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Synthesis and characterisation of $(BiRE)_2O_3$ (RE: Y, Ce) pigments

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Abstract

This paper embodies the results of the investigations carried out on the synthesis of the colored oxides in the Bi_2O_3–RE_2O_3 system. The pigments were prepared by the solid state reaction of mixed oxides $(Bi_2O_3)_{1-x}(RE_2O_3)_x$, where RE: Y or Ce with nominal compositions: $x = 0.2$ and 0.5 for Y and $x = 0.3$ and 0.5 for Ce. The products formed were characterised by the X-ray powder diffraction, scanning electron microscopy, energy dispersive spectrometer analysis and by reflectance spectral data. All the synthesized pigment samples are found to be having color coordinates, low **a** and high **b** and exhibit the color from pale yellow to orange red. Reflectance spectra of the samples show high reflectance percentage in the 600–800 nm range. Because of the homogeneity of the phase formed and the intense coloration, the Y doped pigments have been found to be superior to Ce doped pigments, as possible ecological inorganic pigments.

Keywords: Bismuth-rare earth mixed oxides; Microstructure characterisation; Color properties; Ecological pigments

1. Introduction

The pigments for coloring ceramics, usually inorganic products composed of metal oxides or compounds formed from the host of metal oxides, must possess thermal and chemical stability at high temperature and must be inert to the chemical action of the molten glaze [1]. Inorganic pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels and glasses [2–5]. Unfortunately, the majority of inorganic pigments for the above applications currently employed are the toxic metals such as cadmium, lead, chromium or cobalt. Thus, serious need arises to search for materials of environmentally friendly and economically viable materials for the replacement of toxic inorganic pigments. Pigments based on CeO_2 are inorganic pigments with high temperature stability, but which represent only a small but an important part of the range of inorganic pigments [6]. The high temperature phase of bismuth sesquioxides Bi_2O_3, which is stable in the 730–825 °C temperature range, has been intensively studied because of its high oxygen conductivity [7,8]. This high oxygen vacancy

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concentration gives rise to high oxygen-ion mobility. The δ-phase may be stabilized below room temperature by partial cationic substitution of Bi^{3+}. Thus, the use of rare earth cations has appeared effective though a variety of crystal phases have been observed, depending on the kind and amount of rare earth cation used and the synthesis conditions employed [7].

In the present study, the new pigments having the formula $(Bi_{1-x}RE_x)_2O_3$ (RE = Y or Ce) with various rare earth concentration levels have been prepared and their color properties, as possible ecological inorganic pigments have been investigated.

2. Experimental

2.1. Materials

The raw materials used for the preparation of $(Bi_{1-x}RE_x)_2O_3$ pigments were Bi_2O_3 (99.9%) obtained from Aldrich, CeO_2 (99.9%) and Y_3O_3 (99.9%) obtained from Indian Rare Earths Ltd.

2.2. Methodology

Mixed oxides $(Bi_{1-x}RE_x)_2O_3$, where RE: Ce or Y with nominal compositions: Ce, $x = 0.3$ and 0.5; Y, $x = 0.2$ and 0.5, have been prepared. The above oxides were weighed in the required stoichiometric amounts and then were wet mixed thoroughly in an agate mortar using acetone. The dried mixture was calcined in a platinum crucible in an electrical furnace. The heating of the furnace was programmed increasing the temperature initially at 10 °C/min up to 750 °C and afterwards the heating rate was decreased to 5°C/min up to 900°C. The sample was soaked at that temperature for 3 h. The calcination process was repeated thrice in order to ensure the completion of the reaction with intermittent grinding.

2.3. Characterisation

The calcined powders were characterised by X-ray powder diffraction with a Philips X'Pert X-ray diffractometer. The XRD patterns were recorded in the 20–60° 2θ range using Nickel filtered Cu Kα radiation. Morphological analysis was performed by a JEOL JSM-5600 LV scanning electron microscope. The quantitative microanalysis of the product was carried out by energy dispersive spectrometer (EDAX, USA). Color measurements were done with a Shimadzu UV-2401 spectrophotometer operating in the 400–800 nm range and the color coordinates were determined using CIE-LAB 1976 color scales.

