



# Synthesis and characterization of new environmentally benign tantalum-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ yellow pigments: Applications in coloring of plastics

V.S. Vishnu, Giable George, V. Divya, M.L.P. Reddy\*

National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Thiruvananthapuram 695 019, Kerala, India

## ARTICLE INFO

### Article history:

Received 28 October 2008

Received in revised form

1 November 2008

Accepted 3 November 2008

Available online 12 November 2008

### Keywords:

Novel ecological yellow pigments

$\text{CeO}_2$ – $\text{ZrO}_2$ – $\text{Ta}_2\text{O}_5$

Solid solution

Coloring of plastics

## ABSTRACT

New inorganic pigments having the general formula  $\text{Ce}_{1-(x+y)}\text{Zr}_x\text{Ta}_y\text{O}_{2+\delta}$  ( $x$  ranges from 0.15 to 0.2 and  $y$  ranges from 0 to 0.05) displaying colors ranging from white to yellow have been synthesized by a traditional solid-state route, as viable alternatives to lead, cadmium and chromium based yellow toxic inorganic colorants. The products were characterized by X-ray powder diffraction, UV–vis diffuse reflectance spectroscopy and CIE- $L^*a^*b^*$  1976 color scales. The coloring mechanism is based on the strong absorptions of the pigments in the visible region under 500 nm, which could originate from the additional energy level between  $\text{O}_{2p}$  valence band and the  $\text{Ce}_{4f}$  conduction band by forming a hybrid orbital of  $\text{Ta}_{5d}$  and  $\text{O}_{2p}$ . The designed yellow pigments consist of non-toxic elements and further found to be thermally and chemically stable. The pigments were also found to be suitable candidates for the coloring of plastics.

© 2008 Elsevier Ltd. All rights reserved.

## 1. Introduction

In recent years there is a great demand for the development of new yellow colored inorganic materials to substitute for industrial pigments that are based on heavy metals hazardous to health and environment [1]. Inorganic pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels and glasses [2]. Although  $\text{PbCrO}_4$ ,  $\text{PbMoO}_4$ ,  $\text{Pb}_2\text{Sb}_2\text{O}_7$  and  $\text{CdS}$  have been widely employed as conventional yellow inorganic pigments, the use of these pigments has been restricted because they contain toxic elements [3]. Praseodymium yellow ( $\text{ZrSiO}_4\text{:Pr}$ ) has been known as one of the environmentally benign yellow pigments, which has been applied for many surface coating applications [4–6]. However, this pigment requires high temperature calcinations during preparation, which tends to induce particle growth of the pigment. Hence it is difficult to apply the praseodymium yellow to paints and inks in which fine dispersions of the pigment are essential.

Recently, several rare earth-based yellow inorganic pigments have been proposed by many researchers including our group as viable alternatives to the existing traditional toxic pigments [7–10]. Among several non-toxic yellow pigments,  $\text{CeO}_2$  and related materials have attracted much attention because of their opacity, low toxicity and high thermal stability [11–14]. The coloring mechanism is based on the charge-transfer band from  $\text{O}_{2p}$  to  $\text{Ce}_{4f}$  in the semi-conducting  $\text{CeO}_2$ . The band gap between the anionic  $\text{O}_{2p}$

valence band and the cationic  $\text{Ce}_{4f}$  conduction band can be modified by the formation of solid solutions, which introduces an additional electronic level between the valence and conduction bands. As a result a shift of the charge-transfer band is observed. Crystalline cerium molybdenum oxides have been reported as novel yellow pigments as alternatives to lead, cadmium and chromium based toxic pigments [11]. The reflectance spectrum of the cerium double molybdates indicates strong absorption in both visible and ultraviolet regions, which could originate from the  $\text{O}_{2p}$ – $\text{Ce}_{4f}$  and the  $\text{O}_{2p}$ – $\text{Mo}_{3d}$  double charge transitions and as a result the pigments show yellow color. Amorphous cerium tungstate,  $\text{Ce}_{1-x}\text{M}_x\text{W}_2\text{O}_8$  ( $\text{M} = \text{Zr}$  or  $\text{Ti}$ ,  $0 \leq x \leq 0.6$ ) has been reported as a possible ecological inorganic yellow pigment. This pigment exhibits brilliant yellow color due the effective absorptions in the visible and ultraviolet regions (under 500 nm efficiently), which is originated from the  $\text{O}_{2p}$ – $\text{Ce}_{4f}$  and the  $\text{O}_{2p}$ – $\text{W}_{5d}$  double charge transitions [12]. Earlier investigations reveal that the classical toxic inorganic pigments can be replaced by solid solutions of perovskites  $\text{CaTaO}_2\text{N}$  and  $\text{LaTaON}_2$ , which gives colors ranging from yellow to deep red [9]. Although these pigments are non-toxic and show excellent color hue, it is necessary to heat the starting materials in a flow of toxic and inflammable ammonia gas for a long time (20–60 h) to synthesize them. Therefore, research needs to be performed in developing novel yellow inorganic pigments with various advantages over traditional toxic pigment formulations.

