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Synthesis of fluorite ceria based solid solutions from mixed rare earth carbonates

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Abstract

The synthesis of new class of compound based on CeO_2 as pigments has been reported. The starting material used for preparation of the compound is mixed rare earth carbonate, which is an intermediate product obtained during beneficiation of monazite mineral to separate different rare earth metals. This paper presents direct use of the mixed rare earth carbonate without separation of individual rare earth oxides for pigment preparation, thereby reducing cost and improving eco-efficiency of the process. The effect of dopants, and different mineralizers on colour formation has been studied in detail by XRD, SEM and UV–vis spectrophotometer (CIELAB parameters), particle size analyzer. From this study, we optimized the conditions for the syntheses of mixed rare earth oxide by solid state reaction route to develop the brown colour pigments. Pigment properties such as moisture content, oil absorption, bleed resistance, opacity, gloss, etc., of the product has been evaluated and found to be in acceptable range. Nominal composition of the product was found to be $Ce_{0.75}Pr_{0.05}Ln_{0.20}O_{1.9}$, where Ln includes, La, Nd, Sm, Gd.

Keywords: A. Powders: solid state reaction; C. Colour; C. Optical properties; Mixed rare earths

1. Introduction

Inorganic natural and synthetic pigments that are produced and marketed as fine powders are an integral part of many decorative and protective coatings and are used for the colouration of plastics, fibres, paper, rubber, glass, cement, ceramic bodies, glazes, porcelain enamels, etc. In all these applications, the pigment is dispersed in the media, forming a heterogeneous mixture. In ceramic industry, where pigments are used for the production of traditional coloured glazed and unglazed tiles, the pigments must show thermal and chemical stability at high temperatures (1200–1250 °C) and must be inert to the chemical action of the molten glazes. To be successfully used, a pigment in particular must function as an integral part of the glaze or enamel system. Hence, it must be compatible with the other components: the glaze itself, the opacifiers and other additives.

Most of the inorganic pigments suitable for high temperatures applications are the complex oxides, which belong to a restricted number of structural class [1,2]. These lattices not only posses good thermal and chemical stability but also have a high refractive index, which is important for good optical pigment properties.

The many of these high temperature inorganic pigments use toxic metals such as cadmium, lead, chromium or cobalt. There is a serious need for substituting these metals from environment point of view. One of the alternative materials is based on rare earths, since they are eco-benign and also possess unusual optical properties due to unique electronic configuration of partially filled f orbitals [3–6]. The intense colouration of rare earth based materials arises due to charge transfer interactions between a donor and an acceptor, where metal ions being the acceptor. Pigments based on cerium dioxide are lesser known and represent only a small, but an important range of inorganic pigments. The synthesis of Pr-doped ceria pigment was first reported in a European patent and published by Olazcuaga et al. [7,8]. These pigments are known to have high temperature stability and give various pink-orange to red-brown hues, depending on the quantity of praseodymium incorporation into the host lattice of cerium dioxide, synthesis conditions, calcinations temperature.

$Ce_{1-x}Pr_xO_2$ system has been studied extensively as ceramic pigments by different authors [9–16], where various synthesis

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routes have been adopted. It is further studied by admixture of various lanthanides like La_2O_3, Sm_2O_3, Nd_2O_3 and Gd_2O_3 [13–15]. The present paper describes use of alternative raw material, which contains apart from cerium and praseodymium other lanthanides such as lanthanum, samarium, neodymium, gadolinium in appreciable amount, to prepare pigment. In general, lanthanides occur in the nature together, and because of very similar electronic structure, they exhibit very similar chemical properties, and hence separation of them requires expensive processing routes that add to their cost. Use of mixed metal carbonates as starting material to prepare pigment will reduce the cost of production considerably.

2. Experimental

2.1. Materials

Mixed rare earth carbonates was supplied by Indian Rare Earth Ltd. (IREL), Cochin, India. Nominal composition of the rare earth carbonate, analyzed by qualitative XRF analysis is given in Table 1. To optimize the pigment composition additional praseodymium and different mineralizers such as LiF, Li_2CO_3, Na_2SiF_6, NH_3F_6, NaF, NaCl, K_2CO_3 and mixture thereof were used. All the chemicals used are reagent grades and used without further purification.

