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\textsubscript{6}MoO\textsubscript{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\textsubscript{0.5}La\textsubscript{0.5}Na\textsubscript{0.5}Cu\textsubscript{0.5}Si\textsubscript{4}O\textsubscript{10} and Ba\textsubscript{0.5}La\textsubscript{0.5}Na\textsubscript{0.5}Cu\textsubscript{0.5}Si\textsubscript{2}O\textsubscript{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\textsubscript{0.5}La\textsubscript{0.5}Na\textsubscript{0.5}Cu\textsubscript{0.5}Si\textsubscript{4}O\textsubscript{10} showed the presence of the phases which included (a) BaCuSi\textsubscript{4}O\textsubscript{10} (b) La\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} (c) SiO\textsubscript{2} and La\textsubscript{2}O\textsubscript{3} (trace) whereas Ba\textsubscript{0.5}La\textsubscript{0.5}Na\textsubscript{0.5}Cu\textsubscript{0.5}Si\textsubscript{2}O\textsubscript{6} confirmed the presence of the phases such as (a) BaCuSi\textsubscript{2}O\textsubscript{6} and (b) BaCuSi\textsubscript{2}O\textsubscript{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\textsubscript{x}B\textsubscript{(2−x−y)}Cr\textsubscript{y}O\textsubscript{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\textsubscript{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.

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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...
increased thermal and chemical stability. The pigments based on various mixed oxide structures and also perovskite 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 (Fe₂O₃ in zircon matrices) and lead oxide (Pb₃O₄ 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, CaTiO₃ [8–11]. Many of these materials have important technological applications and interesting physical properties. Most of the compounds with the general formula ABO₃ have this pernological applications and interesting physical properties. Most unfortunately is poisonous and unstable above 900 °C.

Fig. 1. Perovskite structure, ABO₃.

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

It is important to note that in the perovskite structure, the sum of the valencies 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 NdAlO₃–Al₂O₃ [12]. Pisch and Radion [13] have synthesized pigment based on the perovskite CaTiO₃ 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 Letschet [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 alumina in 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, \(\lambda = 0.154060\) 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) \(\text{Er}_6\text{MoO}_{12}\).
(ii) \(\text{Ba}_{0.5}\text{La}_{0.5}\text{Na}_{0.5}\text{Cu}_{0.5}\text{Si}_{4}\text{O}_{10}\).
(iii) \(\text{Ba}_{0.5}\text{La}_{0.5}\text{Na}_{0.5}\text{Cu}_{0.5}\text{Si}_{2}\text{O}_{6}\).
(iv) \(\text{A}_x\text{B}(2−x−y)\text{Cr}_y\text{O}_3\).

4.1. \(\text{Er}_6\text{MoO}_{12}\) pigment

4.1.1. Sample preparation

The powders were mixed according to the equation below:

\[3\text{Er}_2\text{O}_3 + \text{MoO}_3 \rightarrow \text{Er}_6\text{MoO}_{12}\]

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 and 1300 °C for 2 h and 4 h, with slight variations in intensity.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Formula</th>
<th>Calcination temperature (°C)</th>
<th>Soaking time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er</td>
<td>(\text{Er}<em>6\text{MoO}</em>{12})</td>
<td>1100</td>
<td>2</td>
</tr>
<tr>
<td>Er1</td>
<td>(\text{Er}<em>6\text{MoO}</em>{12})</td>
<td>1200</td>
<td>2</td>
</tr>
<tr>
<td>Er2</td>
<td>(\text{Er}<em>6\text{MoO}</em>{12})</td>
<td>1300</td>
<td>2</td>
</tr>
<tr>
<td>Er3</td>
<td>(\text{Er}<em>6\text{MoO}</em>{12})</td>
<td>1300</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 1 Sample name obtained after different calcination temperatures

