

Rare-earth cuprates for ceramic colouring application—An investigation

Jitendra Kumar Kar^{a,*}, Ron Stevens^b, Christopher R. Bowen^b

^a Carborundum Universal Limited, Industrial Ceramics Division, 47 Sipcot Industrial Complex, Hosur 635126, Tamil Nadu, India

^b Materials Research Centre, Department of Mechanical Engineering, University of Bath, Bath BA2 7AY, UK

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Abstract

The possible use of rare-earth cuprates R_2BaCuO_5 and $R_2Cu_2O_5$ (R = rare earth) type compounds for high temperature (above $1000^\circ C$) ceramic pigment application is presented in this paper. The traditional ceramic powder mixing method was adopted for the manufacture of various samples (pigment powders) used in this study. Yellow-green coloured powders with a variation in the intensity were obtained with R_2BaCuO_5 (R = Sm) at different calcination temperatures (950 – $1050^\circ C$) and soaking time up to 12 h. These powders were then optimized in terms of colour by altering the calcinations temperature. The products with the most attractive colour were obtained with the sample calcined at $1050^\circ C$. The same yellow-green colour powders were observed when Sm was replaced by other rare earth oxides such as Ho, Yb, Er and calcined at the same temperature, except for Y. In the case of the Y addition, a dark green coloured powder was observed. The X-ray diffraction pattern of the samples indicated R_2BaCuO_5 (R = rare earth) to be the major phase present in each case, although traces of CuO and the respective rare earth oxides were still present. For $R_2Cu_2O_5$ (R = Dy), a bluish-green coloured pigment powders with a variation in their intensity were observed when calcined between (950 and $1050^\circ C$) with a 2 h soaking time. The best result (as far as intense colour is concerned) was noticed with the sample calcined at $950^\circ C$. The same bluish-green colour powders were observed when Dy was replaced by other rare earths such as Yb, Ho, Er and Y. SEM micrographs of both types of compounds (R_2BaCuO_5 and $R_2Cu_2O_5$) obtained at various calcination temperatures revealed the presence of agglomerates in the samples, with an average grain size in the range 1 – $3\ \mu m$. All the pigment powders of the type R_2BaCuO_5 with the exception of the Sm-doped materials were unstable at $1070^\circ C$ and produced a bubble rich surface (yttrium being the worst) when introduced into an unleaded commercial transparent glaze. In the case of Sm the yellow-green coloured powder turned to a light green. Similarly all the bluish-green coloured powders were unstable in the glaze except R = Dy and Y. In the case of Dy, a raindrop effect was observed on the surface of the ceramic tiles.

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1. Introduction

Rare-earth cuprates and nickelates from the families $R_2Cu_2O_5$ (the so-called blue phases where R = Tb–Lu, Y, Sc) and R_2BaCuO_5 (the so-called green phases where R = Sm–Gd, Dy–Lu and Y) first attracted attention in connection with the development of the high- T_c superconductors [1–3]. The $R_2Cu_2O_5$ type of compound crystallizes in the orthorhombic space group $Pna2_1$ [4–6]. In this case Cu–O pyramids (CuO_5) are joined by the common edges Cu (1) Cu (2) O_8 dimers. These form zigzag chains along the x -axis. These chains are linked by oxygen atoms forming xy planes, where the Cu–Cu distance

along the y -axis ($\cong 3.5\ \text{\AA}$) is close to the largest one in a chain along the x -axis ($\cong 3.2\ \text{\AA}$). The distances between the planes are $6.5\ \text{\AA}$. There are two non-equivalents four-fold low symmetry positions for the R^{3+} ions in a unit cell. R (1) O_6 and R (2) O_6 distorted octahedra are united in a three-dimensional network. The R_2BaCuO_5 type of compound (except R = Nd) crystallizes in the orthorhombic space group $Pbnm$ [1,2]. Nd_2BaCuO_5 crystallizes in the tetragonal space group $P4/mbm$. The green phases R_2BaCuO_5 (R = Sm–Gd, Dy–Lu and Y) and brown phase Nd_2BaCuO_5 of R_2BaCuO_5 super conducting ceramics contain isolated Cu^{2+} ions interconnected by direct bonds through oxygen. Various Cu–O–O–Cu or Cu–O–R–O–Cu super exchange paths dominate in these compounds depending on the particular R^{3+} ion. It has been proposed that a possible application for these compounds is as new ceramic pigments in lead containing glazes in order to obtain various shades of blues and green [7–9]. The

* Corresponding author.

E-mail address: jitendra_kar@hotmail.com (J.K. Kar).

objective of the current research work is to manufacture these types of pigments using solid-state synthesis method and also to investigate the stability of these pigments during application in the un-lead commercial transparent glaze.

2. Method of preparation of the samples

In the present research work, all the samples have been prepared using the traditional powder mixing 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 medium. Subsequently, the milled powders were dried out using an infrared lamp and then sieved through a 150 μm size sieve. The powders were placed in pure alumina crucibles and subjected to calcination at different temperatures and soaking times. Treibacher AURMET, Austria kindly provided all the rare earth oxides (purity > 99%), CuO (99% pure) was provided by A.C.S. reagent, Aldrich Chemical Company Inc., U.S.A. and BaCO₃ (99% pure, GPR) was supplied by BDH Chemical Limited, England.

