^* a^* b^* parameters of Er_6MoO_{12} pigment powders at different calcination temperatures

Symbol	Pigment powder		
	L^*	a^*	b^*
Er1	83.01	6.24	28.60
Er2	83.08	8.92	25.82
Er3	83.02	9.68	26.14

4.1.2. *Results*

Colour measurements were carried out using a spectrophotometer and the values are given below. From Table 2, it was found that intense colour could be obtained with the sample Er1 calcined at 1200 °C for 2 h. X-ray diffraction on the sample Er1 (obtained at 1200 °C for 2 h) was carried out to determine the phases present. XRD shows (Fig. 2), Er_6MoO_{12} to be the only phase present in the sample.

The particle size distribution of the pigment powder (1200 °C for 2 h) after ball milling for 2 h was $d\ (0.1) = 0.31$ μm, $d\ (0.5) = 6.35$ μm, $d\ (0.9) = 14.08$ μm. SEM micrographs (Fig. 3) revealed the presence of agglomeration in the sample, each agglomerate contained a large number of grains with a grain size <1 μm.

The stability of the pigment was tested in commercial unleaded transparent glaze by adding 8-wt% and firing at 1050 °C. The orange–yellow pigment powder turned to light pink in the glaze. The CIE values of the pigment powder and pigment in the glaze are given in Table 3. It was speculated that the transformation of the orange yellow colour powder to light pink in the glaze was due to the breakdown of Er_6MoO_{12} to Er_2O_3 and MoO_3. Er_2O_3 is generally light pink in colour and it

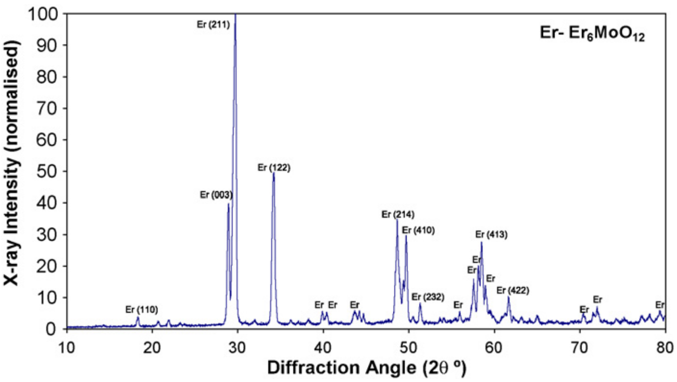
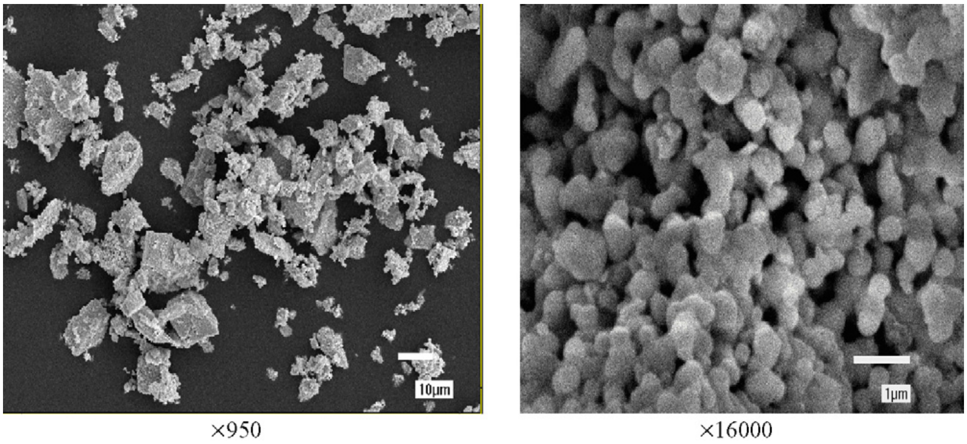


Fig. 2. X-ray diffraction pattern of Er_6MoO_{12} pigment powder obtained at 1200 °C for 2 h.



×950 ×16000

Fig. 3. SEM micrographs of the Er_6MoO_{12} pigment powder after ball milling for 2 h (Magnification 950× and 16,000×).

