Green colored nano-pigments derived from Y 2 BaCuO 5 : NIR reflective coatings

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Green colored nano-pigments derived from $Y_2BaCuO_5$: NIR reflective coatings

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Abstract

A green colored nano-pigment $Y_2BaCuO_5$ with impressive near infra-red (NIR) reflectance (61% at 1100 nm) was synthesized by a nano-emulsion method. The developed nano-crystalline powders were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), UV–vis–NIR diffuse reflectance spectroscopy and CIE-L*a*b* 1976 color scales. The XRD and Rietveld analyses of the designed pigment powders reveal the orthorhombic crystal structure for $Y_2BaCuO_5$, where yttrium is coordinated by seven oxygen atoms with the local symmetry of a distorted trigonal prism, barium is coordinated by eleven oxygen atoms, and the coordination polyhedron of copper is a distorted square pyramid [CuO$_5$]. The UV–vis spectrum of the nano-pigment exhibits an intense d–d transition associated with CuO$_5$ chromophore between 2.1 and 2.5 eV in the visible domain. Therefore, a green color has been displayed by the developed nano-pigment. The potential utility of the nano-pigments as “Cool Pigments” was demonstrated by coating on to a building roofing material like cement slab and PVC coatings.

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1. Introduction

The near infra-red (NIR) reflecting inorganic pigments have been widely employed in the defence, construction, plastic and ink industries [1]. NIR reflective pigments coated on the external walls and roofs of a building have been reported to reduce energy consumption by making the interior of the building cooler [2,3]. These pigments absorb in the visible region and reflect NIR diffusive reflectance (61% at 1100 nm) has not been investigated. Recently there have been a few reports of colored rare earth based NIR reflecting pigments as viable alternatives to existing toxic NIR reflecting colored pigments [14–19]. Thus there is a strong incentive to develop novel colored, NIR reflecting inorganic pigments that are less hazardous to health and environment.

In this paper, NIR reflective nanocrystalline $Y_2BaCuO_5$ green pigment was obtained by a nano-emulsion method and fully characterized. A comparison of optical properties was also made between nano-crystalline $Y_2BaCuO_5$ green pigment, and its corresponding micron-sized pigment. Finally, the coloring performance of the designed pigment is evaluated by applying on to roofing materials like concrete cement blocks and plastic materials.
2. Experimental section

2.1. Materials and methods

The chemical reagents utilized are Y(NO$_3$)$_3$·6H$_2$O (purity; 99.8%, Sigma Aldrich), Cu(NO$_3$)$_2$·2.5H$_2$O (purity; 98%, Alfa Aesar), Ba(NO$_3$)$_2$ (purity; 99.9%, Sigma Aldrich), cetyltrimethylammonium bromide (CTAB) (purity; 99.9%, Sigma Aldrich), 1-butanol (purity; 99.9%, Sigma Aldrich), Na(PO$_3$)$_6$ (calgon: Nice chemicals Pvt. Ltd.) [17]. All other chemicals used in the present work are of analytical grade.

2.1.1. Synthesis of Y$_2$BaCuO$_5$ by nano-emulsion method

The nano-pigment Y$_2$BaCuO$_5$ was synthesized according to the procedure described elsewhere [20]. 0.2 M aqueous solution of yttrium nitrate, barium nitrate and copper nitrate were mixed, respectively in a mole ratio of 2:1:1. The emulsion system was used in the present study consisting of a cationic surfactant, CTAB, with 1-butanol as co-surfactant and n-octane as the solvent. The butanol/CTAB ratio was maintained as 0.75. Nano-emulsion I was prepared by mixing surfactant phase (CTAB + 1-butanol), solvent (n-octane) and aqueous phases (0.2 M nitrate solutions of Y, Ba, and Cu) in a ratio of 32:58:10 (weight fraction). The nano-emulsion II was prepared by mixing surfactant phase (CTAB + 1-butanol), solvent (n-octane) and ammonium oxalate (0.25 M) in the same weight fraction as described above. Then, nano-emulsion I was slowly added into nano-emulsion II and stirred for 2 h. The resulting precipitate was first washed with a 1:1 mixture of methanol and chloroform and finally washed with ethanol and dried in air at 50 °C. The dried precipitates were then calcined in platinum crucibles at 900 °C for 2 h in air atmosphere and characterized.