2.2. Characterization of raw material

Raw material was characterized by thermo-gravimetric study, XRD. The raw material was heat treated at different temperature at 200, 400, 600, 1000, 1300 °C, respectively to see the phase change by XRD. Unless otherwise stated, calcined powder mentioned in the text refers to powder heat treated at 1300 °C, with soaking for 2 h.

2.3. Preparation of pigment

The starting mixtures containing 85–87 wt.% of rare earth carbonate, 3–5 wt.% dopant and 5–10 wt.% of mineralizers were mixed thoroughly in an agate mortar in acetone medium. The powder was then dried in an oven at 110 °C. The dried mixture was calcined in an alumina crucible in muffle furnace. The temperature of the furnace was increased at 5 °C/m up to 1300 °C and was soaked for 2 h. After the calcining process; the products were washed with a near boiling in HCl/water mixture to remove soluble residues of the mineralizers followed by drying, grinding and sieving.

Table 1
Chemical composition of mixed rare earth carbonate.

Composition	wt.%
CeO_2	69.24
La_2O_3	11.33
Nd_2O_3	11.24
Pr_6O_{11}	4.32
Sm_2O_3	2.17
Gd_2O_3	1.10

2.4. Micro-structural characterization of pigment

The calcined powders were characterized by X-ray powder diffraction (Philips X'Pert X-ray diffractometer in the 20–40° 2θ range using Zirconium filtered Mo Kα radiation). Particle size and morphology were analyzed by nano-particle size analyzer (NA-150, Microtrac) and scanning electron microscope (Hitachi S-3400N). The quantitative microanalysis of the product was carried out by energy dispersive (EDAX) analysis. Colour measurements were carried out in a Shimadzu UV-2450 spectrophotometer operating in the 200–900 nm range and the colour co-ordinates were determined using CIE-LAB 1976 colour scales.

2.5. Evaluation of pigment properties

The calcined samples were subjected to various tests in isolation, since there was no reference/master/standard. The colour properties are generally expressed in comparison to agreed reference or standard or in visual terms as well as in numerical.

To test the pigment properties, paint samples were prepared in vibro-shaker where dispersion/grinding was done in 125 ml stainless steel cup using air drying Soya long oil alkyd medium and steel balls of 4 mm diameter as grinding media. The grinding time was maintained for 45 min. The pigment under test were noticed to have hard texture where finish on Hegman Gauge (HG) was 5–6 for 30 min grinding time, hence longer duration was used. The draw downs were drawn using 100 micron bar coater.

3. Results and discussion

3.1. Characterization of mixed rare earth carbonate and calcined product

Fig. 1 shows the thermo-gravimetric study of mixed rare earth carbonate. It can be seen from the graph that the weight loss (~30%) occurred during the temperature range of 400–600 °C, which is due to the removal of volatiles and CO_2. It has been reported [11] that praseodymium oxide, neodymium oxide, lanthanum oxide dissolve in cerium oxide and form a

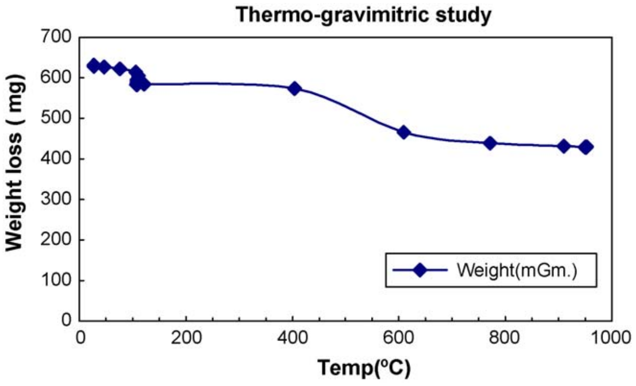


Fig. 1. TG curve for RE carbonate.