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), \(\text{Er}_6\text{MoO}_{12}\) 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 \(\text{Er}_6\text{MoO}_{12}\) to \(\text{Er}_2\text{O}_3\) and \(\text{MoO}_3\). \(\text{Er}_2\text{O}_3\) is generally light pink in colour and it Fig. 2. X-ray diffraction pattern of \(\text{Er}_6\text{MoO}_{12}\) pigment powder obtained at 1200 °C for 2 h.
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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Pigment powder</th>
<th>Pigment in glaze</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L^<em>$ $a^</em>$ $b^*$</td>
<td>$L^<em>$ $a^</em>$ $b^*$</td>
</tr>
<tr>
<td>Er1</td>
<td>83.01 6.24 28.60</td>
<td>83.62 15.92 −0.65</td>
</tr>
<tr>
<td>Er_6MoO_{12}</td>
<td>83.62 15.92 −0.65</td>
<td></td>
</tr>
<tr>
<td>Er_2O_3</td>
<td>83.86 13.05 3.83</td>
<td></td>
</tr>
</tbody>
</table>

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. $\text{Ba}_{0.5}\text{La}_{0.5}\text{Na}_{0.5}\text{Cu}_{0.5}\text{Si}_4\text{O}_{10}$ 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$_2$O$_3$, CuO, Na$_2$CO$_3$, 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$_4$O$_{10}$ (blue colour according to the JCPDS standard).
(ii) La$_2$Si$_2$O$_7$.
(iii) SiO$_2$ and La$_2$O$_3$ (trace).

Table 4

Composition and firing conditions of the samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Formula</th>
<th>Calcination temperature (°C)</th>
<th>Soaking time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>Ba$<em>{0.5}$La$</em>{0.5}$Na$<em>{0.5}$Cu$</em>{0.5}$Si$<em>4$O$</em>{10}$</td>
<td>950</td>
<td>2</td>
</tr>
<tr>
<td>E2</td>
<td>Ba$<em>{0.5}$La$</em>{0.5}$Na$<em>{0.5}$Cu$</em>{0.5}$Si$<em>4$O$</em>{10}$</td>
<td>1050</td>
<td>2</td>
</tr>
<tr>
<td>E3</td>
<td>Ba$<em>{0.5}$La$</em>{0.5}$Na$<em>{0.5}$Cu$</em>{0.5}$Si$<em>4$O$</em>{10}$</td>
<td>1050</td>
<td>3</td>
</tr>
<tr>
<td>E4</td>
<td>Ba$<em>{0.5}$La$</em>{0.5}$Na$<em>{0.5}$Cu$</em>{0.5}$Si$<em>4$O$</em>{10}$</td>
<td>1050</td>
<td>6</td>
</tr>
<tr>
<td>E5</td>
<td>Ba$<em>{0.5}$La$</em>{0.5}$Na$<em>{0.5}$Cu$</em>{0.5}$Si$<em>4$O$</em>{10}$</td>
<td>1050</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 5

$L^* a^* b^*$ parameters of Ba$_{0.5}$La$_{0.5}$Na$_{0.5}$Cu$_{0.5}$Si$_4$O$_{10}$ pigment powders at different calcination temperatures

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Pigment powders</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L^<em>$ $a^</em>$ $b^*$</td>
</tr>
<tr>
<td>E1</td>
<td>66.84 −2.95 −28.53</td>
</tr>
<tr>
<td>E2</td>
<td>65.58 1.92 −38.01</td>
</tr>
<tr>
<td>E3</td>
<td>67.40 −0.43 −33.25</td>
</tr>
<tr>
<td>E4</td>
<td>66.65 1.00 −35.40</td>
</tr>
<tr>
<td>E5</td>
<td>64.87 1.90 −36.78</td>
</tr>
</tbody>
</table>

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

(i) BaCuSi$_4$O$_{10}$ (blue colour according to the JCPDS standard).
(ii) La$_2$Si$_2$O$_7$.
(iii) SiO$_2$ and La$_2$O$_3$ (trace).
Table 6
$L^* a^* b^*$ parameters of $\text{Ba}_{0.5}\text{La}_{0.5}\text{Na}_{0.5}\text{Cu}_{0.5}\text{Si}_4\text{O}_{10}$ pigment powder and pigment in glaze (only at one firing temperature, 1050 °C for 2 h)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigment powder</td>
<td>65.58</td>
<td>1.92</td>
<td>-38.01</td>
</tr>
<tr>
<td>Pigment in glaze</td>
<td>74.78</td>
<td>-12.14</td>
<td>4.74</td>
</tr>
</tbody>
</table>

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. $\text{Ba}_{0.5}\text{La}_{0.5}\text{Na}_{0.5}\text{Cu}_{0.5}\text{Si}_2\text{O}_6$ 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) $\text{BaCuSi}_4\text{O}_{10}$ (blue colour according to JCPDS standard).
(ii) $\text{BaCuSi}_2\text{O}_6$ (violet colour according to JCPDS standard).