2.1. R₂BaCuO₅ type

The first rare earth (R) element to be used was samarium (Sm). The powders were mixed according to the reaction equation given below:



Subsequently the powders were placed in pure alumina crucibles. Two calcining methods were used, one in a crucible with lid and one without. A ramp rate of 300 °C/h and a soaking time of 12 h was used in each case, followed by furnace cooling. The powders were calcined at three different temperatures (950–1050 °C with 12 h soaking) (Table 1) in order to optimize the colour in terms of calcination temperature.

Due to the decomposition of the barium carbonate to barium oxide and carbon dioxide during the calcination, a black substance (possibly due to CuO, which is black in colour) in addition to the yellow-green coloured product, formed at the bottom of the sample when a lid was placed on the crucible. The formation of the black substance can be explained as follows.

In the superconducting lattice copper remains in the 3+ oxidation state due to the oxidation of Cu²⁺ to Cu³⁺. When a lid was placed on the crucible, carbon dioxide (CO₂) from barium carbonate does not entirely escape and creates an inert atmosphere (reduces the oxidizing atmosphere). This subsequently prevents the complete oxidation of Cu²⁺ leaving a large amount

Table 2

Nomenclature of the samples obtained at different calcination temperatures (950–1050 °C with 2 h soaking)

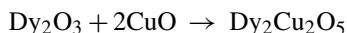
| Sample name | Calcination temperatures (°C) | Soaking time (h) |
|-------------|-------------------------------|------------------|
| B1 | 950 | 2 |
| B2 | 1000 | 2 |
| B3 | 1050 | 2 |

of unreacted CuO. Since CuO is black in colour, black substance was formed in addition to the yellow-green coloured compound.

With no lid applied to the crucible the black substance was hardly produced and the yellow-green coloured powders obtained were then characterized further. These calcined samples were ground and sieved with a 45 μm mesh before further characterization. Nomenclature of the samples obtained after different calcination temperatures is given in Table 1.

2.2. R₂Cu₂O₅ type

In this case the rare earth (R) was dysprosium (Dy) and calcined at similar temperatures (950–1050 °C) and soaking times (both 2 and 12 h), Table 2 in order to optimize the colour. The powders were mixed according to the reaction equation given below:



The powders were then placed in pure alumina crucibles and subjected to firing at temperatures of 950, 1000 and 1050 °C for a holding time of 2 and 12 h (ramp rate of 300 °C/h), followed by furnace cooling. Samples after the 2 h soaking time gave an intense bluish-green colour with slight differences in intensity.

The samples fired at the same temperatures for a 12 h soaking time produced a less intense bluish-green colour compared to 2 h. Nomenclature of the samples obtained at different calcination temperatures with 2 h soaking time is given in Table 2.

3. Experimental techniques

3.1. X-ray diffraction (XRD)

XRD analyses of the samples were carried out on a Philips PW1730/00 diffractometer using monochromatic Cu K α radiation, $\lambda = 0.154060$ nm. A generator voltage and current of 40 kV and 25 mA were used, respectively. X-ray scans were made between 2θ angles of 10° and 80°. A scan speed of 1.0 s per step and a step size of 0.02° were used. The purpose of the XRD was to locate the various phases in the calcined pigment powder samples.

3.2. Particle size

The average particle size of the samples was measured using a Malvern mastersizer X particle size analyzer. This instrument is founded on laser diffraction techniques.

3.3. Spectrophotometry

In the present research work all colour measurements were performed using a Spectra Flash SF600 PLUS spectrophotometer supplied by Datacolor. The diffuse reflectance of the samples at 10 nm intervals within the visible spectrum (360–700 nm) and the colour coordinates ($L^*a^*b^*$), which specify a colour in

Table 1

Name of the sample obtained after different calcination temperatures (950–1050 °C with 12 h soaking)

| Sample name | Calcination temperature (°C) | Soaking time (h) |
|-------------|------------------------------|------------------|
| Sm1 | 950 | 12 |
| Sm2 | 1000 | 12 |
| Sm3 | 1050 | 12 |

uniform colour space can be measured with this instrument. Each colour in the uniform colour space can be denoted by three parameters $L^*a^*b^*$ in rectangular coordinates where

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

3.4. Scanning electron microscopy (SEM)

The SEM used in this study was a JEOL JSM-6310 analytical scanning electron microscope fitted with a 10/85-link microanalysis system manufactured by Oxford Instrument. The SEM was used to detect the surface morphology and grain size of the calcined pigment powders.

3.5. Application of the pigment powders to the glaze

Stability of the pigment powders was tested in commercial transparent lead-less glaze. The glaze was kindly provided by the Ferro Corporation, Stoke on Trent, England (Product No-V7470/A, Lxt 711 frit 900, China clay 100). The precise composition of this glaze could not be obtained for reasons of manufacturing confidentiality of the company.

Glazes were coloured by introducing 8 wt.% of the pigments to the glaze. A homogeneous mixture of the pigment and glaze was achieved by milling the materials constituting the slip for half an hour in a high-density plastic container using zirconia grinding media. The ground mixtures were then sieved through a 100 μm mesh 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 and 0.2 g/cm^2 .

Firings of the glazed samples were 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 and discussion

4.1. $R_2\text{BaCuO}_5$ type

4.1.1. Colour measurement

Colour measurement was carried out on the pigment powder sample (rare earth containing Sm) using a spectrophotometer in order to optimize the colour in terms of calcination temperature. The CIE values $L^*a^*b^*$ are given in Table 3 and the reflectance curves in Fig. 1.