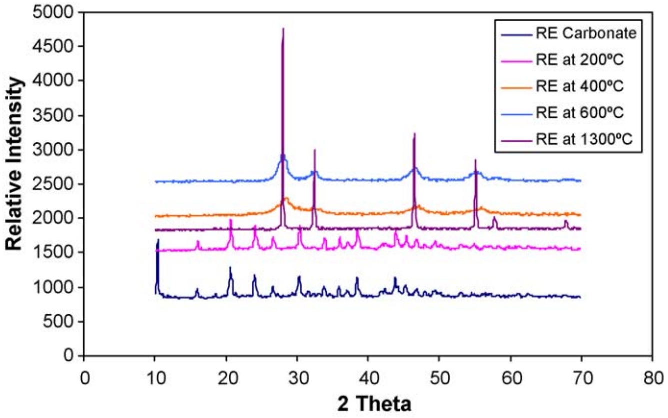


Fig. 2. XRD plots of rare earth carbonate at different temperatures.

solid solution. The tetravalent Pr^{4+}, having smaller radius than Ce^{4+} [$r(Ce^{4+}) = 0.101$ nm, $r(Pr^{4+}) = 0.092$ nm], substitutes Ce^{4+} and forms uncharged defects in the crystal structure. On the other hand the trivalent Nd^{3+} and La^{3+}, having higher radius than Ce^{4+}[$r(Nd^{3+}) = 0.108$ nm, $r(La^{3+}) = 0.115$ nm], substitute Ce^{4+} in the crystal structure and form negatively charged defects which are compensated by positively charged oxygen voids. Fig. 2 shows the XRD patterns of the RE carbonate calcined at different temperatures. It has been found that the phase change started to occur at 400 °C in mixed RE carbonate in agreement with the TG data. However, even at 400 °C, the observed diffraction lines correspond to the characteristic lines of fluorite structure of cerium dioxide, but with much broader peak width, showing poor crystalinity. It

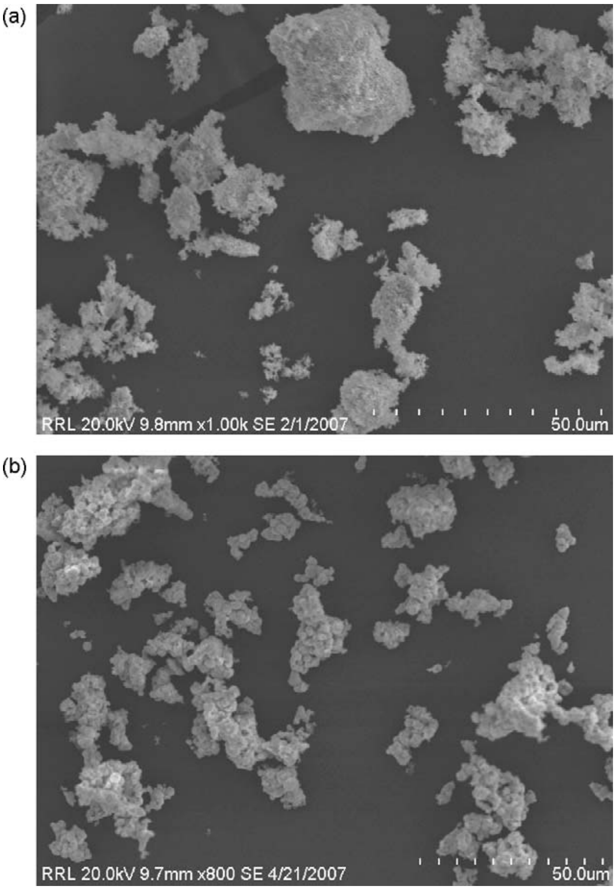
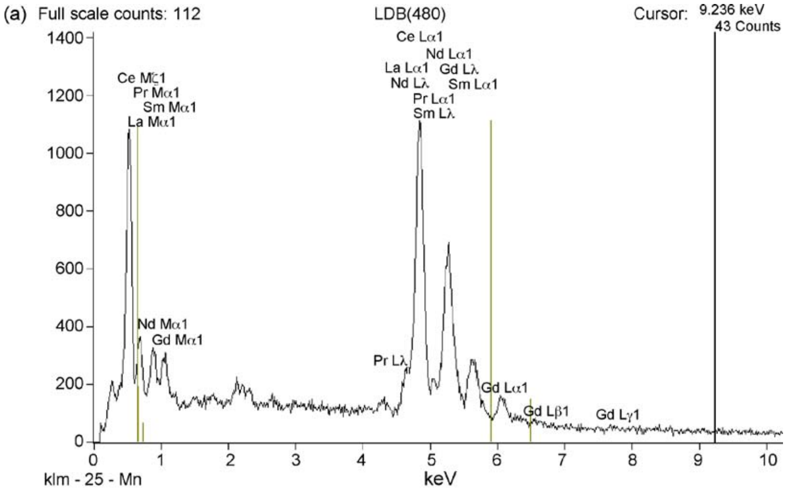
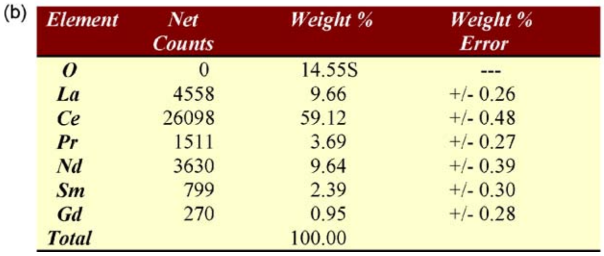