2.1.2. Synthesis of Y$_2$BaCuO$_5$ by calcination method

The green pigment was synthesized by conventional ceramic method [13] in the presence and absence of mineralizers. Stoichiometric ratios of the oxides or carbonates of the precursors were weighed and transferred to an agate mortar and homogenized by wet milling with acetone for 30 min. The resultant powders were then calcined in platinum crucibles in a Nabertherm high temperature electric furnace at a temperature of 1050 °C for 12 h in air atmosphere, followed by auto-cooling inside the furnace. The

2.2. Rietveld refinement

Table 1: Rietveld refinement parameters of Y$_2$BaCuO$_5$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{eq}$ (Å$^2$)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1</td>
<td>4c</td>
<td>0.117(1)</td>
<td>0.289(1)</td>
<td>0.25</td>
<td>0.009(1)</td>
<td>1</td>
</tr>
<tr>
<td>Y2</td>
<td>4c</td>
<td>0.397(1)</td>
<td>0.074(1)</td>
<td>0.25</td>
<td>0.013(1)</td>
<td>1</td>
</tr>
<tr>
<td>Ba</td>
<td>4c</td>
<td>0.930(1)</td>
<td>0.905(1)</td>
<td>0.25</td>
<td>0.013(1)</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>4c</td>
<td>0.714(1)</td>
<td>0.658(1)</td>
<td>0.25</td>
<td>0.017(1)</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>8d</td>
<td>0.163(1)</td>
<td>0.433(1)</td>
<td>0.993(1)</td>
<td>0.006(2)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>8d</td>
<td>0.356(1)</td>
<td>0.227(1)</td>
<td>0.501(1)</td>
<td>0.011(2)</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>4c</td>
<td>0.083(1)</td>
<td>0.102(1)</td>
<td>0.25</td>
<td>0.004(2)</td>
<td>1</td>
</tr>
</tbody>
</table>

Space group: Pbnm; a = 7.134(1) Å, b = 12.184(1) Å, c = 5.661(1) Å.
Reliability Factors (%): R$_{p}$ = 3.58, R$_{wp}$ = 4.82, R$_{f}$ = 8.12, $\chi^2$ = 1.73.
Bond Lengths (Å): Y1–O1 = 2.303(1) × 2, Y1–O2 = 2.347(1) × 2, Y1–O3 = 2.354(1) × 2, Y2–O1 = 2.398(1) × 2, Y2–O2 = 2.358(1) × 2, Y2–O3 = 2.261(1).
Ba–O1 = 3.069(1) × 2, Ba–O1 = 3.263(1) × 2, Ba–O2 = 2.951(1) × 2, Ba–O2 = 3.011(1) × 2.
Ba–O3 = 2.834(1) × 2, Ba–O3 = 2.645(1).
Cu–O1 = 1.978(1) × 2, Cu–O2 = 2.050(1) × 2, Cu–O3 = 2.224(1).
heating of the furnace was programmed to increase the temperature at 5 °C/min. The final products were ground in an agate mortar so as to refine and homogenize the particle size. The green pigment Y$_2$BaCuO$_5$ was also prepared in the presence of different mineralizers like NaF, NaCl, with a view to understand their influence on the calcination temperature and optical properties. The mineralizer was used at 1 wt.% level on the total weight of the precursors.

