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$(TiO_2)_1$ $(CeO_2)_{1-x}$ $(RE_2O_3)_x$ − novel environmental secure pigments

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Abstract

This paper embodies the results of the investigations carried out on the synthesis of titania − rare earth mixed oxide pigments: $(TiO_2)_1$ $(CeO_2)_{1-x}$ $(RE_2O_3)_x$, where RE = Y, Pr, Nd or Sm with nominal compositions: $x = 0.2$ and 0.8 and their characterization by X-ray powder diffraction, scanning electron microscopy, energy dispersive spectrometric analysis and reflectance spectral data. The synthesized pigment samples are having color coordinates, low **a** and high **b** and exhibit the colors ranging from yellow to orange-red. The dominant reflectance of these colorants lies in the wavelength region of 600–800 nm. Among the various colorants prepared, Y and Sm doped pigments are found to be promising candidates as ecological pigments because of their high reflectance, lightness and intense coloration.

Keywords: Titanium; Rare earth; Mixed oxides; Colorants; Environmental secure pigments

1. Introduction

Inorganic pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels and glasses [1–3]. These pigments may impart coloristic properties and protect the coating from the effects of visible as well as ultraviolet and infrared light. In addition to absorbing light, their ability to scatter or reflect light also contributes to their functionality. In order to be suitable in a wide variety of applications, they need to demonstrate a high degree of light fastness and their high temperature stability. The majority of the inorganic pigments, which are currently employed on an industrial scale, generally, comprise toxic metals (cadmium, lead, chromium or cobalt) [4]. The use of the above pigments is becoming increasingly strictly controlled, indeed banned, by government legislation and regulations in many countries due to their reputedly high toxicity. Thus, serious economic and industrial need continues to exist for substituting inorganic pigments devoid of the above drawbacks.

Transition metals are used as a chromophore in a vast number of mixed metal oxide pigments [5,6]. In contrast, rare earths are used quite sparingly in inorganic pigments [7,8]. The intense coloration of rare earth based materials can arise from mostly charge transfer interactions between a donor and acceptor with the metal ions playing generally the role of an acceptor. Dopants based on rare earth elements in mixed oxide systems offer an opportunity to tune the color response through the manipulation of energy gaps and delocalization phenomena in conduction and valence bands. This phenomenon offers wide scope for designing of colorants for specific applications. Nontoxic yellow/orange pigment compositions, well suited for the coloration of a wide variety of substrates, for example paints, varnishes, plastics, ceramics, etc., comprise a major amount of zirconium oxide and an additive amount of cerium, praseodymium and/or terbium values, in the form of oxides, have been developed by Huguenin et al. [5] and assigned to Rhone-Poulenc Chimie, France. Recently, rare earth–transition metal oxide materials, having the general formula:

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$(RE_xTM)O_y$, where RE is rare earth, TM is transitional metal, x ranges from 0.08 to 12 and y ranges from $x + 1$ to $2x + 2$, have been reported as novel inorganic pigments for use in plastics, paints, coatings, glass enamels and other materials with various advantages over the traditional pigment formulations [1]. Chopin and Macaudiere [9] developed thermally/chemically stable and nontoxic inorganic pigments, characteristically green and well suited for the coloration of a wide variety of materials and substrates, having the formula $RE_2M_xM'_yO_5$, where RE is rare earth, M and M′ are Ba and Cu, respectively, x and y are numbers, the sum $x + y = 2$, and assigned to Rhone-Poulenc Chimie, France. However, till date, to our knowledge no reports have been seen on the preparation and characterization of mixed metal oxide pigments, involving titania and mixed rare earth oxides. Accordingly, the major objective of the present investigation is to develop alternate mixed metal oxide pigments for surface coating applications, containing environmental friendly metal ions like rare earths (Ce, Pr, Nd, Sm and Y) and transition metals such as titanium. The new pigments are of the formula $(TiO_2)_1\ (CeO_2)_{1-x}\ (RE_2O_3)_x$, where RE is Y, Pr, Nd or Sm with nominal compositions: $x = 0.2$ and 0.8, have been prepared and characterized for their structure and color properties.