Table 3
L^* a^* b^* parameters of pigment powder and pigment in glaze CIE values of Er_6MoO_{12} and Er_2O_3 pigments in glaze

Symbol	Pigment powder			Pigment in glaze		
	L^*	a^*	b^*	L^*	a^*	b^*
Er1	83.01	6.24	28.60	83.62	15.92	−0.65
Er_6MoO_{12}				83.62	15.92	−0.65
Er_2O_3				83.86	13.05	3.83

Table 5
L^* a^* b^* parameters of $Ba_{0.5}La_{0.5}Na_{0.5}Cu_{0.5}Si_4O_{10}$ pigment powders at different calcination temperatures

Symbol	Pigment powders		
	L^*	a^*	b^*
E1	66.84	−2.95	−28.53
E2	65.58	1.92	−38.01
E3	67.40	−0.43	−33.25
E4	66.65	1.00	−35.40
E5	64.87	1.90	−36.78

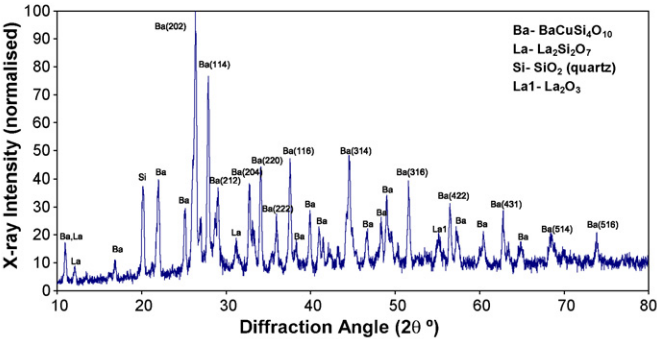


Fig. 4. X-ray diffraction pattern of pigment powder obtained after calcining at 1050 °C for 2 h.

is this, which is considered to impart the pink colour to the glaze. When Er_2O_3 alone was incorporated in the glaze at the 8 wt% level, the same light pink colour was observed. CIE values of Er_6MoO_{12} and Er_2O_3 in the glaze are given in Table 3.

4.2. $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ as vivid blue pigment

4.2.1. Sample preparation

The compositions of the prepared samples are given in Table 4. Precursors used were $BaCO_3$, La_2O_3, CuO, Na_2CO_3, and SiO_2. A ramp rate of 300 °C/h and soaking times of 2 h, 3 h, 6 h and 12 h were used. A vivid blue colour was obtained in each case with variable intensity.

4.2.2. Results

Table 5 gives the CIE values of various pigment powders at different calcination temperatures and soaking times. From Table 5, it is evident that an intense vivid blue colour can be obtained after calcination at 1050 °C for 2 h. From the XRD trace (Fig. 4), the phases below were found to be present:

(i) $BaCuSi_4O_{10}$ (blue colour according to the JCPDS standard).
(ii) $La_2Si_2O_7$.
(iii) SiO_2 and La_2O_3 (trace).

Table 4
Composition and firing conditions of the samples

Sample name	Formula	Calcination temperature (°C)	Soaking time (h)
E1	$Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$	950	2
E2	$Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$	1050	2
E3	$Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$	1050	3
E4	$Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$	1050	6
E5	$Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$	1050	12

Table 6
L^* a^* b^* parameters of $Ba_{0.5}La_{0.5}Na_{0.5}Cu_{0.5}Si_4O_{10}$ pigment powder and pigment in glaze (only at one firing temperature, 1050 °C for 2 h)

Symbol	E2
Pigment powder	
*L**	65.58
*a**	1.92
*b**	−38.01
Pigment in glaze	
*L**	74.78
*a**	−12.14
*b**	4.74