2.1.3. Preparation of nano-coatings

The nano-green pigment, Y$_2$BaCuO$_5$, was used to prepare NIR reflecting coatings on a concrete cement block and plastic [poly(vinyl chloride) (PVC), Sigma Aldrich]. The coating was accomplished by a two-step process according to the procedures described earlier [3,17]. In the first step, the concrete cement block/PVC surface is pre-coated with TiO$_2$, an inexpensive white pigment possessing high NIR reflectance. In the second step, the designed typical pigment is applied to the pre-coated substrate material. The nano-pigment samples were ultrasonicated (Vibronics, 250 W, India) for 10 min to ensure the complete dispersion of the pigment particles in an acrylic–acrylan emulsion. The pigment to binder ratio was maintained as 1:1 by weight. The resulted viscous solution was coated on the concrete cement block/PVC surface and was allowed to dry in air. The thickness of the pigment coating on the concrete cement block/PVC surface was measured by employing LEICA DMRX optical microscope.

2.2. Characterization techniques

The crystalline nature and phase purity of the synthesized green pigment samples were characterized by powder X-ray diffraction using the conventional powder techniques in a diffractometer (Philips X’pert Pro) with Ni–filtered Cu K$_\alpha$ ($\lambda = 0.154060$ nm) radiation. Data were collected by step scanning over a 2θ range from 10 to 70° with a step size of 0.08° and 5 s counting time at each step. Powder X-ray diffraction (PXRD) data for structure refinement were collected by means of a PANalytical X’pert Diffractometer operated at 40 kV and 30 mA using Ni-filtered Cu K$_\alpha$ radiation in the 2θ range 10–120° with a step size of 0.02° and step duration of 50 s. Rietveld refinement of the crystal structure was carried out with the program GSAS [21]. The patterns were typically refined for lattice parameters, atomic coordinates, scale, factors, back ground (Fourier polynomial back ground function), pseudo-Voigt (U, V, W and X) and isothermal temperature factors ($U_{iso}$).

The optical properties of the powdered pigment samples were measured (380–780 nm) with a UV–vis Spectrophotometer (Shimadzu UV-3600 with an integrating sphere attachment, ISR-3100) using barium sulfate as a reference. The measurement conditions were as follows: an illuminant D65, 10° complementary observer and measuring geometry d/8°. The color coordinates were determined by coupling with analytical software (UVPC Color Analysis Fig. 4. SEM images of Y$_2$BaCuO$_5$ green pigment (a) calcined at 1050 °C/12 h and (b) in the presence of mineralizer NaCl, calcined at 900 °C/12 h.

Fig. 5. TGA analysis of nano-emulsion precipitates.

Fig. 6. XRD patterns of Y$_2$BaCuO$_5$ green pigment synthesized by different methods. (NE represents nano-emulsion method, SS represents solid state method).
Personal Spectroscopy Software V3, Shimadzu) to the UV-3600 spectrophotometer. The CIE 1976 L’*a’*b’* colorimetric method was used, as recommended by the Commission Internationale de l’Eclairage (CIE)[22]. In this method, \( L^* \) is the color lightness (\( L^* = 0 \) for black and \( L^* = 100 \) for white), \( a^* \) is the green (–)red (+) axis, and \( b^* \) is the blue (–)yellow (+) axis. The parameter \( C^* \) (chroma) represents saturation of the color and is defined as

\[
C^* = \sqrt{(a^*)^2 + (b^*)^2}.
\]

The hue angle, \( h^* \), is expressed in degrees and ranges from 0 to 360° and is calculated by using the formula

\[
h^* = \tan^{-1}(b^*/a^*).\]

For each colorimetric parameter of a sample, measurements were made in triplicate and an average value was taken as the result. Typically, for a given sample, the standard deviation of the measured CIE \( L^*a^*b^* \) values is less than 0.10, and the relative standard deviation \(<1\%\), indicating that the measurement error can be ignored.

The near-infrared reflectance spectra of the powdered pigment samples and the pigment coated concrete cement block were recorded with a UV–vis–NIR spectrophotometer (Shimadzu, UV-3600 with an integrating sphere attachment, ISR 3100) using poly-tetrafluoroethylene (PTFE) as a reference. Optical measurements were carried out in the 700–2500 nm range.