Thus, the present paper is focused on the development of a novel class of yellow pigments based on tantalum-doped  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  systems as alternatives to the existing toxic inorganic pigments. The new pigments of the general formula  $\text{Ce}_{1-(x+y)}\text{Zr}_x\text{Ta}_y\text{O}_{2+\delta}$  ( $x$  ranges

\* Corresponding author. Tel.: +91 471 2515360; fax: +91 471 2491712.

E-mail address: [mlpredy55@gmail.com](mailto:mlpredy55@gmail.com) (M.L.P. Reddy).

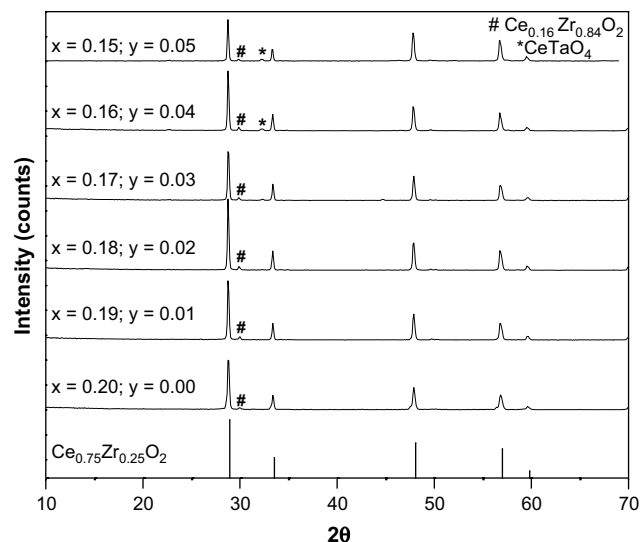


Fig. 1. XRD patterns of  $\text{Ce}_{1-(x+y)}\text{Zr}_x\text{Ta}_y\text{O}_{2+\delta}$  pigments.

from 0.15 to 0.2 and  $y$  ranges from 0.00 to 0.05) have been synthesized by a traditional solid-state reactions of the respective oxides and characterized for their structure and optical properties. The developed pigment was finally applied for the coloration of plastic materials.

## 2. Experimental section

### 2.1. Materials and methodology

Several compositions based on  $\text{Ce}_{1-(x+y)}\text{Zr}_x\text{Ta}_y\text{O}_{2+\delta}$  ( $x$  ranges from 0.15 to 0.2 and  $y$  ranges from 0.00 to 0.05) stoichiometry were prepared by the ceramic method. The precursors employed for the traditional ceramic pigment synthesis route are the corresponding oxides:  $\text{CeO}_2$  (99.9%),  $\text{ZrO}_2$  (99.9%) and  $\text{Ta}_2\text{O}_5$  (99.9%) supplied by Aldrich Chemical Company. In this method, the reactants were mixed and homogenized by wet milling with acetone in an agate mortar for 30 min. The homogeneous mixture was calcined in platinum crucibles in an electric furnace at a temperature of 1300 °C for 6 h. The heating of the furnace was programmed to increase the temperature at 5 °C/min. In order to ensure the completion of the reaction, the calcinations process was repeated thrice for the same sample. To refine and homogenize the particle size after calcinations, the resulting products were ground in an agate mortar.