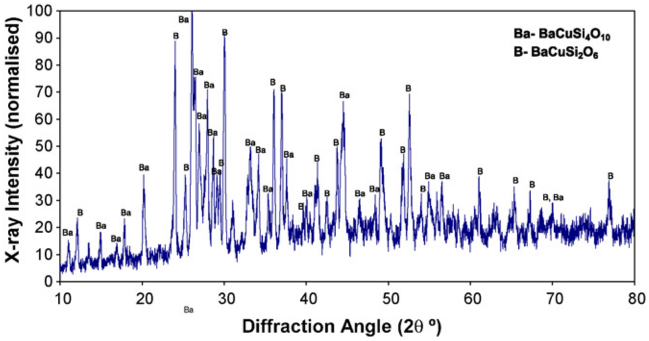


Fig. 5. X-ray diffraction pattern of $Ba_{0.5}La_{0.5}Na_{0.5}Cu_{0.5}Si_2O_6$ violet blue pigment powder calcined at 950 °C for 2 h.

Stability of the pigment (8% by wt) obtained after calcinations at 1050 °C for 2 h, tested in an unleaded commercial transparent glaze gave CIE values of the pigment powder and pigment in the glaze as given in Table 6. It is evident that the pigment in the glaze turned to a light green colour.

4.3. $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ as violet blue pigment

4.3.1. Sample preparation

The compositions of the prepared samples are given in Table 7. Powder samples were fired at 950 °C, 1050 °C with a soaking time of 2 h. A violet blue colour was obtained at 950 °C for 2 h holding time. A glassy product was observed on heating at 1050 °C for 2 h holding time and it was not considered for further characterisation.

4.3.2. Results

The different phases obtained from the XRD trace (Fig. 5) are given below:

(i) $BaCuSi_4O_{10}$ (blue colour according to JCPDS standard).
(ii) $BaCuSi_2O_6$ (violet colour according to JCPDS standard).

Table 8
L^* a^* b^* parameters of $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ pigment powder and pigment in glaze (at firing temperature, 950 °C for 2 h)

Symbol	BV
Pigment powder	
*L**	52.69
*a**	5.81
*b**	−25.40
Pigment in glaze	
*L**	66.6
*a**	−17.21
*b**	2.8

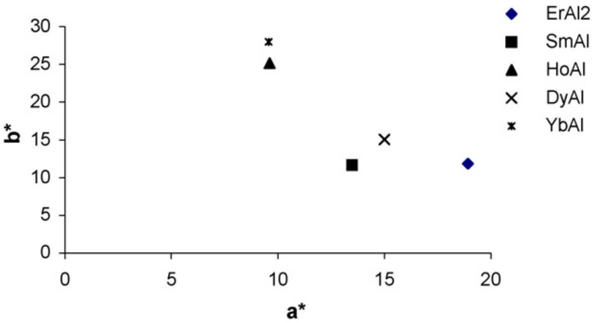


Fig. 6. Variation of the a^* and b^* values of $A_xB_{(2-x-y)}Cr_yO_3$ pigment powders with different rare earths (A = Rare earth, B = Al, $x = 1$, $y = 0.06$) calcined at different temperature and soaking times.

Stability of the pigment (8% by wt) determined after calcination at 950 °C for 2 h was tested in an unleaded commercial transparent glaze. The pigment turned to light green in the glaze. CIE values of the pigment powder and pigment in glaze are given in Table 8.

4.4. $A_xB_{(2-x-y)}Cr_yO_3$ (A = rare earth and B = Al) perovskite compound

4.4.1. Sample preparation

The compositions of the samples prepared are given in Table 9. NaF was used as a mineraliser.

4.4.2. Results

Colour measurements were carried out on pigment powders obtained with different rare earths after various calcinations temperatures and soaking times. The L^*, a^* and b^* parameters are shown in Table 12 and variations of the a^* and b^* values of the pigment powders with different rare earths are given in Fig. 6. From Table 10 it can be seen that a^* and b^* values are similar for ErAl1, ErAl2 and ErAl3 and the value of a^* is higher compared to b^* in each case, but in the case of ErAl the b^* value

Table 7
Compositions and firing conditions of the samples

Sample name	Formula	Calcination temperature (°C)	Soaking time (h)
BV	$Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$	950	2
BV1	$Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$	1050	2

Table 9
Compositions and colour of the samples after calcinations at various temperatures