The NIR solar reflectance \( (R^*) \) in the wavelength range from 700 to 2500 nm was calculated according to ASTM standard number E891–87 as reported elsewhere [6,23,24]. The NIR reflectance or the fraction of solar radiation incident at wavelengths between 700 and 2500 nm that is reflected by a surface is the irradiance-weighted average of its spectral reflectance, \( r(\lambda) \), and can be determined using the relationship

\[
R^* = \frac{\int_{700}^{2500} r(\lambda) i(\lambda) d\lambda}{\int_{700}^{2500} i(\lambda) d\lambda}
\]

where \( r(\lambda) \) is the experimentally obtained spectral reflectance (Wm\(^{-2}\)) and \( i(\lambda) \) is the solar spectral irradiance (Wm\(^{-2}\) nm\(^{-1}\)) obtained from ASTM standard E891–87.

The thermal stability of the colorant was checked in the temperature range of 50–1000 °C by SII Nanotechnology Inc., thermo gravimetric/differential thermal analysis (TG/DTA) 6200 in nitrogen atmosphere. Particle size distribution analysis of the pigment sample developed by calcination route was performed in water medium with calgon as the dispersing agent using the Laser Scattering Particle Size Distribution Analyzer (CILAS 930 Liquid). The samples were ultrasonically homogenized for 240 s during measurement and the signal was evaluated on the basis of Fraunhofer bending. Dynamic Light Scattering experiment was conducted using Malvern Instruments Zeta Sizer nano Zis Model No: ZEN 3600 to determine the particle size of the nano-pigment. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to determine the morphology and particle size. TEM analyses were done on a JEOL 2010 (300 kV). The morphology of the synthesized samples was recorded on a scanning electron microscope (SEM) JEOL JSM–5600 model, with an acceleration voltage of 15 kV.

3. Results and discussion

3.1. Structure and morphology analysis of \( \text{Y}_2\text{BaCuO}_5 \) by solid state method

Rietveld refinement of the crystal structure from powder X-ray diffraction (XRD) data indicates that the developed \( \text{Y}_2\text{BaCuO}_5 \) compound by conventional ceramic method (calcined at 1050 °C for 12 h in air) is essentially a single phase of \( \text{Y}_2\text{BaCuO}_5 \) with an orthorhombic crystal system (Fig. 1, Table 1). Its space group is
Pnma (Z = 4) with lattice parameters $a = 7.134(1)$ Å, $b = 12.184(1)$ Å, $c = 5.661(1)$ Å, which are in good agreement with the earlier reports [25,26]. In this orthorhombic structure, the copper ions are situated in distorted square pyramids [CuO$_5$], connected by Y$_2$O$_{11}$ groups, which are formed from two monocapped trigonal prisms [Y$_7$], sharing a triangular face as can be seen from Fig. 2. The Ba$^{2+}$ is eleven coordinated with oxygen atoms, giving rise to irregular polyhedra.

The influence of mineralizers (NaF/NaCl) on the calcination temperature of Y$_2$BaCuO$_5$ has been investigated and the respective XRD patterns are displayed in Fig. 3. The pigment sample calcined at 1050 °C for 12 h is found to be crystalline and phase pure and the XRD profile can be very well indexed to an orthorhombic structure. Most importantly, the presence of mineralizers activates the formation of an orthorhombic phase of Y$_2$BaCuO$_5$ at a relatively lower temperature of 900 °C for 12 h. Thus it can be concluded that the presence of mineralizers has a profound influence in bringing down the calcination temperature of Y$_2$BaCuO$_5$ green pigment (1050–900 °C). The homogeneous and crystalline nature of the Y$_2$BaCuO$_5$ sample can also be seen from the SEM photographs (Fig. 4).