2. Experimental

2.1. Materials

The starting materials used for the preparation of titania – rare earth oxide pigments – were TiO_2, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3 and Y_2O_3 (99.9% purity) supplied by Aldrich Chemicals Company.

2.2. Methodology

The titania – rare earth oxide samples were prepared in the stoichiometry $(TiO_2)_1\ (CeO_2)_{1-x}\ (RE_2O_3)_x$ where RE: Y, Pr, Nd or Sm with nominal compositions: $x = 0.2$ and 0.8. The above oxides were weighed in the required stoichiometric amounts and were mixed thoroughly in an agate mortar in acetone media. Then, the powder was dried in an air oven. The process of mixing and drying is repeated 3–4 times to get a homogeneous mixture. The calcination of these mixtures was carried out in platinum crucibles in an electrical furnace at a temperature of 1250 °C for 3 h. The heating of the furnace was programmed to increase the temperature initially at 10 °C/min up to 900 °C and afterwards the heating rate was decreased to 5 °C/min up to 1250 °C. In order to ensure the completion of the reaction, calcination process was repeated twice.

2.3. Characterization

The calcined powders were characterized by X-ray powder diffraction with a Philips X'Pert diffractometer. The XRD patterns were recorded in the 20–60° 2θ range using Ni filtered Cu Kα radiation. Morphological analysis of the powders was performed by scanning electron microscope, with a Jeol make JSM – 5600LV. The quantitative microanalysis of the products was carried out by energy dispersive spectrometer (EDAX, USA). The diffused reflectance spectra of the samples were carried out with a Shimadzu UV-2401 spectrophotometer operating in the 400–800 nm and the color coordinates were determined using CIE-LAB 1976 color scales. Among the synthesized pigments, one of the colorants was tested for acid resistance in con. HCl, con. H_2SO_4, and con. HNO_3. The thermal stability of the colorant was also checked by Pyris Diamond TG/DTA Perkin Elmer make.

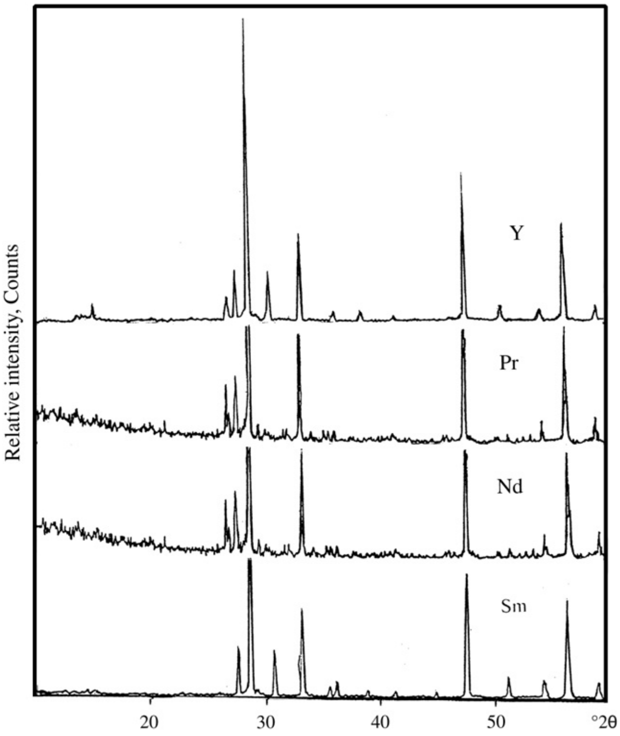


Fig. 1. Powder X-ray diffraction patterns of $(TiCe_{0.8}RE_{0.2})O_{3.9}$, RE = Y, Pr, Nd or Sm.