Fig. 3. (a) SEM of raw material and (b) SEM of calcined sample





Element	Net Counts	Weight %	Weight % Error
O	0	14.55S	---
La	4558	9.66	+/- 0.26
Ce	26098	59.12	+/- 0.48
Pr	1511	3.69	+/- 0.27
Nd	3630	9.64	+/- 0.39
Sm	799	2.39	+/- 0.30
Gd	270	0.95	+/- 0.28
Total		100.00	

Fig. 4. (a) EDAX spectrum analysis of rare earth carbonate. (b) Composition of rare earth carbonate by EDAX analysis.

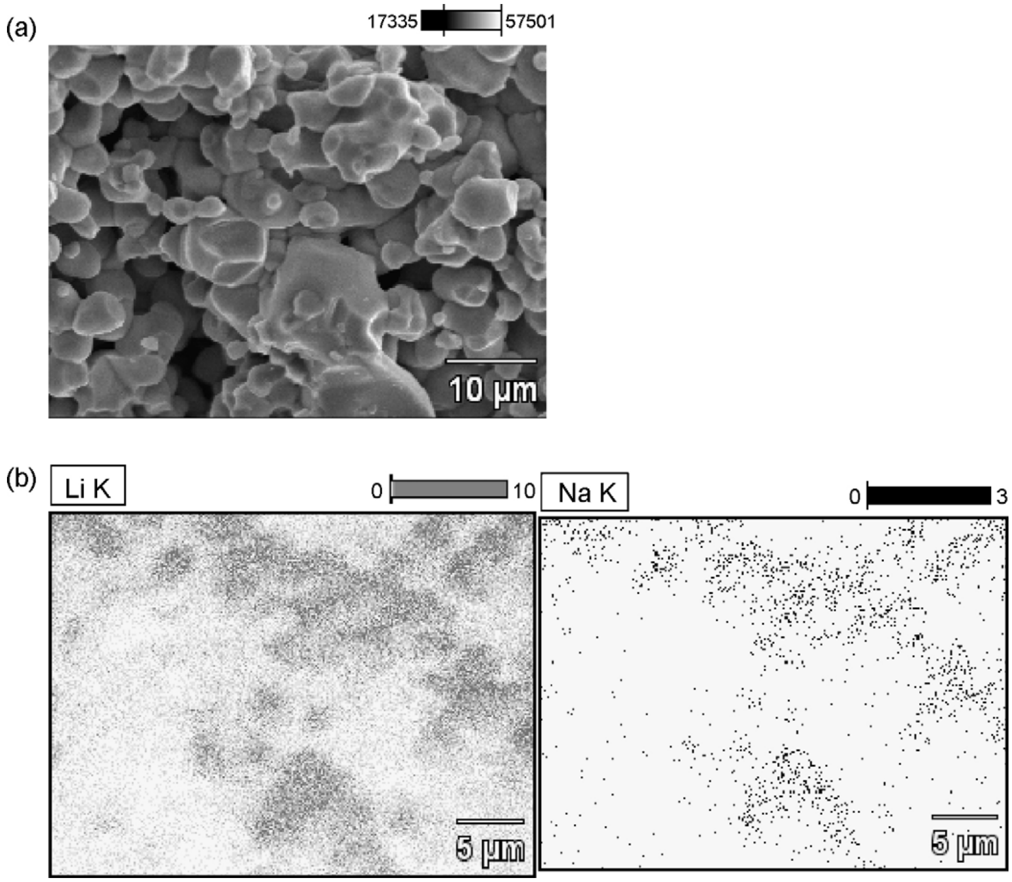


Fig. 5. (a) Microstructure of heat treated pigment sample. (b) Distribution of Na and Li in the structure.

may be mentioned that the colour of the sample at this temperature changed to light brown. At 600 °C, there was not much improvement of the crystalinity. On the other hand sample calcined at 1300 °C for 2 h shows good crystalinity, with sharp and intense peaks coinciding with CeO_2 fluorite structure.