### 2.2. Characterization techniques

Phase analysis of the colored samples was performed by X-Ray powder diffraction using Ni-filtered  $\text{Cu K}\alpha$  radiation with a Philips

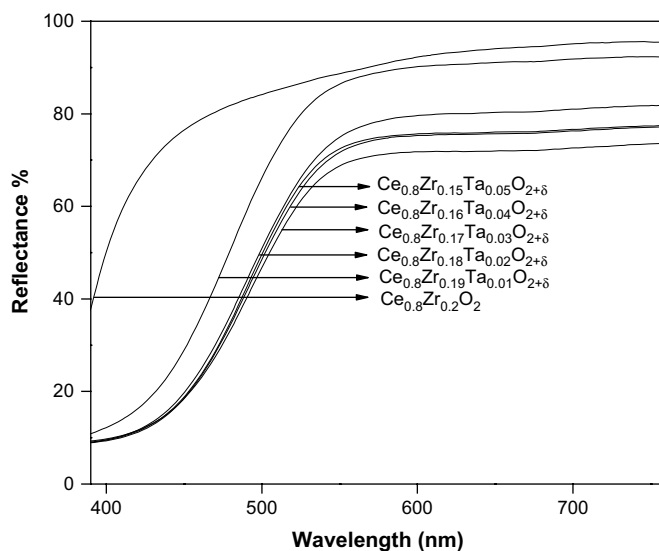


Fig. 3. Reflectance spectra of  $\text{Ce}_{1-(x+y)}\text{Zr}_x\text{Ta}_y\text{O}_{2+\delta}$  pigments.

X'pert Pro diffractometer. Data were collected by step scanning from 10 to 70°  $2\theta$ . Optical reflectance of the synthesized pigment samples was measured (380–780 nm) with an UV-vis spectrometer (Shimadzu UV-2450) using barium sulfate as a reference. The measurement conditions were following: an illuminant D65, 10° complementary observer and measuring geometry  $d/8^\circ$ . The color properties are described in terms of CIE- $L^*a^*b^*$  1976 color scales. Scanning electron micrographs of the samples were taken on a scanning electron microscope (JEOL JSM-5600LV). The thermal stability of the colorant and the polymer incorporated sample was checked by Pyris Diamond TG/DTA Perkin Elmer make. The particle diameter of the sample was measured by the laser scattering particle size distribution analyzer (CILAS 930 Liquid) using Fraunhofer bending.

### 2.3. Coloration of plastics

Poly(methyl methacrylate); (PMMA; Sigma Aldrich) was utilized as a binder phase for fabricating the pigmented compact. The typical pigment sample,  $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$  was ultrasonicated (Vibronics, 250 W, India) in an alcohol/water (1:4) mixture for 10 min to ensure the complete dispersion of the pigment particles. A viscous solution consists of PMMA (95 and 90 wt%) was made using a conventional electrical coil heater. The pigment dispersion was slowly added while stirring and converted into a thick paste. The paste after 2 h of curing, compressed uniaxially into the form of cylindrical discs using a hydraulic press (Lawrence & Maya, India) at a pressure of 25 MPa. Both sides of the pigmented polymer were

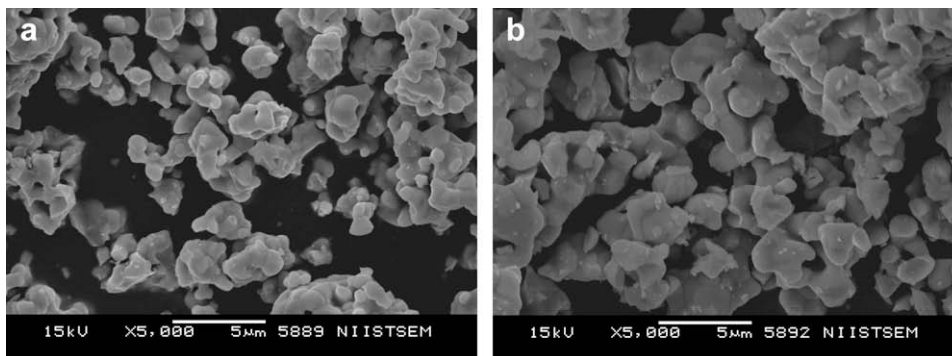


Fig. 2. SEM Micrographs of (a)  $\text{Ce}_{0.8}\text{Zr}_{0.20}\text{O}_2$  and (b)  $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$ .