Table 7
Compositions and firing conditions of the samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Formula</th>
<th>Calcination temperature (°C)</th>
<th>Soaking time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BV</td>
<td>$\text{Ba}<em>{0.5}\text{La}</em>{0.5}\text{Na}<em>{0.5}\text{Cu}</em>{0.5}\text{Si}_2\text{O}_6$</td>
<td>950</td>
<td>2</td>
</tr>
<tr>
<td>BV1</td>
<td>$\text{Ba}<em>{0.5}\text{La}</em>{0.5}\text{Na}<em>{0.5}\text{Cu}</em>{0.5}\text{Si}_2\text{O}_6$</td>
<td>1050</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 5. X-ray diffraction pattern of $\text{Ba}_{0.5}\text{La}_{0.5}\text{Na}_{0.5}\text{Cu}_{0.5}\text{Si}_2\text{O}_6$ violet blue pigment powder calcined at 950 °C for 2 h.

4.4. $\text{A}_x\text{B}_{(2-x-y)}\text{Cr}_y\text{O}_3$ ($\text{A} = \text{rare earth}$ and $\text{B} = \text{Al}$) 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 $\text{ErAl}_1$, $\text{ErAl}_2$ and $\text{ErAl}_3$ and the value of $a^*$ is higher compared to $b^*$ in each case, but in the case of $\text{ErAl}$ the $b^*$ value...
Table 9
Compositions and colour of the samples after calcinations at various temperatures

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Formula</th>
<th>Rare earth</th>
<th>Calcination temperature (°C)</th>
<th>Soaking time (h)</th>
<th>Colour obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErAl</td>
<td>$x = 1, y = 0.06$</td>
<td>Er</td>
<td>1250</td>
<td>1</td>
<td>Yellow</td>
</tr>
<tr>
<td>ErAl1</td>
<td>$x = 1, y = 0.06$</td>
<td>Er</td>
<td>1450</td>
<td>1</td>
<td>Brownish-red</td>
</tr>
<tr>
<td>ErAl2</td>
<td>$x = 1, y = 0.06$</td>
<td>Er</td>
<td>1500</td>
<td>1</td>
<td>Brownish-red</td>
</tr>
<tr>
<td>ErAl3</td>
<td>$x = 1, y = 0.08$</td>
<td>Sm</td>
<td>1500</td>
<td>1</td>
<td>Brownish-red</td>
</tr>
<tr>
<td>SmAl</td>
<td>$x = 1, y = 0.06$</td>
<td>Ho</td>
<td>1500</td>
<td>1</td>
<td>Brick red</td>
</tr>
<tr>
<td>DyAl</td>
<td>$x = 1, y = 0.06$</td>
<td>Dy</td>
<td>1500</td>
<td>1</td>
<td>Brick red</td>
</tr>
<tr>
<td>YbAl</td>
<td>$x = 1, y = 0.06$</td>
<td>Yb</td>
<td>1500</td>
<td>1</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Pigment powders</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErAl</td>
<td></td>
<td>76.92</td>
<td>11.56</td>
<td>21.68</td>
</tr>
<tr>
<td>ErAl1</td>
<td></td>
<td>58.02</td>
<td>18.27</td>
<td>11.24</td>
</tr>
<tr>
<td>ErAl2</td>
<td></td>
<td>59.04</td>
<td>18.92</td>
<td>11.85</td>
</tr>
<tr>
<td>ErAl3</td>
<td></td>
<td>60.15</td>
<td>18.48</td>
<td>11.96</td>
</tr>
<tr>
<td>SmAl</td>
<td></td>
<td>60.34</td>
<td>13.48</td>
<td>11.63</td>
</tr>
<tr>
<td>HoAl</td>
<td></td>
<td>66.73</td>
<td>9.61</td>
<td>25.15</td>
</tr>
<tr>
<td>DyAl</td>
<td></td>
<td>62.87</td>
<td>15.00</td>
<td>15.05</td>
</tr>
<tr>
<td>YbAl</td>
<td></td>
<td>74.75</td>
<td>9.57</td>
<td>27.99</td>
</tr>
</tbody>
</table>