From the reflectance curve and CIE values of the pigment powders (Fig. 1 and Table 3), it could be concluded that the intensity of the colour was a maximum at 1050 °C. It was also seen that increasing the temperature, there is a gradual increase of the absolute value in both b^* and a^* values (Table 3).

Table 3
CIE values of $\text{Sm}_2\text{BaCuO}_5$ pigment powders at various calcination temperatures (950–1050 °C)

| Symbol | Pigment powders | | |
|--------|-----------------|-------|-------|
| | L^* | a^* | b^* |
| Sm1 | 45.14 | −4.09 | 5.56 |
| Sm2 | 46.03 | −4.80 | 6.47 |
| Sm3 | 48.53 | −6.47 | 10.59 |

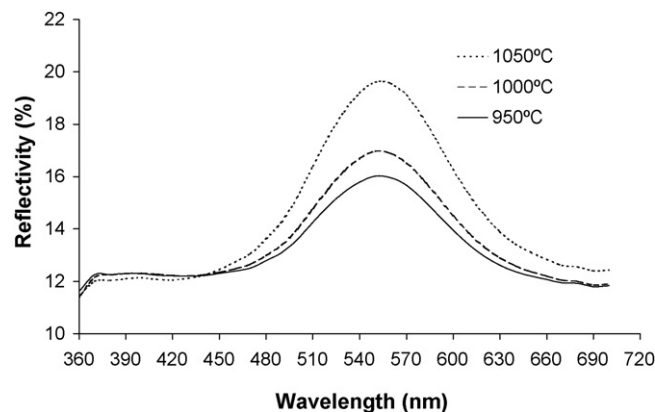
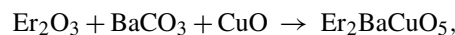
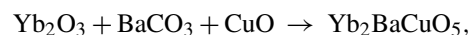


Fig. 1. Diffuse reflectance curves of $\text{Sm}_2\text{BaCuO}_5$ pigment powders at various calcinations temperatures (950–1050 °C) with 12 h soaking.

Subsequently, Sm was replaced by other rare earths (Ho, Yb, Er, Y, and Nd) and was calcined at 1050 °C only for 12 h. The powders were mixed according to the reaction equation given below:



Yellow-green colour powders were obtained with Ho, Yb and Er. Dark green and brown colours were observed for rare earths Y and Nd, respectively. The colour coordinates for these compounds are shown in Table 4. From Table 4, it can be seen that there is an increase in the absolute values of a^* (in negative direction indicating more green) in the glaze compared to the pigment powders. The b^* values indicate the yellow content (positive values of b^*) in the pigment powders and shifts towards blue (negative values of b^*) when put in the glaze.

4.1.2. X-ray diffraction

In order to detect the different phases present in the calcined pigment powder samples, powder X-ray diffraction was carried out. From the XRD traces, the major phases were found to be $R_2\text{BaCuO}_5$ (where R = Ho, Sm, Y and Nd) although traces of CuO were still present. It was also observed that the XRD traces of $R_2\text{BaCuO}_5$ type compounds were similar irrespective of the rare earth content. Typical example of XRD traces of $R_2\text{BaCuO}_5$ type compounds where R = Sm, Nd are given in Figs. 2 and 3.

Table 4
 $L^*a^*b^*$ parameters of the pigment powders and pigments in glaze

| Symbol | Pigment powders | | | Pigments in glaze | | |
|-----------------------------|-----------------|--------|-------|-------------------|--------|-------|
| | L^* | a^* | b^* | L^* | a^* | b^* |
| $\text{Sm}_2\text{BaCuO}_5$ | 48.53 | −6.47 | 10.59 | 67.42 | −19.03 | −0.61 |
| $\text{Ho}_2\text{BaCuO}_5$ | 53.63 | −15.43 | 14.32 | 53.45 | −24.78 | −6.47 |
| Y_2BaCuO_5 | 51.64 | −16.12 | 10.06 | | | |
| $\text{Nd}_2\text{BaCuO}_5$ | 51.84 | 5.51 | 6.91 | 60.31 | −17.63 | −7.63 |

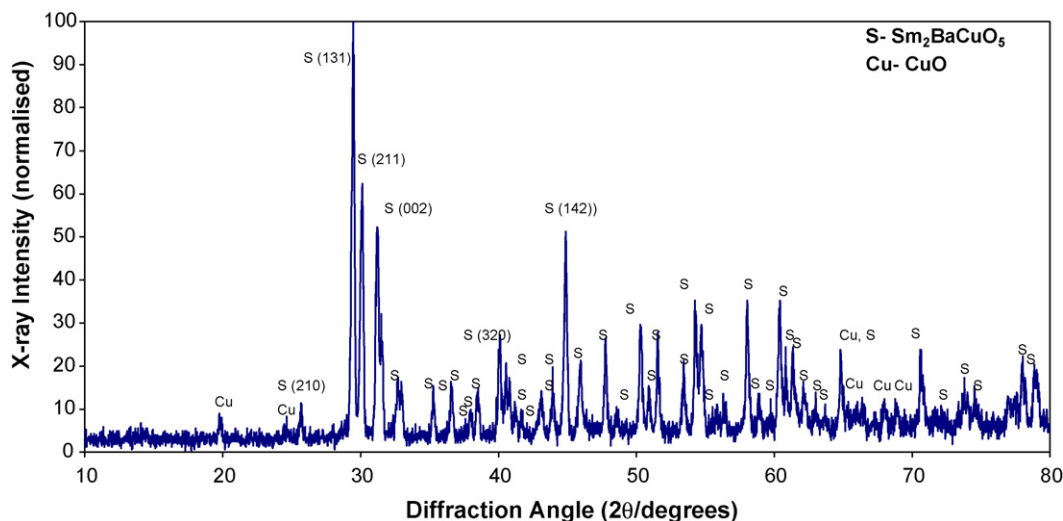


Fig. 2. X-ray diffraction pattern of the $\text{Sm}_2\text{BaCuO}_5$ pigment powder (1050 °C for 12 h).