3.2. Structure and morphology analysis of Y$_2$BaCuO$_5$ by nano-emulsion method

A typical thermogram is depicted in Fig. 5 for the precipitate ([Y$_2$BaCu oxalate]) produced by the nano-emulsion method. For the nano-emulsion product, the initial weight loss occurred between 30 and 120 °C corresponding to the dehydration of precipitates. The second weight loss is attributed to the excess surfactant cetyltrimethylammonium bromide (CTAB) decomposition, which occurred around 280 °C. The third loss was attributed to oxalate decomposition, which occurred in the temperature range of 300–650 °C. Finally, a small weight loss above 650 °C may be due to the decomposition of barium carbonate [27]. A bright green pigment was obtained after heat treatment of the ([Y$_2$BaCu]
oxalate] precipitate at 900 °C for 2 h. This temperature was lower than the normal solid state Y2BaCuO5 phase formation temperature (without mineralizer) of 1050 °C. The XRD pattern of the typical green pigment is shown in Fig. 6, and indicates the formation of single phase of Y2BaCuO5 with an orthorhombic crystal system. All the diffraction peaks are broadened, indicating samples falls within the nano domain. The average crystallite size calculated from the Scherrer equation is 46 nm. The morphology and particle sizes of the developed pigment powders can be observed by TEM. As shown in Fig. 7(a), the pigment samples are granular in nature and present a homogeneous nano scale particle size. Excellent dispersion is observed with narrow grain sizes with the distribution in the range of 60–100 nm. Diffraction pattern of the powder showed the products were polycrystalline, as displayed in Fig. 7(b). The energy dispersive spectral (EDS) analysis of the typical nano-pigment sample is given in Fig. 8 and the results demonstrated the composition of the Y2BaCuO5 particles (yttrium: barium: copper ratio = 2:1:1). From the dynamic light scattering method (DLS measurement), it is evident that the developed pigment particles have an average particle size of 50 nm (Fig. 9). These results are in good agreement with crystallite sizes calculated by the XRD technique.

3.3. Diffuse reflectance and chromatic properties of Y2BaCuO5 pigment powders

To understand the origin of the green color of the developed pigment powders, the diffuse reflectance spectrum of Y2BaCuO5 has been measured and the data is depicted in Fig. 10. The results demonstrated that the optical reflectance spectrum of Y2BaCuO5 exhibits a broad band at 680 nm and a low energy shoulder at 850 nm. From the crystal field energy levels for d-orbitals in the square pyramidal (C4v) symmetry of Cu2+, the band maximum at 680 nm can be assigned to the dxy/dx²−y² electronic transition and the shoulder at 850 nm can be due to dz²/dx²−y² transition. Further, the presence of high energy maximum in the optical absorption spectrum of Y2BaCuO5 indicates the local symmetry of Cu2+ in Y2BaCuO5 is a distorted square pyramid, which is in good agreement with the crystal structure analyzed by Rietveld refinement. The absence of absorption in the 2.1–2.5 eV (green region) of the spectrum results in the green color (Fig. 11). It is interesting to note that the reflectance of the nano-pigment is about 2 fold higher than that of the pigment sample derived from solid state ceramic route. Although the XRD profiles of the green pigments developed by nano-emulsion as well as by ceramic methods are identical, the diffuse reflectance data indicate that the nano-emulsion samples of Y2BaCuO5 formed by aggregates of small particles show a brighter green color due to their greater surface light reflection.

Figs. 12 and 13 illustrate the NIR reflectance and the corresponding NIR solar reflectance spectra of Y2BaCuO5 green pigment samples developed by different methods. The average reflectance

![Fig. 12. NIR reflectance spectra of Y2BaCuO5 green pigment synthesized by different methods. (NE represents nano-emulsion method, SS represents solid state method).](image1)

![Fig. 13. NIR solar reflectance spectra of Y2BaCuO5 green pigment synthesized by different methods. (NE represents nano-emulsion method, SS represents solid state method).](image2)

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color coordinates</th>
<th>Band gap (eV)</th>
<th>NIR reflectance at 1100 nm</th>
<th>NIR solar reflectance R' (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y2BaCuO5</td>
<td>L* a* b* C* h0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>58.51 –31.36 20.98 37.73 146</td>
<td>2.35</td>
<td>41</td>
<td>35</td>
</tr>
<tr>
<td>NE</td>
<td>67.08 –33.33 21.59 39.71 147</td>
<td>2.33</td>
<td>61</td>
<td>50</td>
</tr>
<tr>
<td>aCr2O3</td>
<td>42.00 –15.39 16.75 – –</td>
<td>2.30</td>
<td>55</td>
<td>50</td>
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</tbody>
</table>

* Reported green pigment.