Sample name	Formula $A_xB_{(2-x-y)}Cr_yO_3$ (A = rare earth and B = Al)	Rare earth	Calcination temperature (°C)	Soaking time (h)	Colour obtained
ErAl	$x=1$, $y=0.06$	Er	1250	1	Yellow
ErAl1	$x=1$, $y=0.06$	Er	1450	1	Brownish-red
ErAl2	$x=1$, $y=0.06$	Er	1500	1	Brownish-red
ErAl3	$x=1$, $y=0.08$	Er	1500	1	Brownish-red
SmAl	$x=1$, $y=0.06$	Sm	1500	1	Brown
HoAl	$x=1$, $y=0.06$	Ho	1500	1	Brick red
DyAl	x = 1, $y=0.06$	Dy	1500	1	Brick red
YbAl	$x=1$, $y=0.06$	Yb	1500	1	Yellow

Table 10
*L** *a** *b** parameters of the pigment powders containing various rare earths and calcined at different temperature and soaking times

Symbol	Pigment powders		
	*L**	*a**	*b**
ErAl	76.92	11.56	21.68
ErAl1	58.02	18.27	11.24
ErAl2	59.04	18.92	11.85
ErAl3	60.15	18.48	11.96
SmAl	60.34	13.48	11.63
HoAl	66.73	9.61	25.15
DyAl	62.87	15.00	15.05
YbAl	74.75	9.57	27.99

was found to be higher. Positive value of *b** represents the yellow colour in CIELAB space and hence the *b** value will be higher for a yellow colour compared to a brownish-red colour samples.

The single-phase nature of the sample was revealed X-ray diffraction (Fig. 7). Fig. 8 shows the presence of agglomerates with an average grain size of 2–3 μm. Two types of crystals (as far as morphology is concerned) were observed. EDX spectra of the crystals denoted as *x* and *y* in the SEM micrograph indicated that both had the same composition. The stability of the pigment powder (8 wt%) was tested in an unleaded transparent commercial glaze. The brownish-red colour turned to a pale yellow in the glaze (Table 11).

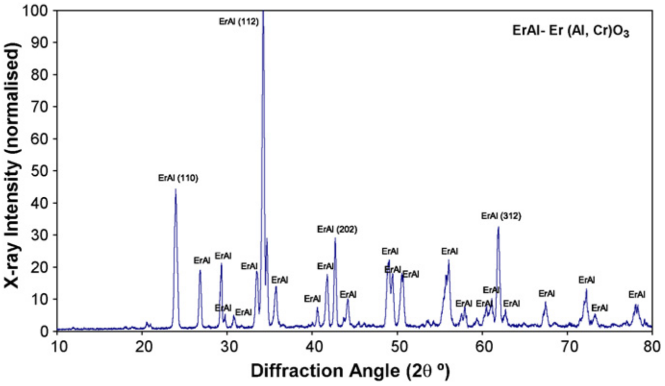


Fig. 7. Typical X-ray diffraction pattern of the pigment powder Er(Al,Cr)O_3.

Table 11
*L** *a** *b** parameters of the pigment powder and the pigment in glaze

Symbol	ErAl2
Pigment powder	
*L**	59.04
*a**	18.92
*b**	11.85
Pigment in glaze	
*L**	69.70
*a**	7.24
*b**	23.61