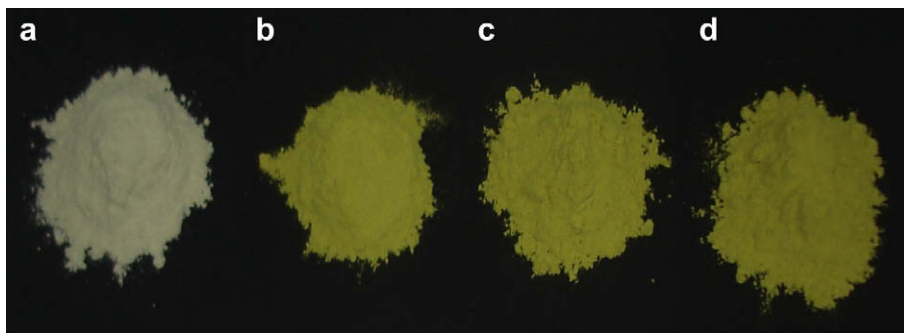
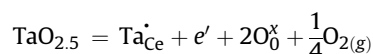


Fig. 4. Photographs of (a)  $\text{Ce}_{0.8}\text{Zr}_{0.20}\text{O}_2$  (b)  $\text{Ce}_{0.8}\text{Zr}_{0.19}\text{Ta}_{0.01}\text{O}_{2+\delta}$  (c)  $\text{Ce}_{0.8}\text{Zr}_{0.17}\text{Ta}_{0.03}\text{O}_{2+\delta}$  (d)  $\text{Ce}_{0.8}\text{Zr}_{0.15}\text{Ta}_{0.05}\text{O}_{2+\delta}$  pigments.

lapped using a fine grade emery sheet for obtaining a polished surface. The intensity of the color of plastics will depend on the concentration of the pigment.

### 3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of the  $\text{Ce}_{1-(x+y)}\text{Zr}_x\text{Ta}_y\text{O}_{2+\delta}$  ( $x$  ranges from 0.15 to 0.2 and  $y$  ranges from 0.00 to 0.05) pigment samples. The XRD pattern of  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  can be very well indexed to the cubic fluorite structure of  $\text{CeO}_2$  with a lattice constant of 0.5363 nm. Addition of  $\text{Zr}^{4+}$  into  $\text{CeO}_2$  produces intrinsic strain which results in a decrease of lattice parameter of  $\text{CeO}_2$  from 0.5411 nm (JCPDF 34-394) to 0.5363 nm [13]. This is due to the smaller ionic radii of  $\text{Zr}^{4+}$  (0.84 Å) compared to  $\text{Ce}^{4+}$  (0.97 Å) [15]. The decrease in lattice parameter further confirms the solid-solution formation. The progressive substitution of  $\text{Ta}^{5+}$  for  $\text{Zr}^{4+}$  in  $\text{Ce}_{0.8}\text{Zr}_{0.2}$  solid solution, did not change the cell parameter values significantly since the ionic radii of  $\text{Ta}^{5+}$  (0.74 Å) is moderately smaller than  $\text{Zr}^{4+}$ . With the increase of tantalum doping in  $\text{Ce}_{1-(x+y)}\text{Zr}_x\text{Ta}_y\text{O}_{2+\delta}$  ( $x$  ranges from 0.17 to 0.15 and  $y$  ranges from 0.03 to 0.05) beyond 3%, a minor phase of  $\text{CeTaO}_4$  has also been noticed from the XRD patterns along with the major cubic fluorite phase of  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ . The formation of the  $\text{CeTaO}_4$  can be explained due to the low solubility of Ta in ceria matrix at higher concentrations of Ta [16]. Further, the minor peak observed in the XRD patterns of all the compositions at a  $2\theta$  of  $\sim 30$  is due to the tetragonal phase of  $\text{Ce}_{0.16}\text{Zr}_{0.84}\text{O}_2$  (JCPDF 38-1437) [17]. Fig. 2 refers to the SEM micrographs of typical pigment samples,  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  and  $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$ . The homogeneous nature of the pigments can be understood from the SEM images. From the SEM photograph, it is clear that there is an even grain distribution; the average grain size is less than 5  $\mu\text{m}$ . The presence of excess oxygen in the present system can be accommodated as structural oxygen and not as interstitial sites [18]. The overstoichiometry due to oxygen is, therefore, compensated by cation vacancies. The defect equilibrium in ceria doped with  $\text{Ta}_2\text{O}_5$ , in terms of Kroger–Vink notation [19] can be represented as