Table 3

<table>
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<tr>
<th>Mineralizer</th>
<th>Color coordinates</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L* a* b* C* h0</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>58.51 –31.36 20.98 37.73 146</td>
<td>2.35</td>
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<tr>
<td>NaF</td>
<td>50.96 –35.94 23.27 42.82 147</td>
<td>2.33</td>
</tr>
<tr>
<td>NaCl</td>
<td>50.81 –32.02 22.28 39.01 145</td>
<td>2.34</td>
</tr>
</tbody>
</table>

Scherrer equation is 46 nm. The morphology and particle sizes of the developed pigment powders can be observed by TEM. As shown in Fig. 7(a), the pigment samples are granular in nature and present a homogeneous nano scale particle size. Excellent dispersion is observed with narrow grain sizes with the distribution in the range of 60–100 nm. Diffraction pattern of the powder showed the products were polycrystalline, as displayed in Fig. 7(b). The energy dispersive spectral (EDS) analysis of the typical nano-pigment sample is given in Fig. 8 and the results demonstrated the composition of the Y2BaCuO5 particles (yttrium: barium: copper ratio = 2:1:1). From the dynamic light scattering method (DLS measurement), it is evident that the developed pigment particles have an average particle size of 50 nm (Fig. 9). These results are in good agreement with crystallite sizes calculated by the XRD technique.
of the green pigment in the NIR region (74% for nano-pigment and 58% for micron sized pigment) is much greater than that of UV—vis region (20% for nano-pigment and 9% for micron sized-pigment). The NIR reflectance as well as solar reflectance of the developed green nano-pigment ($R = 61\%$ at 1100 nm, $R^* = 50\%$) is found to be significantly higher than that of micron sized-pigment powders ($R = 41\%$ at 1100 nm, $R^* = 35\%$). It is interesting to note that the NIR reflectance of the developed green nano-pigment ($R = 61\%$ at 1100 nm) is also found to be higher than that of commercially available nano-green chromium oxide pigment powders ($R = 55\%$ at 1100 nm) [6]. Thus the above results clearly indicate the potential applications of the designed green pigments as “Cool Pigments” for various surface coating applications.

The chromatic properties of the developed $Y_2\text{BaCuO}_5$ pigment powders can be evaluated from their CIE 1976 color coordinate values displayed in Table 2. The lightness ($L^*$) as well as NIR reflectance (at 1100 nm) of the nano-green pigment powders are found to be superior to that of corresponding $Y_2\text{BaCuO}_5$ green pigment powders derived by traditional ceramic route. However, the $-a^*$ and $b^*$, which represents the green and yellow hue of the pigment samples are almost identical to each other. As a consequence, the $C^*$ value, which denotes the saturation of the color hue is also found to be the same for both the nano- and micron-sized green pigment samples. The observed hue angle of the designed pigments are found to be in the green region of the cylindrical color space ($h^* = 120–180$ for green). It is notable that the color coordinates of the designed green pigment samples are found to be significantly higher than that of commercially available $\text{Cr}_2\text{O}_3$ green and the earlier reports [6,11]. The data illustrated in Table 3, clearly shows that there is no change in the color coordinates of the micron-sized green pigment powders synthesized in the presence and absence of mineralizers by ceramic methods. Thus by proper selection of the mineralizers, the green colored pigments can be synthesized at relatively lower temperatures without compromising on their chromatic properties.