3. Results and discussion

3.1. $(Bi_{1-x}Y_x)_2O_3$

The XRD patterns of $(Bi_{0.8}Y_{0.2})_2O_3$ and $(Bi_{0.5}Y_{0.5})_2O_3$ are given in Fig. 1a,b. In the XRD pattern of pigment sample with Y, for $x = 0.2$ doping level, a compound of Bi_3YO_6 is formed which has an fcc structure. Most of the peaks of high intensity can be assigned to the compound Bi_3YO_6 (PDF No: 33-223), which reveals that it is the major phase formed, along with $BiYO_3$ as the

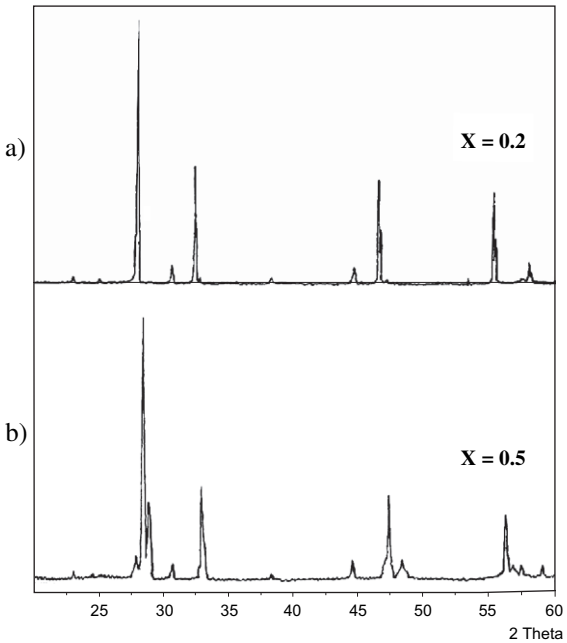
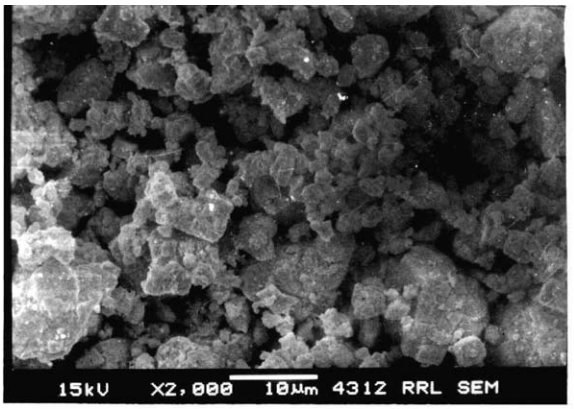
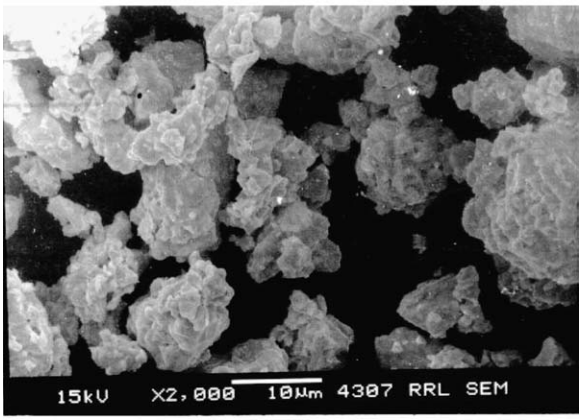


Fig. 1. X-ray diffraction patterns of (a) $(Bi_{0.8}Y_{0.2})_2O_3$ and (b) $(Bi_{0.5}Y_{0.5})_2O_3$.