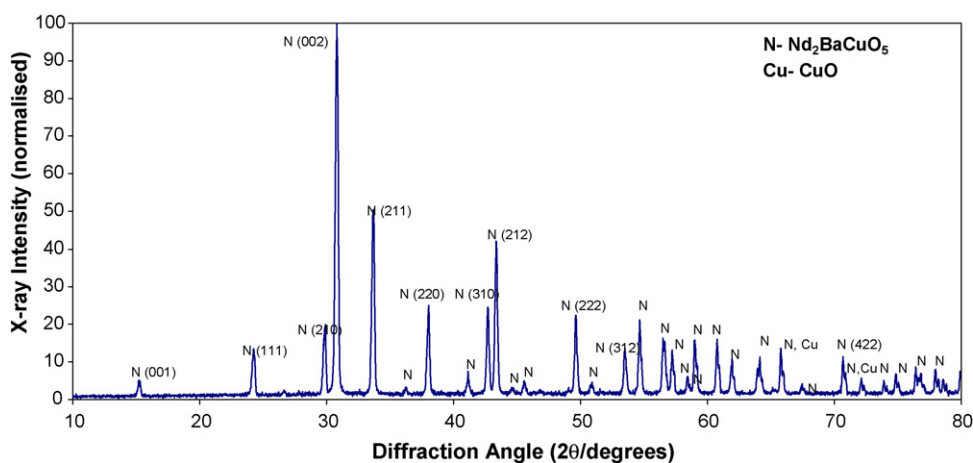


Fig. 3. X-ray diffraction pattern of $\text{Nd}_2\text{BaCuO}_5$ pigment powder (1050 °C for 12 h).

4.1.3. Scanning electron microscopy (SEM)

SEM was carried out on the calcined pigment powder samples in order to find out the surface morphology and the grain size. From the scanning electron microscopy micrographs, Fig. 4, it was evident that the sample contained agglomerates, each composed of small round particles with a grain size of 1–2 μm .

4.1.4. Particle size

Particle sizes of the pigment powder samples (R_2BaCuO_5 , R = Ho, Sm, and Y) after grinding for 1 h are given in Table 5.

Table 5

Particle sizes of all the rare earth cuprate pigment powder samples (R_2BaCuO_5 , R = Sm, Ho, and Y) after grinding for 1 h and $\text{Nd}_2\text{BaCuO}_5$ (after 2 h grinding)

| Sample name | Particle sizes (μm) | | |
|-----------------------------|----------------------------------|----------|----------|
| | $d(0.5)$ | $d(0.1)$ | $d(0.9)$ |
| $\text{Sm}_2\text{BaCuO}_5$ | 11.17 | 4.38 | 29.74 |
| $\text{Ho}_2\text{BaCuO}_5$ | 10.47 | 4.28 | 26.82 |
| Y_2BaCuO_5 | 12.83 | 5.55 | 30.97 |
| $\text{Nd}_2\text{BaCuO}_5$ | 4.03 | 0.28 | 11.82 |

From Table 5, it is seen that, d_{50} varies between 10 and 13 μm , d_{90} varies between 26 and 30 μm and d_{10} varies between 4 and 6 μm .

For $\text{Nd}_2\text{BaCuO}_5$ (after 2 h grinding) the particles lie between 0.28 and 11.82 μm with an average particle size of 4 μm .

4.1.5. Application of the pigment powders onto the glaze

The stability of the yellow-green pigments and brown pigment was tested in an unleaded commercial transparent glaze by addition of 8 wt% of pigment at 1070 °C. The green coloured pigment powders in the case of Sm and Ho turned into light green. The brown coloured pigment powder in the case of Nd also turned into light green in the glaze. Y_2BaCuO_5 gave a bubbled surface in the glaze. It was not possible to carry out colour measurement on Y containing compound after application in the glaze because of the bubbled surface whereas compound-containing Nd completely altered the colour when put in the glaze. The explanation for the presence of bubbles is described in the general discussion. The L^* , a^* and b^* parameters of the pigment powders and pigments in the glaze are given in Table 4. On examination of the values of L^* , a^* and b^* in powder form