### 3.4. Chemical and thermal stabilities of the pigments

To evaluate the chemical stability of the developed nano-crystalline green pigment, the acid/alkali resistance towards the pigment samples was investigated in 2% $\text{H}_2\text{SO}_4$, $\text{HNO}_3$ and $\text{NaOH}$. A pre—weighed amount of the pigment was treated with acid/alkali and soaked for 30 min with constant stirring on a magnetic stirrer. The resultant pigment was then filtered, washed with water, dried, and weighed. Negligible weight loss of pigment was noticed for all the acids and alkali tested. The color coordinates of the pigment samples, which are subjected to chemical resistivity tests are measured and compared with the untreated sample. The total color difference $\Delta E_{ab}^*$ was calculated and the values are summarized in Table 4. The industrially acceptable limits of $\Delta E_{ab}^*$ are as follows: when $\Delta E_{ab}^* \leq 1$ unit indicates that the color change is almost indistinguishable from the original color, whereas, $\Delta E_{ab}^* \leq 2$ units are considered to be very small difference, only obvious to a trained

<table>
<thead>
<tr>
<th>Acid/alkali</th>
<th>Color coordinates</th>
<th>$\Delta E_{ab}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>67.01 -33.35 21.64</td>
<td>0.08</td>
</tr>
<tr>
<td>$\text{NaOH}$</td>
<td>66.84 -32.15 21.08</td>
<td>1.30</td>
</tr>
<tr>
<td>$\text{HNO}_3$</td>
<td>67.89 -33.92 20.44</td>
<td>1.46</td>
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<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>67.77 -32.89 21.94</td>
<td>0.89</td>
</tr>
</tbody>
</table>

$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$

Fig. 14. Thermogram of $Y_2\text{BaCuO}_5$ green pigment carried out under $N_2$ atmosphere.

Fig. 15. Thermogram of $Y_2\text{BaCuO}_5$ green pigment in air atmosphere.

Fig. 16. NIR reflectance spectra of concrete cement coatings and PVC coatings.
eye. The negligible values of $\Delta E^*_{ab}$ observed in the current study reveal that the pigments are chemically stable towards the acid/alkali investigated. The thermal stability (TG-DTA analysis) of the developed nano-crystalline $Y_2BaCuO_5$ pigment was examined in the temperature range 50°C to 1000°C in N$_2$ as well as in air atmosphere and the results are depicted in Figs. 14 and 15, respectively. The thermo gravimetric results clearly demonstrate that there is negligible weight loss and phase transition of the synthesized pigment up to 1000°C.

3.5. NIR solar reflectance analysis of the nano-pigment coatings on a concrete cement block and polymer (PVC) surfaces

The NIR reflectance and the corresponding NIR solar reflectance spectra of the green colored nano-pigment sample coated on the cement slab as well as on polymer PVC with and without TiO$_2$ base coat are shown in Figs. 16 and 17, respectively. The photographs of the coating materials are displayed in Fig. 18. The CIE 1976 color coordinates and average reflectance in UV–vis and NIR region of the green nano-pigment coatings are depicted in Table 5. It is interesting to note that the NIR reflectance ($R = 55\%$ at 1100 nm) and the corresponding solar reflectance ($R^* = 38\%$) of the pigment coated cement block is found to be higher than that of bare concrete cement block ($R = 30\%$ at 1100 nm, $R^* = 30\%$). The pigment coatings on concrete cement slab and PVC without TiO$_2$ base coat were also give high NIR reflectance value as evident from Fig. 16. These findings demonstrate the potential utility of the currently designed green nano-pigments as “Cool pigments” for building roofing materials. The impressive NIR reflectance displayed by the PVC-pigment coatings may find applications in automobile and electrical industries for reducing the heat build-up of heat.

4. Conclusions

In conclusion, a bright green colored nano-inorganic pigment $Y_2BaCuO_5$ (~ 50 nm) with impressive NIR reflectance (61% at 1100 nm) was developed using the nano-emulsion method at relatively lower temperatures as compared to micron sized-pigment, synthesized by traditional ceramic route. Notably, the developed green nano-pigment sample exhibits NIR solar reflectance ($R^* = 38\%$), when coated on cement concrete block, thus having a great potential in applications such as cool materials used for buildings with energy saving performance. The current green nano-inorganic pigment also possesses high chemical and thermal stability. The potential utility of the synthesized nano-pigment formulations was also evaluated by coating on polymer materials like PVC with an aim to develop polymer NIR coatings for use in automobile and electrical cable industries.

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