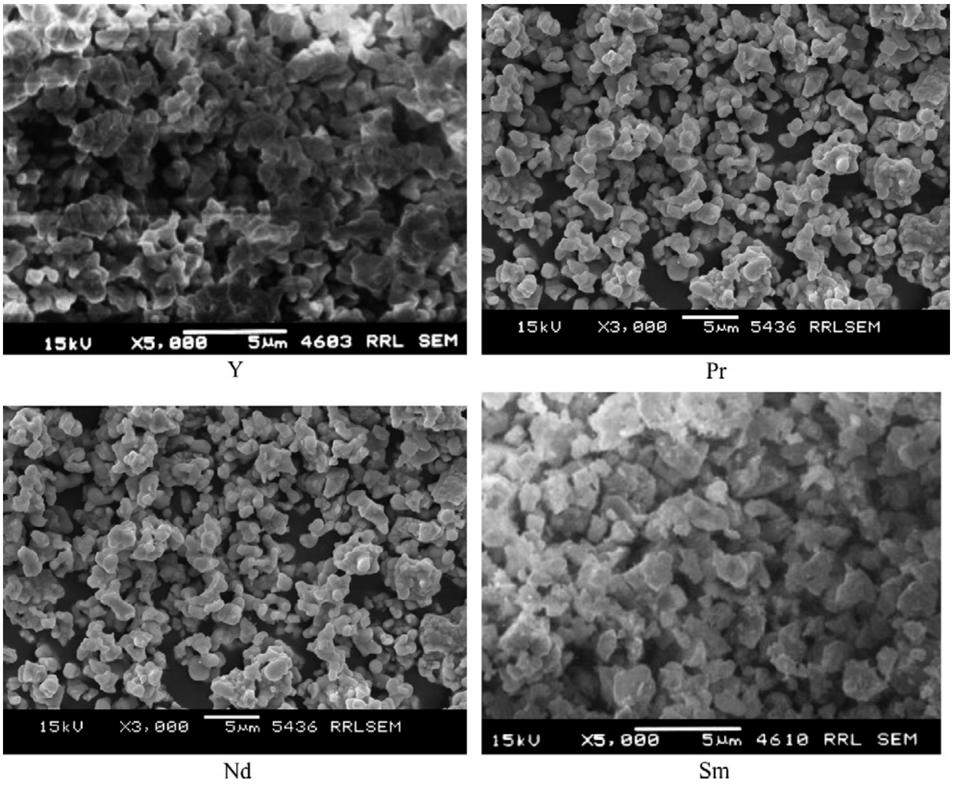
3. Results and discussion

3.1. $(TiO_2)_1\ (CeO_2)_{1-x}\ (RE_2O_3)_x$, where RE = Y, Pr, Nd or Sm and $x = 0.2$

Fig. 1 presents the XRD patterns of $(TiCe_{0.8}RE_{0.2})O_{3.9}$ compounds. In these patterns, all the major peaks can be assigned to the fluorite group ceriamite compound CeO_2 as per PDF No. 34-394. These patterns are also in good agreement

Table 1
Particle size of pigments

Theoretical formula of the pigment	Major phase formed	Particle size (nm)
$(TiCe_{0.8}Y_{0.2})O_{3.9}$	CeO_2	60–80
$(TiCe_{0.8}Pr_{0.2})O_{3.9}$	CeO_2	56–76
$(TiCe_{0.8}Nd_{0.2})O_{3.9}$	CeO_2	56–76
$(TiCe_{0.8}Sm_{0.2})O_{3.9}$	CeO_2	60–70
$(TiCe_{0.2}Y_{0.8})O_{3.6}$	$Ti_2Y_2O_7$	40–50
$(TiCe_{0.2}Sm_{0.8})O_{3.6}$	$Ti_2Sm_2O_7$	80–90



Y Pr

Nd Sm

Fig. 2. SEM photographs of $(TiCe_{0.8}RE_{0.2})O_{3.9}$, RE = Y, Pr, Nd or Sm.