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 $2–3\mu m$. 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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Pigment powder</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErAl2</td>
<td>Pigment powder</td>
<td>59.04</td>
<td>18.92</td>
<td>11.85</td>
</tr>
<tr>
<td></td>
<td>Pigment in glaze</td>
<td>69.70</td>
<td>7.24</td>
<td>23.61</td>
</tr>
</tbody>
</table>

5. Discussion

5.1. Er$_6$MoO$_{12}$ pigment

Orange yellow colours were observed with a variation in intensity on mixing a suitable amount of Er$_2$O$_3$ and MoO$_3$ followed by calcining at the appropriate temperatures ($1200^{\circ}C$ and $1300^{\circ}C$) and soaking times (2 h, 4 h and 6 h). From the X-ray diffraction trace (obtained after calcination at $1200^{\circ}C$, 2 h), Er$_6$MoO$_{12}$ 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$_2$O$_3$ is light pink and hence it was speculated that this colour alteration might be due to the breakdown of Er$_6$MoO$_{12}$ to Er$_2$O$_3$ and MoO$_3$ in the glaze. Er$_2$O$_3$ introduced in the glaze generated the same light pink colour. Therefore it is postulated that the coloured rare earth oxides, such as Nd$_2$O$_3$ 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$_4$O$_{10}$ and Ba$_{0.5}$La$_{0.5}$Na$_{0.5}$Cu$_{0.5}$Si$_2$O$_6$ type pigments

Ba$_{0.5}$La$_{0.5}$Na$_{0.5}$Cu$_{0.5}$Si$_4$O$_{10}$ and Ba$_{0.5}$La$_{0.5}$Na$_{0.5}$Cu$_{0.5}$Si$_2$O$_6$ 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$_4$O$_{10}$ 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$_4$O$_{10}$. Similarly Ba$_{0.5}$La$_{0.5}$Na$_{0.5}$Cu$_{0.5}$Si$_2$O$_6$ was...
obtained by replacing Ba with Ba$_{0.5}$La$_{0.5}$ and Cu with Na$_{0.5}$Cu$_{0.5}$ in the compound BaCuSi$_2$O$_6$. 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$_2$O$_6$ 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$_4$O$_{10}$ 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$_2$O$_6$, BaCuSi$_2$O$_6$ 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$_4$O$_{10}$ was found to consist of two different phases, BaCuSi$_2$O$_6$ and BaCuSi$_4$O$_{10}$. The colour of the BaCuSi$_2$O$_6$ and BaCuSi$_4$O$_{10}$ phases are violet and blue, respectively according to the JCPDS standard. Since from the X-ray diffraction pattern BaCuSi$_2$O$_6$ 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$_3$O$_{10}$ and BaCuSi$_2$O$_6$ 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 the 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$_x$B(2−x−y)Cr$_y$O$_3$, A = rare earth and B = Al

Trials were performed on the perovskite structure A$_x$B(2−x−y)Cr$_y$O$_3$ (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...
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 confirmed that both types of crystals had the same composition. X-ray diffraction pattern of Ba0.5La0.5Na0.5Cu0.5Si2O6 also showed the presence of the phases (a) BaCuSi4O10 and (b) BaCuSi2O6.

- These pigment powders were unstable and light-green colours were observed in the unleaded transparent glaze.

6.3. AxB(2−x−y)Cr3O3 (A = rare earth and B = Al) perovskite-type compound

- AxB(2−x−y)Cr3O3 (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)O3 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