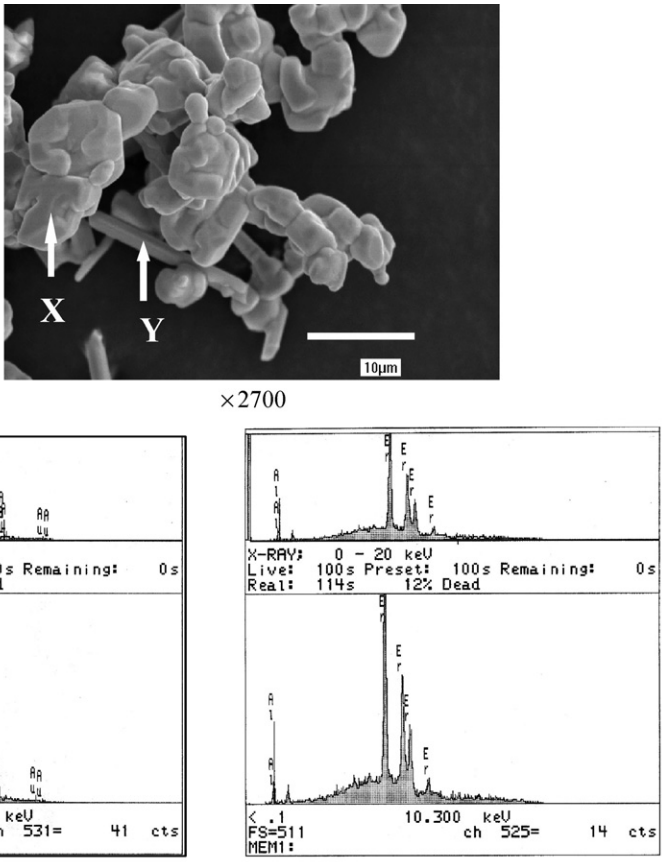
5. Discussion

5.1. Er_6MoO_{12} pigment

Orange yellow colours were observed with a variation in intensity on mixing a suitable amount of Er_2O_3 and MoO_3 followed by calcining at the appropriate temperatures (1200 °C and 1300 °C) and soaking times (2 h, 4 h and 6 h). From the X-ray diffraction trace (obtained after calcination at 1200 °C, 2 h), Er_6MoO_{12} was found to be the only phase present, which in the unleaded transparent glaze turned to a light pink. The colour of the precursor Er_2O_3 is light pink and hence it was speculated that this colour alteration might be due to the breakdown of Er_6MoO_{12} to Er_2O_3 and MoO_3 in the glaze. Er_2O_3 introduced in the glaze generated the same light pink colour. Therefore it is postulated that the coloured rare earth oxides, such as Nd_2O_3 can be used directly in certain ceramic applications when a “washy pale” colour hue is required. The colour developed in this case is attributed to the crystal field splitting of the d orbitals of the Mo^{6+} ion.

5.2. $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ and $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ type pigments

$Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ and $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ produced vivid blue and violet blue coloured powder at different calcination temperatures and soaking times. The pigment powders were optimised in terms of calcination temperature and soaking times before further characterisation. $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ was produced by replacing the Ba ion with $Ba_{0.5}La_{0.5}$ and Cu with $Na_{0.5}Cu_{0.5}$ in the compound $BaCuSi_4O_{10}$. Similarly $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ was



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X-RAY:    0 - 20 keV
Live:   100s Preset:   100s Remaining:     0s
Real:   123s      19% Dead

< .2            10.420  keV
FS=  1K              ch  531=      41  cts
MEM1:
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X

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X-RAY:    0 - 20 keV
Live:   100s Preset:   100s Remaining:     0s
Real:   114s      12% Dead

< .1            10.300  keV
FS=511               ch  525=      14  cts
MEM1:
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Y

Fig. 8. SEM micrograph of the sample Er(Al,Cr)O_3 after calcination at 1500 °C for 1 h (2700×) together with the EDX spectrum of the samples.

obtained by replacing Ba with $Ba_{0.5}La_{0.5}$ and Cu with $Na_{0.5}$ $Cu_{0.5}$ in the compound $BaCuSi_2O_6$. It was interesting to note that a violet colour powder was obtained with $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ calcined at 950 °C for 2 h, but on increasing the temperature to 1050 °C, a glassy phase developed. $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ formed vivid blue colours with a variation in the intensity when calcined at temperatures between 950 °C and 1050 °C with a soaking time of 2 h, 4 h and 6 h.

From the X-ray diffraction of the powder samples, mixtures of phases were found to be present. In the case of $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$, $BaCuSi_4O_{10}$ was found to be the dominant phase and the colour of this compound (phase) is, according to the JCPDS standard, blue and in the experiments a blue colour was noticed. Similarly $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ was found to consist of two different phases, $BaCuSi_2O_6$ and $BaCuSi_4O_{10}$. The colour of the $BaCuSi_2O_6$ and $BaCuSi_4O_{10}$ phases are violet and blue, respectively according to the JCPDS standard. Since from the X-ray diffraction pattern $BaCuSi_2O_6$ was found to be the dominant phase, in the experiment a violet colour with a blue hue was observed in the sample. These pigments were found to be unstable in the unleaded commercial transparent glaze and again this might be due to the reaction of the pigment with the glaze or the breaking down of the compound into individual compounds such as the constituent oxides.