with the earlier patterns of the CeO_2 [10]. The sharp and high intense peaks reveal the crystalline nature of the products. The particle size of the colorants was determined using Debye–Scherrer formula $D = 0.9\lambda/\beta \cos\theta$ from the respective XRD patterns. In the formula, where D is the particle size, λ is the wavelength of X-ray used, β and θ are the half width of XRD diffraction lines and half diffraction angle of 2θ, respectively. The particle size was found to be ranging from 55 to 80 nm (Table 1). The EDS microchemical analysis has been carried out at different regions of the sample and found the presence of all the expected elements. The stoichiometric formula calculated from the semi-quantitative EDS analysis is in close agreement with the respective theoretical formula (Table 1). The homogeneous nature of the samples can be seen from the SEM micrographs (Fig. 2). Further, the particle size of the powder samples is around 1 µm as observed from the SEM photographs.

The reflectance spectra of the TiO_2–CeO_2 with various rare earth dopants are depicted in Fig. 3. The high reflectance of the $TiCe_{0.8}RE_{0.2}O_{3.9}$ pigments lies in the 600–800 nm region. Further, a maximum $R\%$ of 90 was observed especially for $TiCe_{0.8}Y_{0.2}O_{3.9}$ pigment, as compared to 80 ($R\%$) reported elsewhere [8] for $Ce_{0.8}Pr_{0.2}O_2$ pigments. The color coordinates of the above pigments are given in Table 2. The addition of titanium to CeO_2–RE_2O_3 significantly enhances the lightness (L) of the pigments (L for $Ce_{0.8}Pr_{0.2}O_2$ is 56.82 [11]). The prepared pigments exhibit colors ranging from pale yellow to orange-red hue. On the other hand, it has been reported elsewhere that $Ce_{0.8}Pr_{0.2}O_2$ [11] exhibits only orange-red hue, whereas Swiler Daniel [1] reports white color for the $Ti_2Ce_2O_7$ pigment. Thus it is clear from the above study that the addition of small amount of various rare earth cations (Y, Pr, Nd or Sm) to TiO_2–CeO_2 produces not only colors ranging from pale yellow to orange-red, but also improves the lightness of the pigment significantly.

3.2. $(TiO_2)_1$ $(CeO_2)_{1-x}$ $(RE_2O_3)_x$, where RE = Y or Sm and $x = 0.8$

Powder X-ray diffraction patterns of $(TiCe_{0.2}Y_{0.8})O_{3.6}$ and $(TiCe_{0.2}Sm_{0.8})O_{3.6}$ are given in Fig. 4. The sharp and high

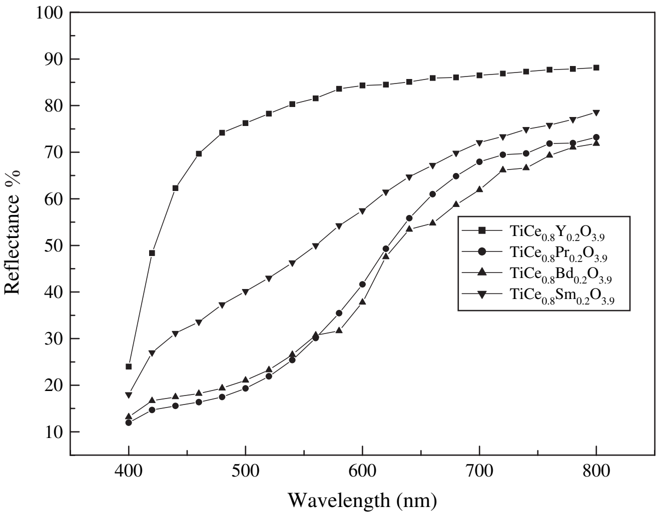


Fig. 3. Reflectance spectra of $(TiCe_{0.8}RE_{0.2})O_{3.9}$, RE = Y, Pr, Nd or Sm.