Particle morphology of raw powder and the calcined powder were studied by scanning electron microscope and the morphology of the sample are shown in Fig. 3a and b. After calcinations the product grows as an agglomerate of smaller spherical particle of size 2–4 μm. However, aggolomerate size varies from 10 to 30 μm. Hence, for a pigment application size reduction is required.

Chemical composition of calcined rare earth carbonate was quantitatively analyzed by EDAX. The results are shown in Fig. 4a and b. It can be seen from Fig. 4b that the calcined powder contains 6 wt.% praseodymium, which is the chromophore and responsible for the colour formation.

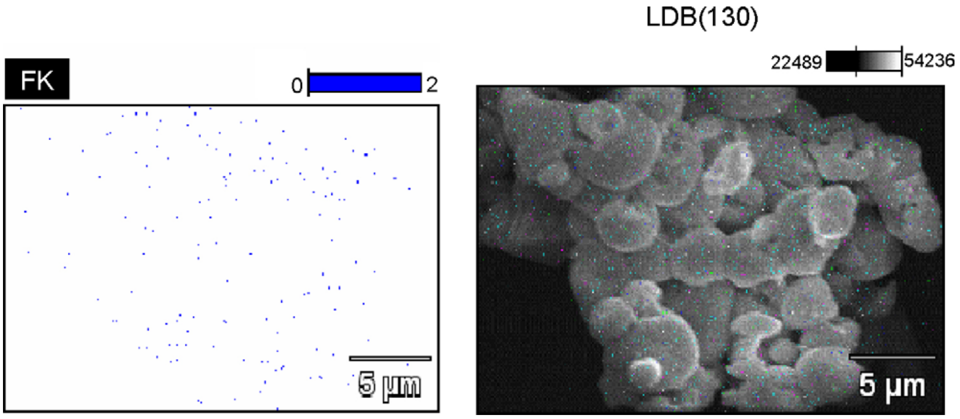


Fig. 6. Elemental mapping of fluorine in RE carbonate by EDAX analysis.

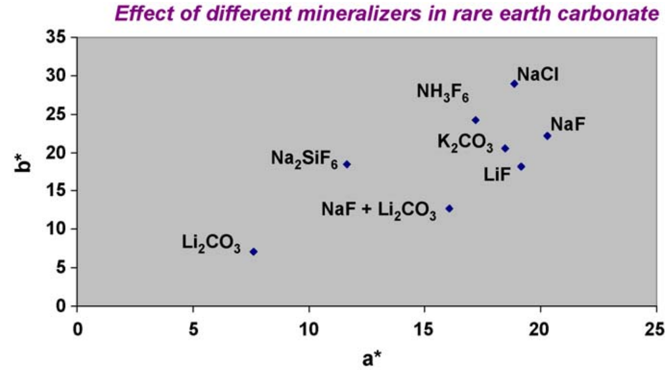


Fig. 7. The effect of the mineralizers on the colour hue of the mixed rare earth oxide pigments in a^*, b^* coordinates.

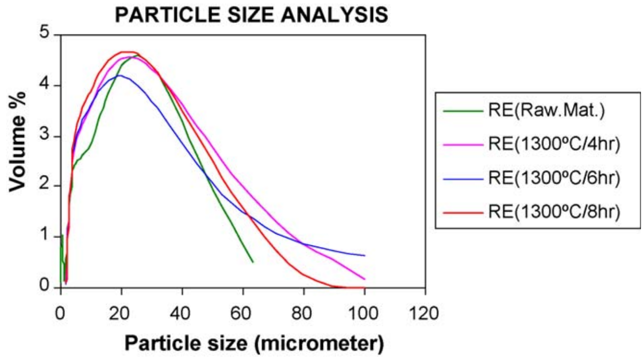


Fig. 8. Particle size distribution of RE carbonate at different soaking time.