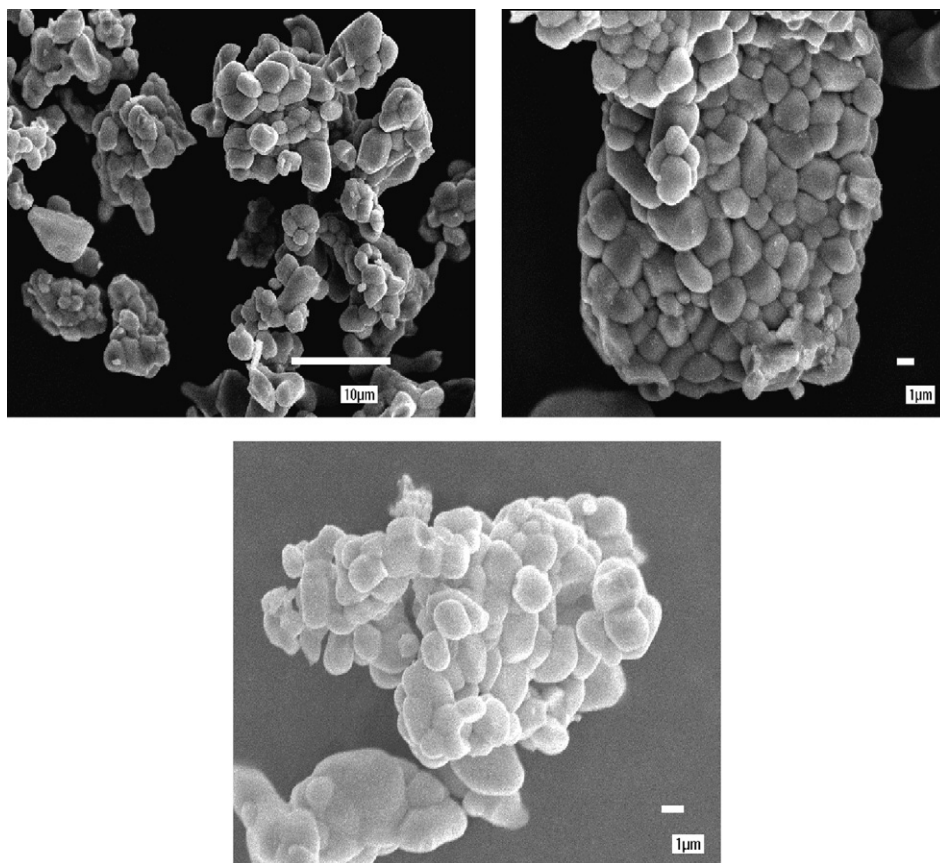


Fig. 4. SEM micrographs of the pigment powder samples at 1050 °C: (a) Y₂BaCuO₅ with 2000×; (b) Y₂BaCuO₅ with 6000×; (c) Ho₂BaCuO₅ with 6000×.

and in the glaze a change in the intensity of the colour in addition to a complete change in the colour in case of Nd₂BaCuO₅ can be noticed.

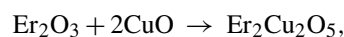
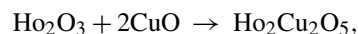
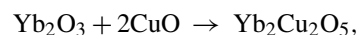
4.2. R₂Cu₂O₅ type

4.2.1. Colour measurement

The *L**, *a** and *b** parameters and the diffuse reflectance spectrum of Dy₂Cu₂O₅ at various calcination temperatures are given in Table 6 and Fig. 5. From Table 6, it was observed that there is a gradual decrease in both *L** and absolute *a** values with increase in temperature whereas *b** values remain almost same. It was also evident that, the most intense colour could be obtained in the compound Dy₂Cu₂O₅ at a temperature of 950 °C with a soaking time of 2 h.

The rare earth Dy was then replaced by other rare earths (Yb, Ho, Y and Er) and calcined at the same temperature and soaking

time. The composition for which the powders were mixed is given below:



A similar bluish-green colour was observed in each case.

CIE values and the diffuse reflectance spectrums of the various rare earth cuprate powders are given in Table 7 and Fig. 6. From Table 7, it is seen that there is a steady increase in the *b** value of the rare earth cuprate pigment powders containing rare

Table 6
*L***a***b** parameters of Dy₂Cu₂O₅ pigment powders at different calcination temperatures (950–1050 °C) with 2 h soaking

| Symbol | Pigment powders | | |
|--------|-----------------|-----------|-----------|
| | <i>L*</i> | <i>a*</i> | <i>b*</i> |
| B1 | 49.63 | −15.21 | −1.92 |
| B2 | 48.37 | −14.08 | −2.00 |
| B3 | 47.12 | −12.58 | −1.88 |

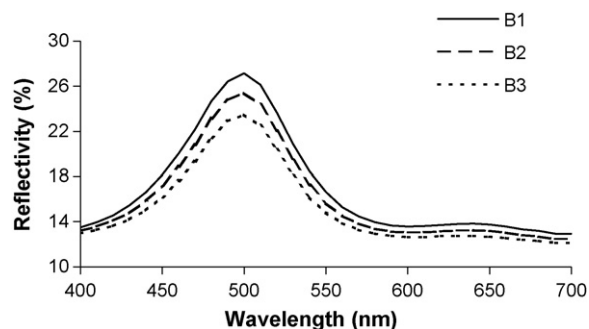


Fig. 5. Diffuse reflectance curves of Dy₂Cu₂O₅ pigments at different calcination temperatures (950–1050 °C) with 2 h soaking time.

Table 7

$L^*a^*b^*$ parameters of various rare earth cuprate pigment powders at the same calcination temperature (950 °C) and soaking times (2 h)

| Formula | Pigment powders | | |
|------------------------------------|-----------------|--------|-------|
| | L^* | a^* | b^* |
| $\text{Yb}_2\text{Cu}_2\text{O}_5$ | 51.22 | -20.25 | -2.10 |
| $\text{Ho}_2\text{Cu}_2\text{O}_5$ | 49.61 | -17.47 | -2.03 |
| $\text{Er}_2\text{Cu}_2\text{O}_5$ | 47.73 | -13.3 | -2.66 |
| $\text{Dy}_2\text{Cu}_2\text{O}_5$ | 49.63 | -15.21 | -1.92 |
| $\text{Y}_2\text{Cu}_2\text{O}_5$ | 51.10 | -16.89 | -4.15 |