Table 2
Color properties of the pigments

Theoretical formula of the pigment	Color coordinates			Dominant reflectance band	Max. *R%*	Color
	a	**b**	**L**			
$(TiCe_{0.8}Y_{0.2})O_{3.9}$	−3.34	12.78	89.49	500–800	90	Pale yellow
$(TiCe_{0.8}Pr_{0.2})O_{3.9}$	14.33	18.75	55.91	650–800	72	Orange-red
$(TiCe_{0.8}Nd_{0.2})O_{3.9}$	11.92	15.87	55.51	650–800	72	Pale orange-red
$(TiCe_{0.8}Sm_{0.2})O_{3.9}$	4.81	16.24	72.02	700–800	77	Orange-red
$(TiCe_{0.2}Y_{0.8})O_{3.6}$	−0.07	12.33	85.06	625–800	85	Orange-red
$(TiCe_{0.2}Sm_{0.8})O_{3.6}$	−3.73	19.18	86.55	600–800	87	Yellow

intense peaks found in the diffraction patterns reveal the crystalline nature of the products. In both the compounds, all the peaks can be indexed to the cubic pyrochlore type structure and further the patterns are also identical to earlier reported pyrochlore type compounds such as $Ln_2Mo_2O_7$ [12] and $Ca_3RE_3Ti_7Nb_2O_{26.5}$ [13]. The particle size calculated using Debye–Scherrer formula is found to be ranging from 80 to 90 nm for Sm compound and from 40 to 50 nm for Y compound (Table 1). The uniform particle size and homogeneous morphology are also observed in the SEM micrographs (Fig. 5a, b). The EDS analysis was carried out at different regions and the composition is found as per the theoretical formula proposed (Table 1). This also confirms the homogeneity of the phase formed.

The effect of Sm and Y doping in ceria and titania pigment was analyzed from the diffuse reflectance spectra and the

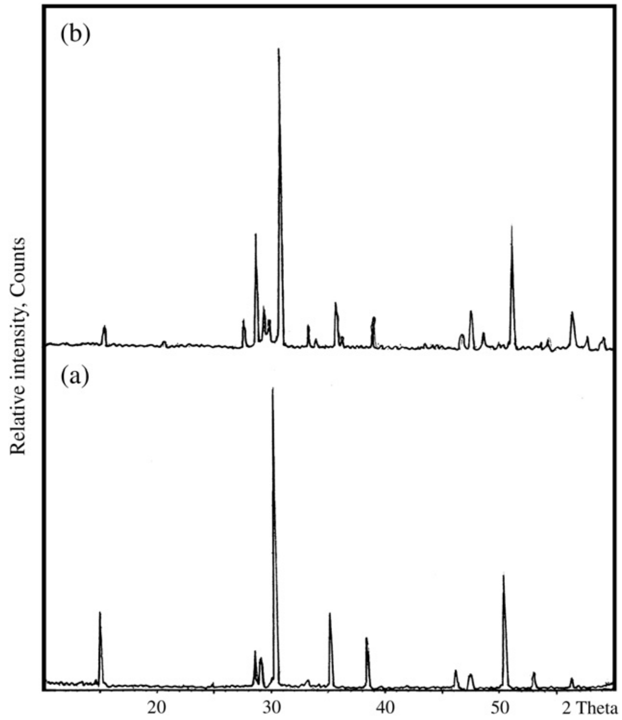


Fig. 4. X-ray diffraction patterns recorded from (a) $TiCe_{0.2}Y_{0.8}O_{3.6}$ and (b) $TiCe_{0.2}Sm_{0.8}O_{3.6}$.