3.2. Effect of mineralizers and dopants on hue of rare earth pigments

The presence of mineralizers was found to be markedly effective in improving colour hue of the pigment [16,17]. With the addition of mineralizers, the pigments become darker hue, in terms of CIE Lab parameters, it amounts to a decrease of L and an increase of the a^* value. Amongst the various mineralizer studied, lithium carbonate produced darkest hue (when a single mineralizer was used), however, the tendency of sintering was increased. On the other hand, simultaneous presence of Li and K-carbonate gives the darkest hue, also lowered the reaction temperature so that product got fused. Usually mineralizers are added to improve the reactivity, but it may also form the glass phase in grain boundaries that may in turn help in reducing the sintering temperature of the pigment. To verify this, the pigment powder was pressed in form of a pellet and sintered at 1400 °C for 1 h, Fig. 5a) shows the microstructure, which did not show any evidence of glass phase formation. EDAX analysis (Fig. 5b) shows Na and Li are uniformly incorporated in the structure. Amongst the different combinations tried, the mixture of NaF and Li_2CO_3 gave the best result. The pigment colour shifted to a red-brown hue and the tendency of sintering decreased when both NaF and Li_2CO_3 were present. Also, it was observed that the presence of fluorine improved the colour hue. The incorporation of fluorine in the lattice was confirmed by EDAX analysis (Fig. 6). The effect of mineralizers on the colour parameters is depicted in Fig. 7.

The addition of praseodymium used as a chromophore improved the colour hue as expected. Its presence of about 5 mol% in the composition is found to be optimum. Increasing further praseodymium content slightly shifts colour parameters to lower values, as reported earlier [18]. The colour co-ordinates and band gap energy values of the pigments are tabulated in Table 2. Nominal composition of the optimized product was found to be $Ce_{0.75}Pr_{0.05}Ln_{0.20}O_{1.9}$, where Ln includes, La, Nd, Sm, Gd, with addition of Pr.

Combination of mineralizer and dopant in the rare earth carbonate gave the best results with respect to the colour parameters. These results are further confirmed with a low band gap energy (Eg) value for the sample (RE-108) in the presence of dopant and mineralizers (2.066 eV).

3.3. Particle size and morphology

The particle size and shape of the powders were examined by scanning electron microscope. The rare earth carbonate (with mineralizer and dopant) after calcinations formed agglomerates of smaller spherical particles of size (2–4 μm), whereas the agglomerate size varies from 10 to 40 μm. To study the effect of soaking time on the particle size, the experiments were carried out with RE carbonate, where the powder was subjected to calcinations for 4, 6, and 8 h duration at temperature of 1300 °C. The products were characterized using Malvern Particle Size Analyzers. Fig. 8 shows the particle size distribution. It was observed that there was no appreciable particle size growth as the soaking time increased.

3.4. Grinding studies of the pigment

Heat treatment of mixed RE carbonate produced agglomerates of size 25–40 μm, where the individual particle size varied from average 2 μm to more than 4 μm. The calcined pigment powders were ground by using Fritsch planetary ball

Table 2
Colour co-ordinates and band gap energy values of the brown colour rare earth pigments.

Sample no.	Composition of starting mixture (wt.%)			CIE LAB values			Band gap values	
	RE carbonate	Dopants	Mineralizers	*L**	*a**	*b**	dWL	Band gap (eV)
RE-33	100	–	–	52.56	18.42	27.98	589.3	2.097
RE-56	95	5	–	48.41	13.38	22.35	587.7	2.103
RE-107	90	–	8 (NaF) + 2 (Li_2CO_3)	41.15	18.89	19.02	594.2	2.080
RE-108	90	3	8 (NaF) + 2 (Li_2CO_3)	36.81	13.14	9.41	598.2	2.066