Color depends on several material properties of a pigment, among which particle size of the pigment is of prime importance. Decrease in particle size of the pigment increases the surface area which further contributes to high surface coverage, higher number of reflectance points and hence more scattering. The particle size distribution of the typical pigment,  $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$  was investigated in water with calgon as the dispersing agent. The results reveal a distribution with 90% of the particles with size smaller than 7.54  $\mu\text{m}$ , 50% smaller than 2.59  $\mu\text{m}$  and 10% smaller than 0.36  $\mu\text{m}$ . The mean particle diameter of the pigment sample was found to be 5.65  $\mu\text{m}$ .

The effect of tantalum doping on the optical properties of  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  was analyzed from the diffuse reflectance spectra of the pigment samples (Fig. 3). The optical absorption edge critically depends on the concentration of tantalum present in the pigment samples and all these samples absorb blue light efficiently, which is originated from the  $\text{O}_{2p}$ – $\text{Ce}_{4f}$  charge transitions. As a result, the color of the pigment samples becomes yellow because blue is a complimentary color to yellow (Fig. 4). Furthermore, the doping of  $\text{Ta}^{5+}$  into the  $\text{CeO}_2$ – $\text{ZrO}_2$  lattice will result in an additional energy level between  $\text{O}_{2p}$  valence band and the  $\text{Ce}_{4f}$  conduction band by forming a hybrid orbital of  $\text{Ta}_{5d}$  and  $\text{O}_{2p}$  [20]. The band gap of the colorants as determined from the absorbance spectra is given in Table 1 and was obtained simply by a straightforward extrapolation method [21]. It can be clearly seen that the band gap of the  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  (3.0 eV) decreases to 2.34 eV with the progressive doping of  $\text{Ta}^{5+}$  for  $\text{Zr}^{4+}$  in  $\text{Ce}_{1-(x+y)}\text{Zr}_x\text{Ta}_y\text{O}_{2+\delta}$  ( $x$  ranges from 0.17 to

Table 1

The color coordinates of the powder pigments and polymer discs and band gap values.

Pigment composition	Color coordinates					Band gap (eV)
	$L^*$	$a^*$	$b^*$	$C^*$	$h^\circ$	
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	97.9	−2.2	12.1	12.3	79.5	3.00
$\text{Ce}_{0.8}\text{Zr}_{0.19}\text{Ta}_{0.01}\text{O}_{2+\delta}$	90.4	−10.4	49.2	50.3	78.1	2.40
$\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$	87.0	−10.9	52.0	53.1	78.2	2.38
$\text{Ce}_{0.8}\text{Zr}_{0.17}\text{Ta}_{0.03}\text{O}_{2+\delta}$	86.7	−9.2	54.7	55.5	80.5	2.34
$\text{Ce}_{0.8}\text{Zr}_{0.16}\text{Ta}_{0.04}\text{O}_{2+\delta}$	83.6	−9.0	52.3	53.0	80.2	2.35
$\text{Ce}_{0.8}\text{Zr}_{0.15}\text{Ta}_{0.05}\text{O}_{2+\delta}$	82.6	−9.8	50.6	51.6	79.0	2.36
$\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$ (5%) + PMMA	58.8	−3.6	32.3	32.5	83.5	
$\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$ (10%) + PMMA	64.0	−2.9	46.0	46.1	86.4	