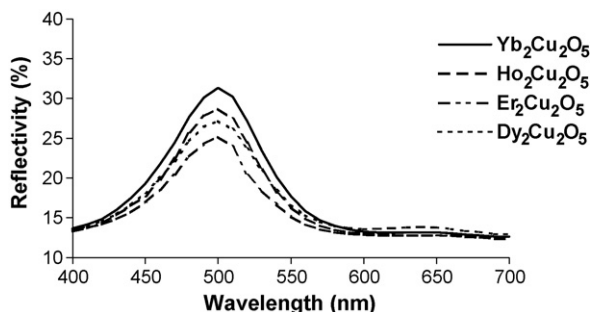


Fig. 6. Diffuse reflectance spectra of various rare earth cuprate powders (at the same calcinations temperature 950 °C with 2 h soaking).

earth in the order, Dy, Ho, Yb, Er and Y, respectively. No regular trend was observed with L^* and absolute a^* values but they vary between 49–51 and 13–20, respectively.

4.2.2. X-ray diffraction

Calcined powder samples were subjected to X-ray diffraction to determine the different phases. From Fig. 7, $\text{Dy}_2\text{Cu}_2\text{O}_5$ was found to be the major phase, although traces of unreacted Dy_2O_3 were still present. Similar diffraction patterns were observed by increasing the temperature to 1000 and 1050 °C. Similarly from the XRD traces of the samples, Figs. 8 and 9, rare-earth cuprates

$\text{R}_2\text{Cu}_2\text{O}_5$ (R = Ho and Y) were identified as the main phase in each case, although traces of CuO were still observed indicating incomplete reaction.

4.2.3. Scanning electron microscopy (SEM)

The SEM micrograph of the sample ($\text{Dy}_2\text{Cu}_2\text{O}_5$ pigment powder obtained at 950 °C for 2 h) is shown in Fig. 10 and revealed the presence of rounded particles having average grain size 1–2 μm .

4.2.4. Particle size

The pigment powder samples obtained after calcination was sieved through a 45 μm sieve and the particle size measurement were then carried out. The particle sizes of different samples are given in Table 8. From Table 8, it is evident that the average particle size (d_{50}) various rare earth cuprate pigment powders vary between 10 and 13 μm , d_{90} between 22 and 32 and d_{10} between 4 and 6 μm .

4.2.5. Application in the glaze

Stability of the pigments was tested in an unleaded commercial transparent glaze. Pigments were applied at a level of 8 wt% of the dry glaze. $\text{Ho}_2\text{Cu}_2\text{O}_5$ and $\text{Yb}_2\text{Cu}_2\text{O}_5$ gave a bubble rich surface when fired in the glaze and the explanations are given in the general discussion parts. The L^* , a^* and b^* parameters of $\text{Dy}_2\text{Cu}_2\text{O}_5$ and $\text{Y}_2\text{Cu}_2\text{O}_5$ are given in Table 9 and Fig. 6. From both the table and figure it is observed that when the pigment powders are put in the glaze, there is an increase in the b^* value whereas a^* values remain same. The increase in the b^* values in the negative axis indicates that the glazed tiles are more bluish in colour compared to the raw pigment powders.

5. Mechanism of colour formation

The creation of colour in $\text{R}_2\text{BaCu}_2\text{O}_5$ and $\text{R}_2\text{Cu}_2\text{O}_5$ type compounds is considered to be due to the crystal field splitting of