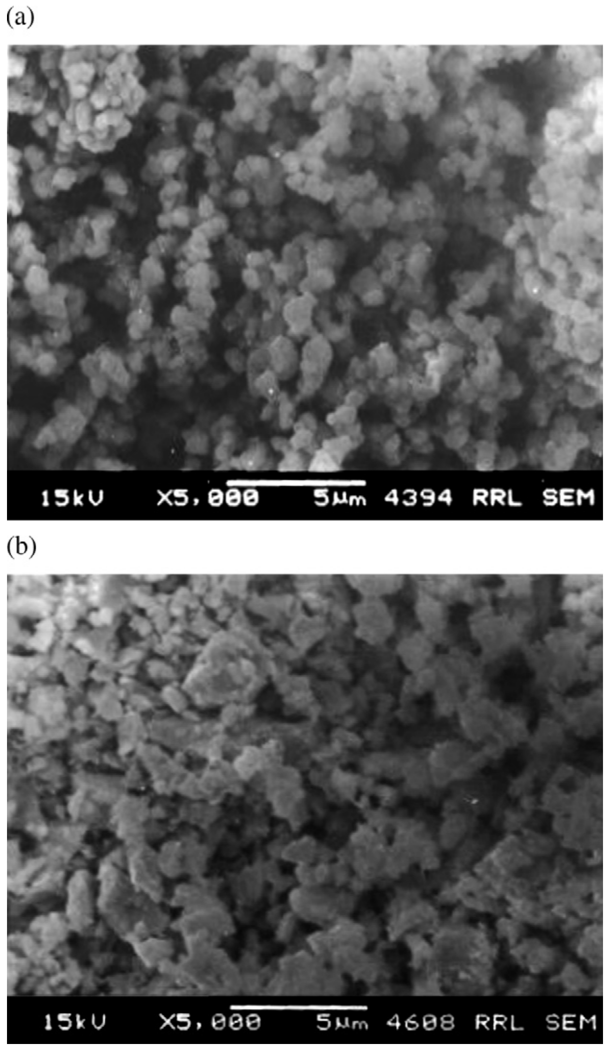


Fig. 5. SEM photographs of (a) $TiCe_{0.2}Y_{0.8}O_{3.6}$ and (b) $TiCe_{0.2}Sm_{0.8}O_{3.6}$.

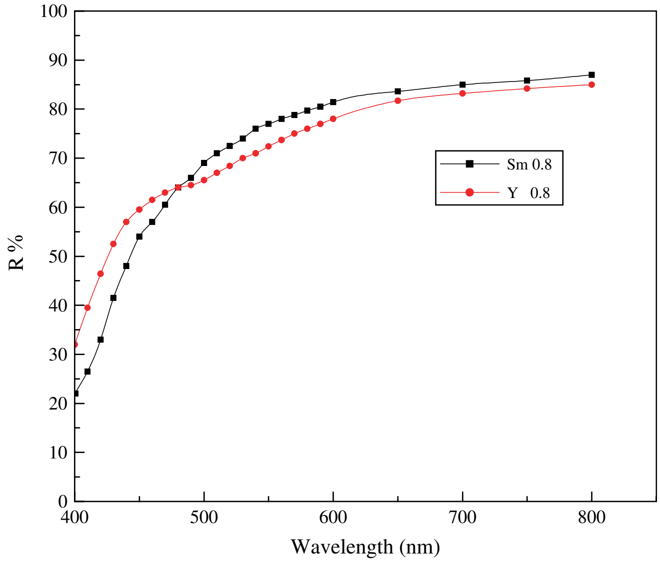


Fig. 6. Reflectance spectra for $(TiCe_{0.2}Sm_{0.8})O_{3.6}$ and $(TiCe_{0.2}Y_{0.8})O_{3.6}$ pigments.