minor one. On the other hand, for the sample with $x = 0.5$, the XRD pattern shows high intensity peaks and can be assigned to the compound $BiYO_3$ (PDF No: 27-1047) with a minor phase of Bi_3YO_6. The very sharp and high intense peaks found in the diffraction patterns reveal the crystalline nature of the product. The homogeneous and crystalline nature of the samples for Y with $x = 0.2$ and 0.5 can also be observed in the SEM photographs (Fig. 2a,b). The agglomerates found in the photographs are essentially clusters of primary particles. The particle size of the calcined powders was determined using Debye–Scherrer formula $D = 0.9\lambda/\beta\cos\theta$ from the respective XRD patterns [9]. In the formula, where D is the particle size, λ is the wavelength of X-ray used, β and θ are half width of XRD diffraction lines and half diffraction angle of 2θ, respectively. The calculated particle size from the formula for different *hkl* planes was found to be 8–17 nm size (Table 1). The EDS analysis was carried out at different regions of the samples. The stoichiometric formulae calculated from the semiquantitative EDS results are $Bi_{1.7}Y_{0.5}O_3$ when $x = 0.2$ and $BiYO_3$ when $x = 0.5$ which are in close agreement with the theoretical formulae. This also further confirms the homogeneity of the phase formed.



a)



b)

Fig. 2. SEM photographs of (a) $(Bi_{0.8}Y_{0.2})_2O_3$ and (b) $(Bi_{0.5}Y_{0.5})_2O_3$.

The effect of rare earth doping on the color of the Bi based pigments was analyzed from the diffuse reflectance spectra shown in Fig 3. The color coordinates data are given in Table 2. The reflectance spectra of pigment sample with Y, for $x = 0.2$ doping level shows a steep slope from 500–600 nm wavelength. The high reflectance region lies in the region 600–800 nm and shows maximum R% 80 (Fig. 3). The Y^{3+} ion imparts high intense yellow–orange hue to the pigment (high coordinate **b** value), reduces the red hue (very low coordinate **a** value). The reflectance in this region indicates that the pigment appears to be yellow–orange color. On the other hand, compounds with Y, for $x = 0.5$ doping, the reflectance curve is not giving such a steep slope as observed in $Y_{0.2}$ doping.

The maximum R% is 77 at 725 nm. The dominant reflectance band lies in the 650–800 region. The increase of Y^{3+} ion enhances the red hue (slight increase of **a** coordinate) and reduces the yellow hue (slight decrease of **b** coordinate). The very high reflectance in this wavelength region explains the intense yellow–orange color with a reddish shade of the pigment with Y, for $x = 0.5$ doping. From

Table 1
Particle size of the $(Bi_{1-x}RE_x)_2O_3$ pigments from the XRD results

Theoretical formula of the pigment	Major phase formed	Particle size (nm)
$(Bi_{0.7}Ce_{0.3})O_3$	$Bi_3Ce_{0.74}O_3$	8–12
$BiCeO_3$	$Bi_{1.3}Ce_2O_3$	8–15
$(Bi_{0.8}Y_{0.2})O_3$	$Bi_{1.5}Y_{0.5}O_3$	13–17
$BiYO_3$	$BiYO_3$	8–12

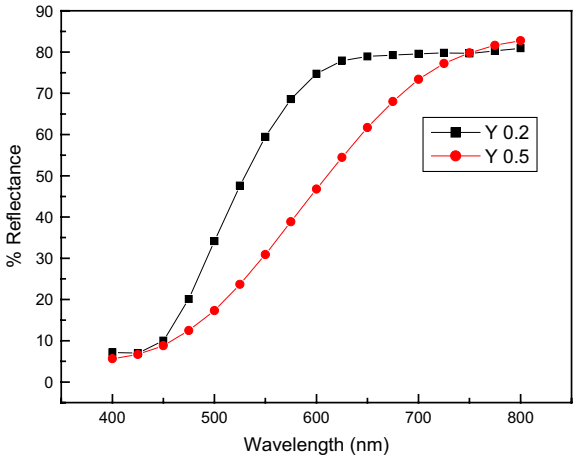


Fig. 3. Reflectance spectra for $(Bi_{0.8}Y_{0.2})_2O_3$ and $(Bi_{0.5}Y_{0.5})_2O_3$.

these analyses, it is clear that with the increase of Y concentration, the color of the pigment also increases, however the lightness **L** decreases slightly.