The colours of the compounds $BaCuSi_4O_{10}$ and $BaCuSi_2O_6$ are blue and purple, respectively [17]. These compounds have recently been shown to be complex copper silicates. The compounds are ring silicates in which the colour is derived from crystal field splitting of the Cu^{2+} d orbitals in a square planar environment. Hence experiments were carried out on these compounds, replacing Ba with $Ba_{0.5}La_{0.5}$ and Cu with $Na_{0.5}$ $Cu_{0.5}$ in order to see the effect of this replacement on the colour as well as intensity of the colour produced. This replacement was expected to affect the d–d electronic transitions of Cu^{2+} and consequently change in the Cu–O bond lengths.

5.3. Pigments based on perovskite structure $A_xB_{(2-x-y)}Cr_yO_3$, A = rare earth and B = Al

Trials were performed on the perovskite structure $A_xB_{(2-x-y)}Cr_yO_3$ (A = rare earth and B = Al). Yellow and different shades of brownish-red colour were observed after calcining at different temperatures and soaking times. CIELAB measurements were carried out on the pigment powder samples and the best results were obtained with the rare earth Er. When incorporated into the unleaded transparent glaze, a stability problem was encountered and the colour turned to a dirty yellow.

In the structure (ABO_3) where B = Al and A = rare earths, the relative sizes of atoms are such that ternary oxides develop according to a non-ideal perovskite-type crystal structure with a tolerance index $t \approx 0.8$–0.9. X-ray diffraction patterns confirmed

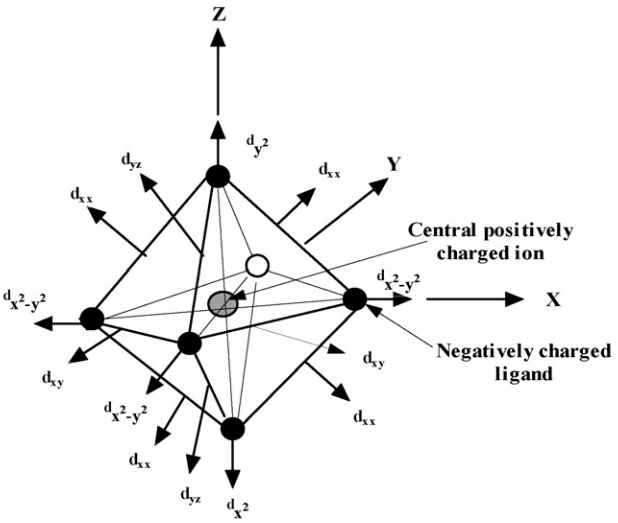

Fig. 9. Ligand field: d orbital interaction of central ion with six ligands of an octahedral neighbourhood.

the crystallization of the compound in the orthorhombic system. The colour developed in the system $A_xB_{(2-x-y)}Cr_yO_3O_3$ is attributed to the crystal field splitting of the energy bands [30].

The chromium ion having an ionic radius (0.69 Å) larger than that of the aluminium ion (0.50 Å), finds itself with tetragonally deformed oxygen (ligands) (Fig. 9). As a result of this, the ligands along the z-axis are more distant from the central ion in comparison with the others. Consequently splitting of the d-orbitals of the Cr^{3+} ion and the transition of energy from the higher energy level to lower energy level gives rise to the colour. When the central ion, inside an octahedrally co-ordinated cage is chromium, the field is strong enough to allow absorption in the visible spectrum, for wavelengths located in the blue and green region.

6. Conclusions

6.1. Er_6MoO_{12} pigment

- Orange–yellow colours were observed at calcinations temperatures of 1200 °C and 1300 °C with various soaking times.
- The X-ray diffraction pattern at 1200 °C for 2 h showed the single-phase nature of the compound.
- The pigment powder turned to light pink when used in an unleaded transparent glaze.