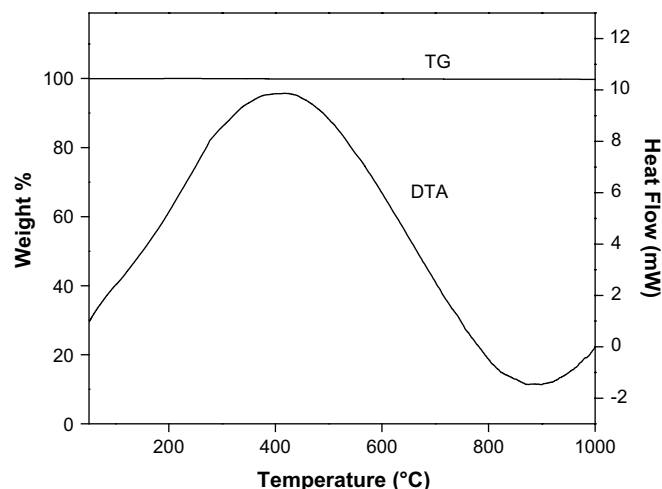


Fig. 5. The TG-DTA of  $\text{Ce}_{0.8}\text{Zr}_{0.16}\text{Ta}_{0.04}\text{O}_{2+\delta}$  pigments.

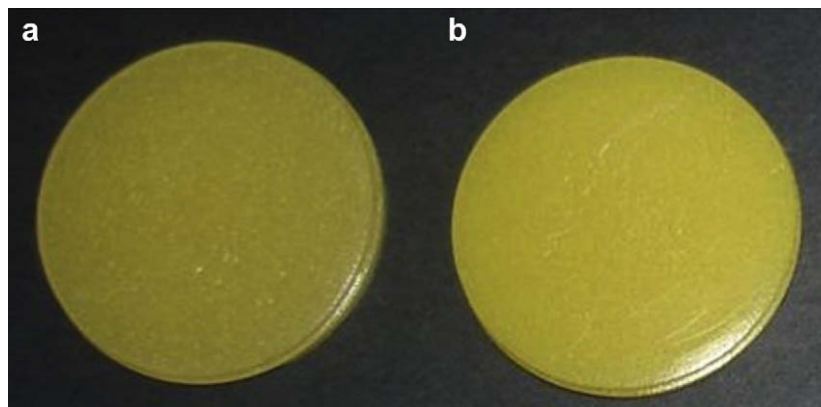


Fig. 6. Photograph of (a)  $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$  (5%) + PMMA and (b)  $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$  (10%) + PMMA.

0.20 and  $y$  ranges from 0 to 0.03) samples. Thus the color of the pigment samples gently changes from white to yellow. On the other hand, the band gap of the colorants moderately increases above 3% doping of Ta due to the formation of minor phase of  $\text{CeTaO}_4$ .

The CIE 1976 color coordinates of the powdered pigments are summarized in Table 1. The increase of  $b^*$  value with the increase of dopant concentration from  $y=0$  to 0.03 in  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ , indicates that the color of the pigment gently changes to yellow. It can be seen that there is no appreciable change in  $a^*$  which is responsible for the green tinge of the pigment sample after the progressive doping of tantalum into  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ . At higher tantalum concentrations, the chroma of the pigment decreases slightly may be due to the formation of minor phase of  $\text{CeTaO}_4$  [16]. The color coordinates of the typical pigment,  $\text{Ce}_{0.8}\text{Zr}_{0.17}\text{Ta}_{0.03}\text{O}_{2+\delta}$  ( $L^* = 86.7$ ,  $a^* = -9.2$ ,  $b^* = 54.7$ ,  $C^* = 55.5$ ,  $h^\circ = 80.5$ ), especially the chroma was found to be much higher than that of the commercially available pigment ( $L^* = 90.0$ ,  $a^* = -3.5$ ,  $b^* = 43.3$ ,  $C^* = 43.5$ ,  $h^\circ = 85.4$ ) Zircon Yellow (Zircon 1561:  $(\text{Zr},\text{Pr})\text{SiO}_4$  of M/s Kawamura Chemicals, Japan). However, the chroma of the present pigment samples is found to be inferior to that of commercial cadmium yellow ( $L^* = 75.7$ ,  $a^* = -7.9$ ,  $b^* = 99.1$ ,  $C^* = 99.4$ ,  $h^\circ = 85.4$ ) [9]. The hue angles ( $h^\circ$ ) of the present pigments were found to be in the yellow region of the cylindrical color space.