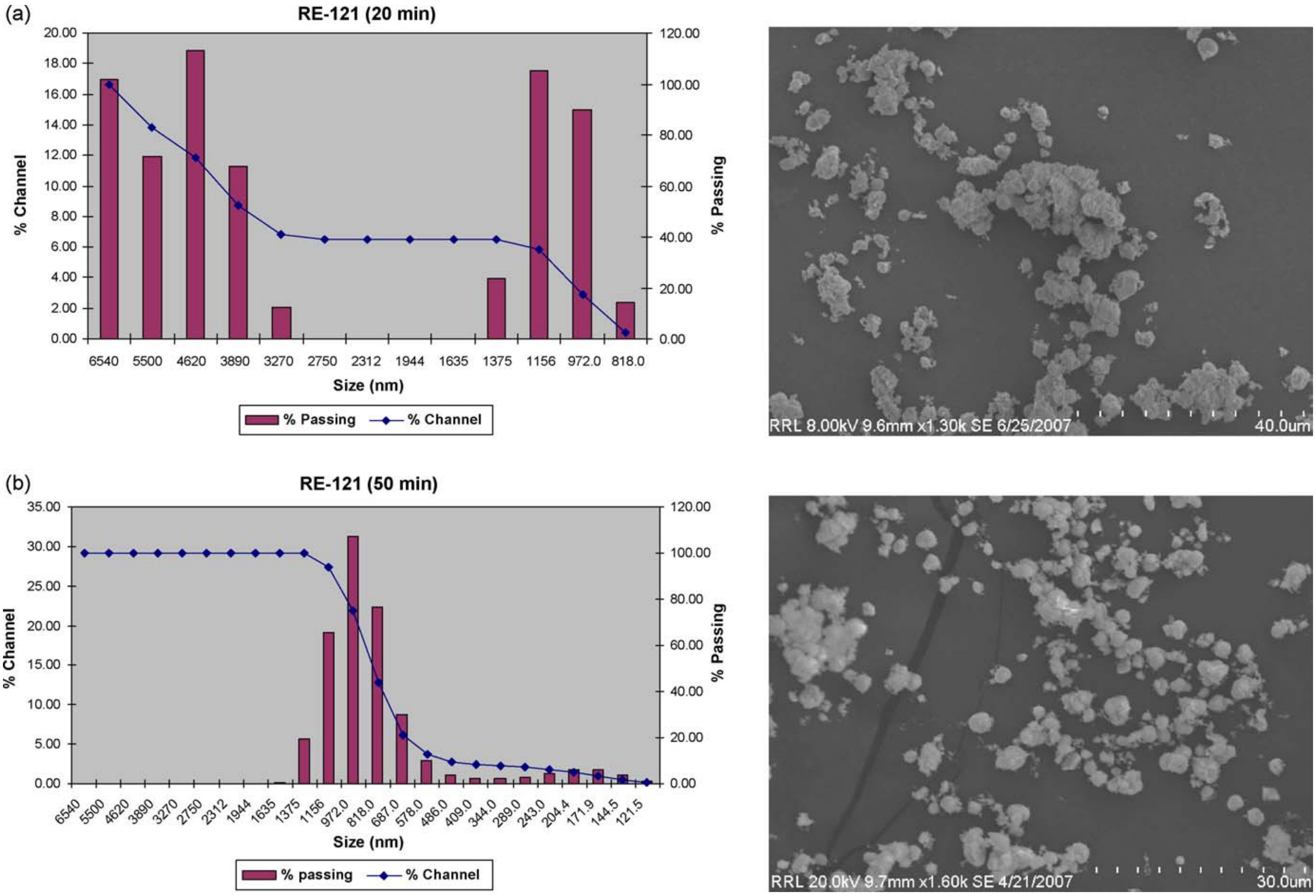


Fig. 9. (a) Particle size distribution and SEM image of grinded pigment sample after 20 min. (b) Particle size distribution and SEM image of grinded pigment sample after 60 min.

mill P6 using agate bowl and balls. Ball mill speed was fixed at 500 rpm. Duration of milling was varied from 10 min to 1 h with the ball to powder ratio kept at 3:1. The ground materials were characterized by particle size analyzer, SEM and UV–vis spetrophotometer. Calcined sample showed bimodal distribution after 20 min of grinding and distribution did not change till after 40 min of grinding. After 50 min of grinding, particle size reduced between 1 and 2 μm. Higher grinding time reduced the particle size further, as expected, in expense of finer (<1 μm) particles. The particle size distribution and SEM image of