6.2. $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ and $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ pigments

- $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ gave vivid blue colour powders when calcined between 950 °C and 1050 °C for different soaking times and $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ produced violet–blue colour powders when calcined at 950 °C for 2 h.
- X-ray diffraction pattern for $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_4O_{10}$ showed the presence of the phases (a) $BaCuSi_4O_{10}$ (b) $La_2Si_2O_7$ and (c) SiO_2 and La_2O_3 (trace) whereas the X-ray diffraction pattern of $Ba_{0.5}La_{0.5}$ $Na_{0.5}$ $Cu_{0.5}Si_2O_6$ also showed the presence of the phases (a) $BaCuSi_4O_{10}$ and (b) $BaCuSi_2O_6$.
- These pigment powders were unstable and light-green colours were observed in the unleaded transparent glaze.

6.3. $A_xB_{(2-x-y)}Cr_yO_3$ (A = rare earth and B = Al) perovskite-type compound

- $A_xB_{(2-x-y)}Cr_yO_3$ (A = rare earth and B = Al) produced different shades of red and yellow colour depending on the rare earth, value of x and y, and calcination temperature. An intense brownish-red colour was obtained with Er and with $x = 1$, $y = 0.06$.
- From the X-ray diffraction spectrum, Er(Al Cr)O_3 was found to be only phase present.
- SEM micrographs indicated the presence of agglomerates as well as of two different types of crystals. EDX spectra confirmed that both types of crystals had the same composition.
- The pigment was unstable and the brownish-red colour turned to very pale yellow in the glaze when used in an unleaded transparent glaze.

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References

[1] G. Buxbaum, Industrial Inorganic Pigments, 2nd ed., Wiley-Vch, 1997.
[2] A. Burgyan, Characterization and identification of the mixed metal oxides and ceramic pigments manufactured in the U.S., Interceram. NR. 1 (1979) 30–32.
[3] E.Sh. Kharashvili, Trends in developing ceramic pigments, Glass Ceram. 42 (9/10) (1985) 459.
[4] R.W. Batchelor, Trans. Br. Ceram. Soc. 73 (8) (1974) 297.
[5] R.A. Eppler, Solid State Reactions in the Preparation of Zircon Stains, in: L.L. Hench, D.B. Dove (Eds.), Physics of Electronic Materials. Part B, Marcel Dekker Inc., New York, 1972, pp. 1021–1045.
[6] W. Brugger, "Process of producing ceramic colouring substances", British Patent 1,181494, February 18 (1970).
[7] D.V. Sanghani, G.R. Abrams, P.J. Smith, Trans. J. Br. Ceram. Soc. 80 (1981) 210.
[8] Francis S. Galasso, Perovskites and High T_c Superconductors, Gordon and Breach Science Publishers, 1990.
[9] F.S. Galasso, Structure, Properties and Preparation of Perovskite-Type Compounds, Pergamon Press, London, 1969.
[10] H.D. Megaw, Ferroelectricity in Crystals, Methuen, London, 1957.
[11] A.S. Bhalla, R. Guo, R. Roy, The Perovskite structure—a review of its role in ceramic science and technology, Mater. Res. Inn. 4 (2000) 3–26.
[12] M. Kato, T. Takahashi, J. Mater. Sci. Lett. 20 (2001) 413.
[13] V. Pishch, E.V. Radion, Glass Ceram. 55 (1998) 9.
[14] I. Marinova, E. Cordoncillo, V. Kozhukharov, J.B. Carda, Proceedings of the 7th European Ceramics Society Conference Brugge, Belgium, September 9–13, 2001, p. 379.
[15] M. Jansen, H.P. Letschert, Nature 404 (2000) 980.
[16] G. Baldi, Colorobia Italia S.p.A, European Patent EP96/01029, March 11 1996.
[17] Richard Tilley, Colour and the Optical Properties of Materials, John Wiley and Sons, Ltd, 1999, p. 168.