3.2. $(Bi_{1-x}Ce_x)_2O_3$

Fig. 4a,b presents the XRD patterns of $(Bi_{1-x}Ce_x)_2O_3$, $x = 0.3$ and 0.5, respectively. $Bi_{1.4}Ce_{0.6}O_3$ pattern indicates the presence of major phase of substituted Bi_2O_3 in accordance with the PDF No. 27-52. From this, it is clear that CeO_2 is almost completely dissolved in the Bi_2O_3 since, all the high intensity peaks can be assigned to δ-Bi_2O_3. This means that even after Ce doping the fluorite structure of δ-Bi_2O_3 is retained. On the other hand, with the increase of CeO_2 content, the presence of heterogeneous phases like CeO_2 and BiCe was also detected from the XRD pattern as per PDF No. 34-394 and 15-817. With the increase of Ce content, the possibility of formation of heterogeneous phases is increased considerably.

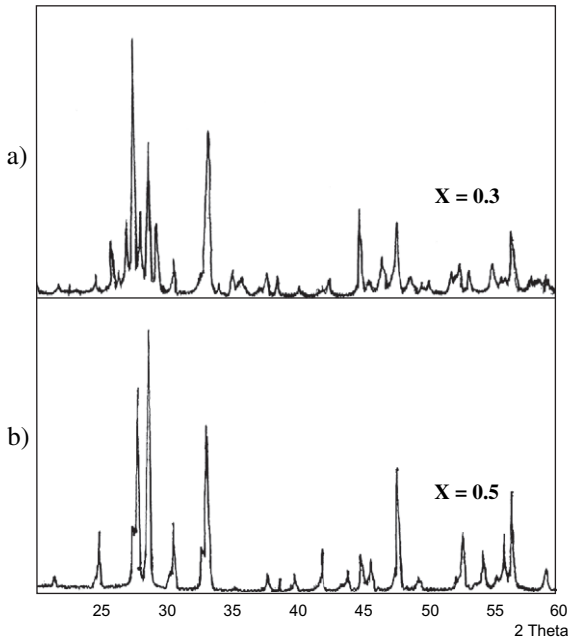
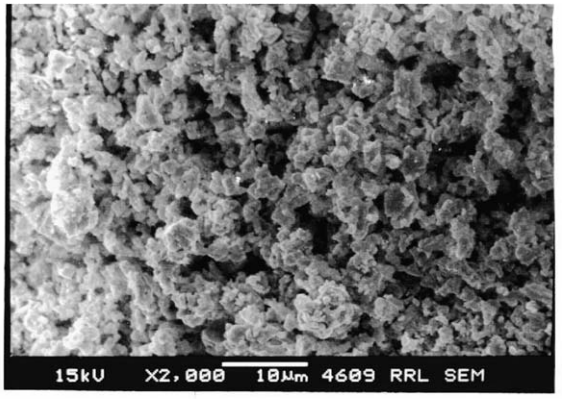


Fig. 4. X-ray diffraction patterns of (a) $(Bi_{0.7}Ce_{0.3})_2O_3$ and (b) $(Bi_{0.5}Ce_{0.5})_2O_3$.

The particle size calculated from the XRD pattern of Ce doped samples lies in 8–15 nm range (Table 1). High intense, sharp and symmetrical peaks were selected for calculating the particle size. Fig. 5a,b shows the micrographs of the calcined powder of Ce, with $x = 0.3$ and 0.5 compounds. This also supports the heterogeneity of the morphological characters with increased Ce doping. The agglomerates observed are clusters of primary particles of 8–15 nm in size supported by the XRD results. The EDS analysis at different micro-regions indicates the presence of the different phases formed, and their compositions were analyzed. These results also support the formation