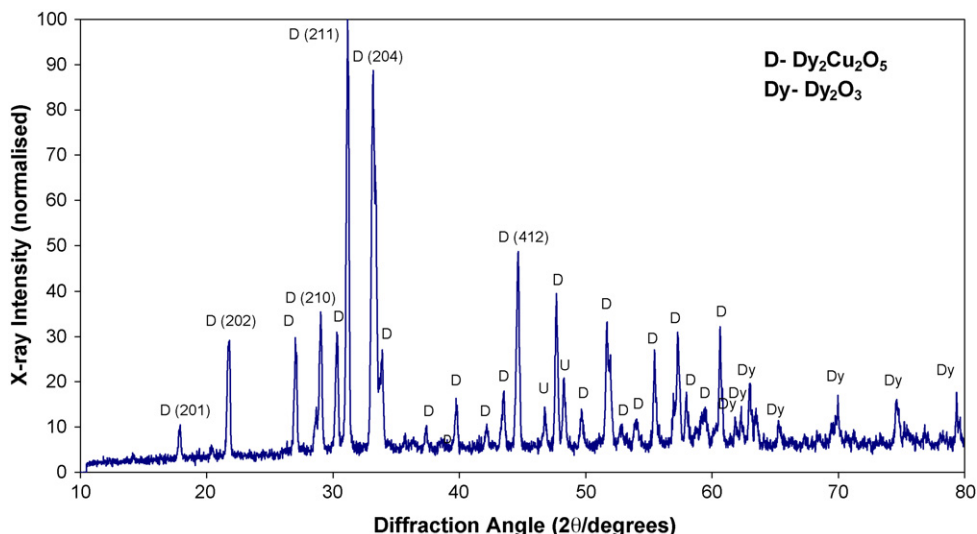
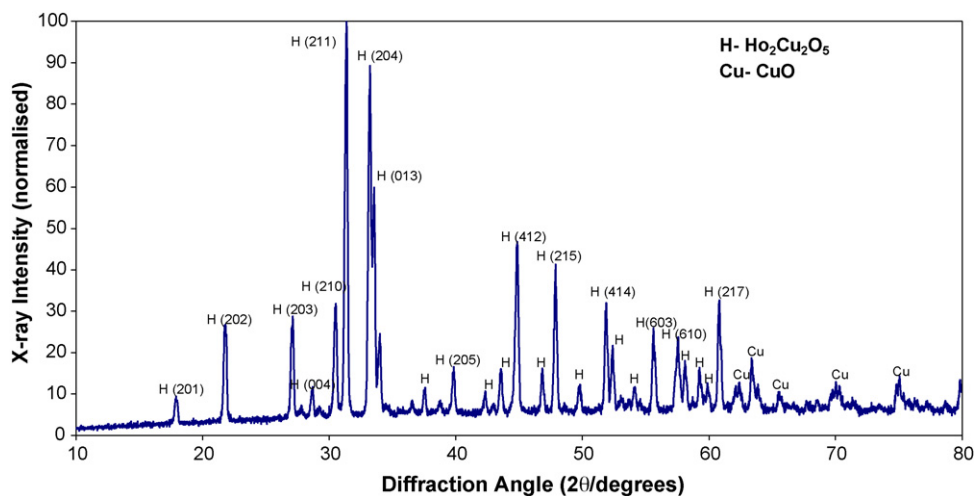
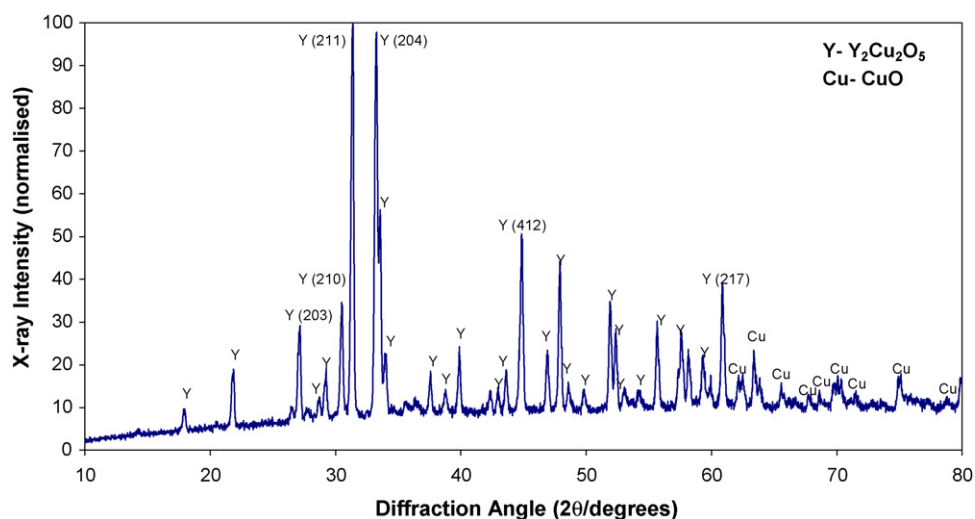
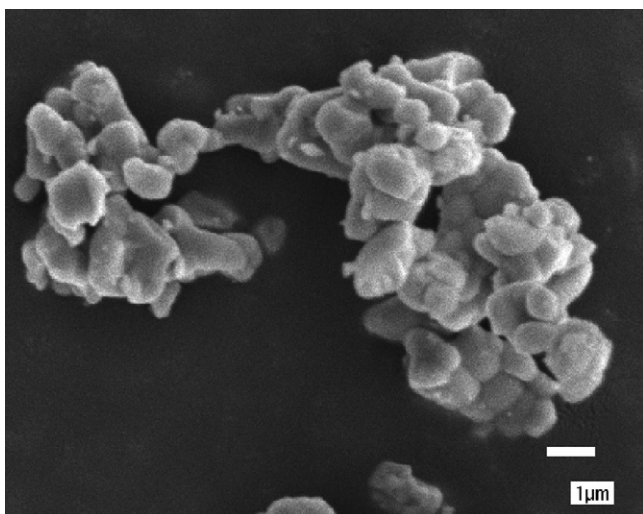


Fig. 7. X-ray diffraction pattern of $\text{Dy}_2\text{Cu}_2\text{O}_5$ pigment powder (950 °C for 2 h).

Fig. 8. X-ray diffraction pattern of $\text{Ho}_2\text{Cu}_2\text{O}_5$ pigment powder (950°C for 2 h).Fig. 9. X-ray diffraction pattern of $\text{Y}_2\text{Cu}_2\text{O}_5$ pigment powder (950°C for 2 h).Fig. 10. Typical SEM micrograph of $\text{Dy}_2\text{Cu}_2\text{O}_5$ pigment powder obtained at 950°C for 2 h.

the d-orbitals of Cu^{2+} . It is believed that the d–d electronic transitions give rise to the colour in both cases. The magnitude of the splitting of the d-orbitals into appropriate energy levels was dissimilar in both types of compounds because 3d-electrons would be expected to interact differently with the surrounding environment (due to the changes in geometrical arrangement). Hence, the changes in the colour were observed. The same colour with a variation in the intensity was noticed