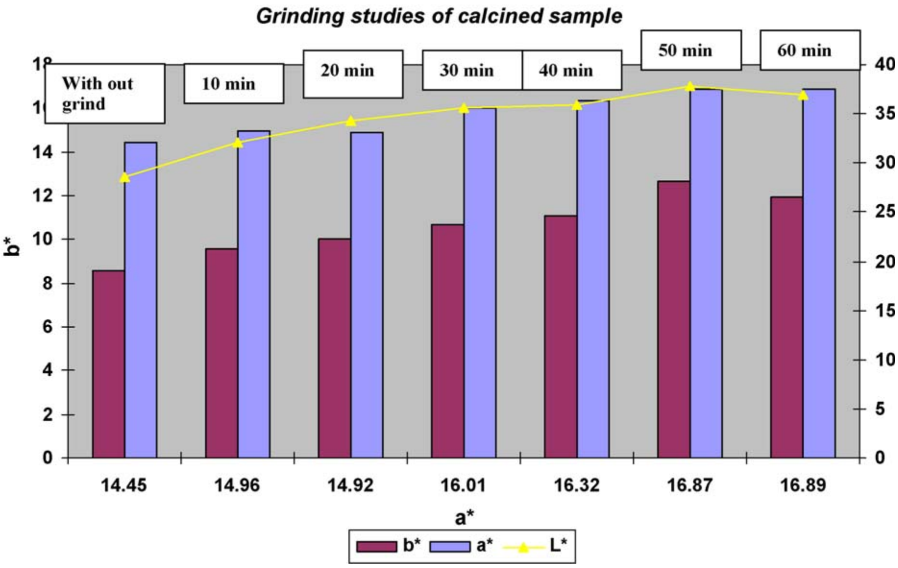


Fig. 10. CIE LAB parameters of ground sample at different timings.

calcined samples ground for 20 and 60 min duration, respectively, are shown in Fig. 9a and b. Fig. 10 shows the variation of colour parameters with grinding time. Presence of finer particle (higher grinding time) increased the lightness (L^*) value appreciably, whereas a^* & b^* increased marginally.

3.5. Evaluation of pigment properties

It was observed that the powder tested has acceptable moisture content, oil absorption, bleed resistance, opacity, gloss at 20° and 60°. It also has acceptable water resistance, but inferior acid and alkali resistance. It has been reported that ceria based pigments prepared by solid state reactions are unstable in porcelainised stoneware [19], also due to outgassing problem not suitable in all glazes [20]. This is due to the decomposition of cerium oxide at higher temperature ($2CeO_2 \rightarrow Ce_2O_3 + 1/2\ O_2$). In the present case, ceria contains appreciable amount of La and Nd in addition to Pr, Sm, Gd (Table 1). Most stable valence state of these lanthanides are at +3 valence state, thereby introducing high oxygen ions vacancies in the structure, even at room temperature. Hence, heating of pigments at higher temperature will induce hopping of oxygens in different vacant sites and may reduce outgassing.

4. Conclusions

The paper presents the preparation of environmentally friendly pigment of orange-brown hue from a low valued raw material. The chromophore Pr responsible for colour formation was present in the raw material. Colour formation is due to the incorporation of Pr^{4+} into the Ce^{4+} lattice thereby forming uncharged defects in the crystal structure. The colour shifted to darker hue with the addition of dopants (additional Pr) and mineralizers because of decreasing band gap energies. Amongst different combination of mineralizer tested, the mixture of NaF & Li_2CO_3 gave best result with respect to colouring capabilities. Also presence of Flourine seemed to enhance the intensity of the colour. Na and Li are also get incorporated in the structure. Optimum particle size for acceptable colouring capabilities (good hiding, opacity) was found to be between 2 and 4 μm.

Combination of mineralizer and dopant in the rare earth carbonate gave the best results with respect to the colour parameters. Nominal composition of the optimized product was found to be $Ce_{0.75}Pr_{0.05}Ln_{0.20}O_{1.9}$, where Ln includes, La, Nd, Sm, Gd, with addition of Pr.

These results are further confirmed with a low band gap energy (Eg) value for the sample (RE-108) in the presence of dopant and mineralizers (2.066 eV).

The optimized product has acceptable moisture content, oil absorption, bleed resistance, opacity, gloss at 20° and 60°. It also has acceptable water resistance, but inferior acid and alkali resistance.

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