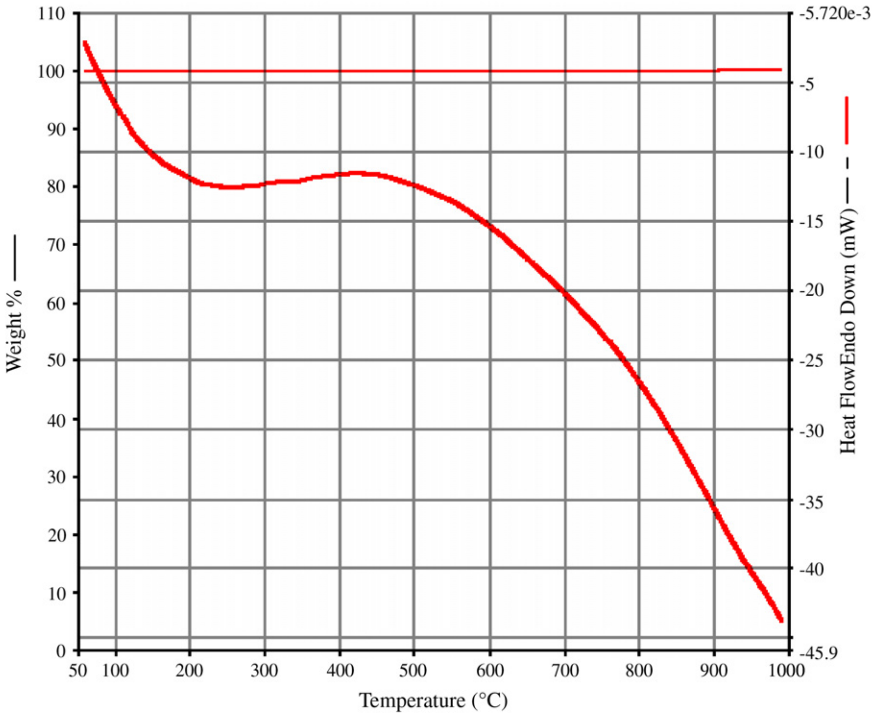


Fig. 7. TG/DTA curves of $TiCe_{0.2}Y_{0.8}O_{3.6}$.

results are depicted in Fig. 6 and Table 2. The Sm^{3+} ion imparted an intense yellow hue to the pigment (high coordinate **b** value) and reduces green hue (very low coordinate −**a** value). The high reflectance lies in the 600–800 nm region and shows a maximum *R*% of 87 at 783 nm. On the other hand, the Y^{3+} ion imparted an intense orange-red hue to the pigment (moderate coordinate **b** value and low coordinate −**a** value). The high reflectance band lies in the 700–800 nm region and shows a maximum *R*% of 85 at 774 nm. The reflectance in this region indicates that the pigment may appear orange-red in color and appears visibly the same color. From this analysis, it is clear that the addition of Sm or Y to the pigments containing titanium and cerium (less in content) produces different colors ranging from yellow to orange-red hue with high reflectance and lightness. On the other hand, white pigments have been reported elsewhere with mixed oxides containing TiO_2 and Sm_2O_3 or Y_2O_3 [1].

It is clear from the TG/DTA analysis (Fig. 7) of $TiCe_{0.2}Y_{0.8}O_{3.6}$ that there is no loss of weight and phase transformation in the temperature range (50–1000 °C). Among the various synthesized pigment samples, typically $TiCe_{0.2}Y_{0.8}O_{3.6}$ was tested for its acid resistance. A small quantity of weighed pigment sample is mixed with 10% concentrated HNO_3, HCl or H_2SO_4 and soaked for half an hour with constant stirring using a magnetic stirrer. Then, the pigment was filtered, washed with water, dried and weighed. Negligible weight loss was observed for all the acids tested. This indicates that the pigment samples are resistant to the various mineral acids.

4. Conclusion

The present investigation demonstrates that various colorants with different hues ranging from yellow to orange can be produced from mixed metal oxides containing titanium and rare earths. The developed pigments are found to have high reflectance and lightness, especially with Sm or Y in addition to TiO_2–CeO_2, as compared to earlier reported colorants TiO_2–Sm_2O_3 or Y_2O_3 [1]. Further, these colorants are also thermal and chemical resistant. Thus, the above pigments may find potential alternative to the conventional toxic inorganic pigments, for use in paints, coatings, plastics and glass enamels.

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