Table 8

Particle sizes of the different rare earth cuprate pigment powders (at the same calcinations temperature 950°C with 2 h soaking)

| Sample name | Particle sizes (μm) | | |
|------------------------------------|----------------------------------|----------|----------|
| | $d(0.5)$ | $d(0.1)$ | $d(0.9)$ |
| $\text{Dy}_2\text{Cu}_2\text{O}_5$ | 11.76 | 4.28 | 25.07 |
| $\text{Ho}_2\text{Cu}_2\text{O}_5$ | 10.09 | 4.26 | 22.55 |
| $\text{Yb}_2\text{Cu}_2\text{O}_5$ | 11.87 | 5.10 | 24.64 |
| $\text{Y}_2\text{Cu}_2\text{O}_5$ | 13.38 | 5.97 | 31.37 |

Table 9
 $L^*a^*b^*$ parameters of the $\text{Dy}_2\text{Cu}_2\text{O}_5$ and $\text{Y}_2\text{Cu}_2\text{O}_5$ pigment powders, and also in the glaze

| Sample name | Pigment powders | | | Pigments in glaze | | |
|------------------------------------|-----------------|--------|-------|-------------------|--------|-------|
| | L^* | a^* | b^* | L^* | a^* | b^* |
| $\text{Dy}_2\text{Cu}_2\text{O}_5$ | 49.63 | -15.21 | -1.92 | 53.71 | -15.08 | -9.71 |
| $\text{Y}_2\text{Cu}_2\text{O}_5$ | 51.10 | -16.89 | -4.15 | 46.27 | -11.12 | -3.48 |

by changing the rare earths in one type of compound. This is again considered to be due to the slight change in the energy levels (due to the crystal field splitting) caused by individual rare earths attached to the compound altering the energy of the bonds.

6. Stability of the pigments manufactured and general discussion

R_2BaCuO_5 (R=rare earth) and $\text{R}_2\text{Cu}_2\text{O}_5$ (R=rare earth) type pigments have been prepared using a solid-state synthesis method. Intense yellow-green colour powders were obtained with R_2BaCuO_5 where R=rare earth, except Y where a dark green coloured powder was observed. Bluish-green powders were obtained with $\text{R}_2\text{Cu}_2\text{O}_5$ (R=rare earth). Y_2BaCuO_5 pigment powder was put into the commercial unleaded transparent glaze to test its stability. It gave a bubble rich surface, which contradicts the results reported by Fernandez et al. [10] where they claimed Y_2BaCuO_5 as a stable pigment in the specially designated glaze (lead containing glaze). They also mentioned that the colour of the pigment powder turned into light green in the glaze which means its not a stable pigment. The diversity in the results may be due to the difference in the glaze. Each glaze has a different composition and the presence of some elements in the glaze, even if in small amounts, can react with the pigment to produce a bubble rich surface. It was difficult to know the precise composition of the glaze because of the manufacturing secrecy of the company and therefore hard to predict the exact cause of the bubbles. Similarly intense yellow-green coloured powders turned into light green in the glaze, which disagrees with the results reported by Thierry [11,12]. This may again be due to the difference in the glaze and processing method of the pigments. Bluish-green colours also were not stable in the glaze except the compounds containing Dy and Y as the rare earth element.

All the pigment powders of the type R_2BaCuO_5 with the exception of the Sm-doped materials were unstable and gave a bubble rich surface (yttrium being the worst) in the unleaded commercial transparent glaze. In the case of Sm the yellow-green coloured powder turned to a light green. This may be due to the breakdown of some of the $\text{Sm}_2\text{BaCuO}_5$ resulting in a lesser amount of Cu^{2+} ion in the compound and hence producing a lighter colour. Similarly all the bluish-green coloured powders were unstable in the glaze except R=Dy and Y. In the case of Dy, a raindrop effect was observed on the surface of the ceramic tiles. This stability problem may

well be due to the reaction of the pigment with certain elements/compounds present in the glaze with the evolution of oxygen.

7. Conclusions

- (1) Intense yellow-green and bluish-green colour powders were obtained from the R_2BaCuO_5 and $\text{R}_2\text{Cu}_2\text{O}_5$ type compounds (R = rare earth) respectively for a range of calcination temperature and soaking times. In the case of Y and Nd (R_2BaCuO_5 type) dark green and brown colour powders were observed.
- (2) From the X-ray diffraction patterns of the samples (both types of compounds), rare-earth cuprates were found to be the major phase although traces of CuO and sometimes rare earth oxides were still present.
- (3) The scanning electron microscopy micrographs of both R_2BaCuO_5 and $\text{R}_2\text{Cu}_2\text{O}_5$ type of compound revealed the presence of agglomerates; each composed of small round particles with a grain size of 1–2 μm .
- (4) All the pigment powders of the type R_2BaCuO_5 with the exception of the Sm-doped materials were unstable and gave a bubble rich surface (yttrium being the worst) in the unleaded commercial transparent glaze. In the case of Sm the intense yellow-green coloured powder turned to a light green. Bluish-green colours (obtained from $\text{R}_2\text{Cu}_2\text{O}_5$ type of compound) also were not stable in the glaze except the compounds containing Dy and Y as the rare earth element. In the case of Dy, a raindrop effect was observed on the surface of the ceramic tiles. This can be considered as a limitation of these compounds for application in unleaded commercial transparent glaze.
- (5) The generation of colour in R_2BaCuO_5 and $\text{R}_2\text{Cu}_2\text{O}_5$ type compounds is considered to be due to the crystal field splitting of the d-orbitals of Cu^{2+} followed by d–d electronic transitions. The changes in the colour in both types of compound was observed because of the difference in the magnitude of the splitting of the d-orbitals into appropriate energy levels because 3d-electrons would be likely to interact differently with the neighboring environment (due to the changes in geometrical arrangement).

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