It is clear from the TG/DTA analysis (Fig. 5) of the typical pigment  $\text{Ce}_{0.8}\text{Zr}_{0.16}\text{Ta}_{0.04}\text{O}_{2+\delta}$  that there is no loss of weight and phase transformation in the temperature range 50–1000 °C. The typical pigment  $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$  was tested for its acid and alkali resistances. A pre-weighed quantity of the pigment was treated with 10%  $\text{HCl}/\text{H}_2\text{SO}_4/\text{HNO}_3$  and  $\text{NaOH}$ , and soaked for half an hour with constant stirring using a magnetic stirrer. The pigments were then filtered, washed with water, dried and weighed. Negligible weight loss was noticed for the range of acids and alkali tested. The typical total color difference value ( $\Delta E^*$ ) [22] after acid and alkali resistance tests were found to be negligible ( $\Delta E^* = 1.3$  for  $\text{HNO}_3$ ;  $\Delta E^* = 1.2$  for  $\text{H}_2\text{SO}_4$ ;  $\Delta E^* = 0.9$  for  $\text{HCl}$  and  $\Delta E^* = 0.7$  for  $\text{NaOH}$ ). Thus the designed yellow pigments are found to be chemically and thermally stable.

The coloring performance of the pigments ( $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$ ) was investigated for its coloring application in a PMMA substrate. Typically 5 or 10 wt% of the pigment sample was dispersed in PMMA and compressed to a cylindrical disc (Fig. 6). The color coordinates of the test pieces were measured at different locations and an average value is depicted in Table 1. The  $L^*a^*b^*$  values obtained are more or less the same, indicating the uniform distribution of the pigment particles in the polymer matrix. The intensity of the color of the plastic depends upon the concentration of the pigment being incorporated. Thermogravimetric analysis of the pigmented polymer sample was carried out in the range of

50–500 °C. The TG clearly indicates the thermal stability of the colored polymer up to 225 °C. The light resistance of the above  $\text{Ce}_{0.8}\text{Zr}_{0.18}\text{Ta}_{0.02}\text{O}_{2+\delta}$  dispersed PMMA matrix was tested by exposing it to sunlight at various time intervals and measured the color coordinates. The typical total color difference value ( $\Delta E^*$ ) after exposing to sunlight was negligible ( $\Delta E^* = 1.5$  after 24 h;  $\Delta E^* = 0.9$  after 48 h;  $\Delta E^* = 0.7$  after 72 h). This indicates that the pigmented polymer is light resistant. Thus the developed pigments may find potential applications in the coloring of various plastic materials.

#### 4. Conclusion

In summary, new environmentally benign yellow inorganic pigments have been successfully synthesized by doping tantalum into zirconia matrix of  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ . The band gap of these colorants gently changes from 3.0 to 2.34 eV with increasing doping of tantalum. The developed pigments are found to be thermally and chemically stable and also do not contain toxic metals. Thus, the present pigments may find potential alternative to the classical toxic yellow inorganic pigments for various surface coating applications.

#### Acknowledgements

This work was supported by Indian Rare Earths Limited Technology Development Council (IRELTDC). The authors wish to thank Prof. T.K. Chandrasekhar, Director, National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram, India for his constant encouragement.