Table 2
Reflectance data of the $(Bi_{1-x}RE_x)_2O_3$

Theoretical formula of the pigment	Dominant reflectance band (nm)	R%	R_{400}%	R_{700}%	Color coordinates		
					L	**a**	**b**
$(Bi_{0.8}Y_{0.2})_2O_3$	600–800	77–80	7.15	79.56	76.81	0.55	41.08
$BiYO_3$	700–800	65–77	5.66	73.39	58.15	11.79	28.63
$(Bi_{0.7}Ce_{0.3})_2O_3$	650–800	61–69	7.24	69.47	70.73	1.66	28.61
$BiCeO_3$	650–800	69–73	9.65	62.5	64.82	4.65	30.69



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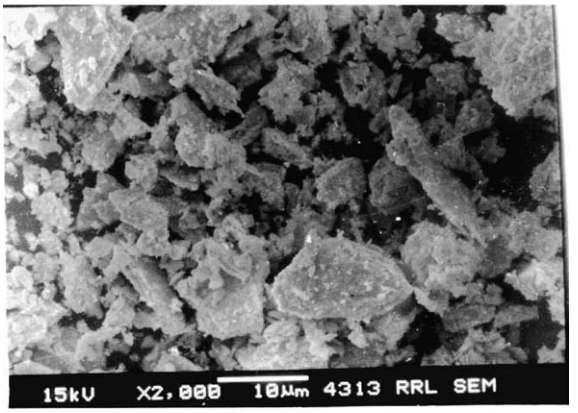

b)

Fig. 5. SEM micrographs of (a) $(Bi_{0.7}Ce_{0.3})_2O_3$ and (b) $(Bi_{0.5}Ce_{0.5})_2O_3$.

of heterogeneous phases with increased Ce doping. The stoichiometric formulae deduced from the semiquantitative EDS results are $Bi_{1.3}Ce_{0.74}O_3$ when $x = 0.3$ and $Bi_{1.3}Ce_2O_3$ when $x = 0.5$. The reflectance spectra corresponding to Ce with $x = 0.3$ and 0.5 doping are shown in Fig. 6. The pigment with $x = 0.3$ doping level shows high reflectance in the broad region of 625–725 nm with maximum reflectance 71% at 800 nm.

The color parameters are given in Table 2. The low **a** coordinate and high **b** coordinate suggest pale yellow color and the sample appears to be the same, even though the maximum reflection is at

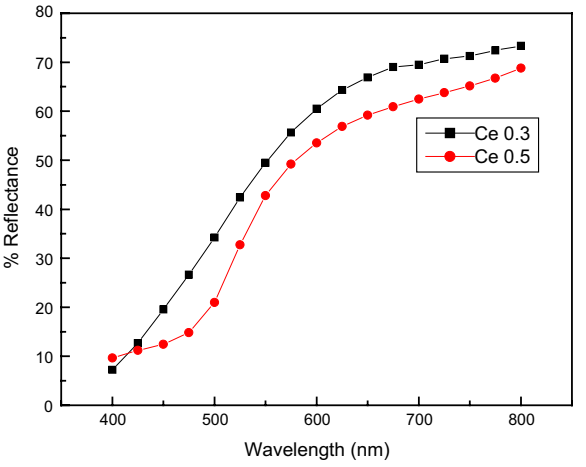

Fig. 6. Reflectance spectra for $(Bi_{1-x}Ce_x)_2O_3$, $x = 0.3$ and 0.5.

the high wavelength region. For Ce with $x = 0.5$ doping level, slight increase of **a** coordinate and slight decrease of **b** coordinate reduce the yellow color and increase the red component and appears to result in more intense coloration than with $x = 0.3$ doping. The maximum R% is 68.81, at wavelength 725 nm. The lightness **L** decreases with the increase of Ce content.

4. Conclusion

The comparative study of the results obtained from the Y and Ce substituted Bi_2O_3 pigments shows that Y doped pigments exhibit better properties like phase purity and intense coloration and high reflectance. From these analyses, it is also clear that with the increase of the rare earth concentration, the intensity of the color increases and lightness **L** decreases moderately. These pigments are heat and chemical resistant and can be used even in high temperature glazes and represent potential alternate inorganic pigments from the environmental point of view.

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