#### References

- [1] Smith HM. High performance pigments. Weinheim: Wiley-VCH; 2002.
- [2] Swiler DR, Terry JD, Axtell, Enos A. Rare earth transition metal oxide pigments. U.S. Patent 6,582,814; 2003.
- [3] Badenes JA, Llusar M, Tena MA, Calbo J, Monros G. Praseodymium-doped cubic  $\text{Ca-ZrO}_2$  ceramic stain. Journal of the European Ceramic Society 2002;22:1981–90.
- [4] Nero GD, Cappelletti G, Ardizzone S, Fermo P, Gilardoni S. Yellow Pr–zircon pigments: the role of praseodymium and of the mineralizer. Journal of the European Ceramic Society 2004;24:3603–11.
- [5] Hill K, Lehman R, Swiler D. Effects of selected processing variables on color formation in praseodymium-doped zircon pigments. Journal of the American Ceramic Society 2000;83:2177–82.
- [6] Blonski RP. Stable heavy metal free zircon pigments for use in plastics and paints and method for coloring thereof. U.S. Patent 5,316,570; 1994.
- [7] Prabhakar Rao P, Reddy MLP.  $(\text{TiO}_2)(\text{CeO}_2)_{1-x}(\text{RE}_2\text{O}_3)_x$ -novel environmental secure pigments. Dyes and Pigments 2007;73:292–7.
- [8] George G, Sandhya Kumari L, Vishnu VS, Ananthakumar S, Reddy MLP. Synthesis and characterization of environmentally benign calcium-doped  $\text{Pr}_2\text{Mo}_2\text{O}_9$  pigments: applications in coloring of plastics. Journal of Solid State Chemistry 2008;181:487–92.

- [9] Jansen M, Letschert HP. Inorganic yellow-red pigments without toxic metals. *Nature* 2000;404:980–2.
- [10] Gauthier G, Jobic S, Evain M, Koo HJ, Whangbo MH, Fouassier C, et al. Syntheses, structures and optical properties of yellow  $\text{Ce}_2\text{SiS}_5$ ,  $\text{Ce}_6\text{Si}_4\text{S}_{17}$  and  $\text{Ce}_4\text{Si}_3\text{S}_{12}$  materials. *Chemistry of Materials* 2003;15:828–37.
- [11] Sreeram KJ, Radhika S, Devi JM, Nair BU, Ramasami T. Cerium molybdenum oxides for environmentally benign pigments. *Dyes and Pigments* 2007;75:687–92.
- [12] Furukawa S, Masui T, Imanaka N. Synthesis of new environment-friendly yellow pigments. *Journal of Alloys and Compounds* 2006;418:255–8.
- [13] Furukawa S, Masui T, Imanaka N. New environment-friendly yellow pigments based on  $\text{CeO}_2$ – $\text{ZrO}_2$  solid solutions. *Journal of Alloys and Compounds* 2008;451:640–3.
- [14] Masui T, Tategaki H, Imanaka N. Preparation and characterization of  $\text{SiO}_2$ – $\text{CeO}_2$  particles applicable for environment-friendly yellow pigments. *Journal of Materials Science* 2004;39:4909–11.
- [15] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A* 1976;32:751–67.
- [16] Clemente DA, Lucchini E, Meriani S, Furlan N. Crystal structures of  $\text{CeO}_2$ – $\text{ZrO}_2$ – $\text{Ta}_2\text{O}_5$  ternary system studied by Rietveld method. *Journal of the European Ceramic Society* 2005;25:1863–76.
- [17] Reddy BM, Khan A. Raman and X-ray photoelectron spectroscopy study of  $\text{CeO}_2$ – $\text{ZrO}_2$  and  $\text{V}_2\text{O}_5/\text{CeO}_2$ – $\text{ZrO}_2$  catalysts. *Langmuir* 2003;19:3025–30.
- [18] van Roosmalen JAM, Cordfunke EHP. A new defect model to describe the oxygen deficiency in perovskite-type oxides. *Journal of Solid State Chemistry* 1991;93:212–9.
- [19] Kroger FA, Vink HJ. In: Sietz F, Turnbull D, editors. *Solid state physics*, vol. 3. New York: Associated Press; 1956. p. 307.
- [20] Arranz A, Perez-Dieste V, Palacio C. Electronic structure of stoichiometric and reduced  $\text{Ta}_2\text{O}_5$  surfaces determined by resonant photoemission. *Physical Review B* 2002;66:075420–5.
- [21] George HC, Ming-Ling L, Li-Dong C, Fu-Qiang H, Daniel EB, Daniel MW, et al. Syntheses, crystal structures, and physical properties of  $\text{La}_5\text{Cu}_6\text{O}_4\text{S}_7$  and  $\text{La}_5\text{Cu}_{6.33}\text{O}_4\text{S}_7$ . *Inorganic Chemistry* 2008;47:4368–74.
- [22] Buxbaum G, Pfaff G. *Industrial inorganic pigments*. Weinheim: Wiley-VCH; 2005.