The synthesis and characterization of alkaline-earth metal doped Pr$_2$Mo$_2$O$_9$ pigments: Applications in coloring of plastics

Summary

A new class of inorganic pigments based on praseodymium molybdate having the general formula Pr$_{2-x}$A$_x$Mo$_2$O$_{9-δ}$ (where A = Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ and x ranges from 0 to 1.0), displaying colors ranging from green to greenish-yellow were synthesized by traditional solid-state route, as alternatives to lead, cadmium and chromium based 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 blue and red regions due to electronic transitions between 4f$^2$→4f$^1$5d$^1$ states of Pr$^{3+}$. The designed pigments consist of non-toxic elements and are further found to be thermally and chemically stable. The greenish-yellow pigments were found to be interesting alternatives to existing toxic pigments for coloration of plastics.

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4.1. Introduction

There is a strong incentive to design new colorants based on inorganic materials to substitute for industrial pigments that are based on heavy elements hazardous to health and the environment [Smith 2002]. Green and yellow are particularly important colors in the pigment industry with high performance in their thermal and chemical stability and the consumption of the green and yellow exceeds that of any other colored pigments. There are various important yellow pigment families: tin vanadium yellow (11-22-4 DCMA, dry color manufacturers association), praseodymium zircon (14-43-4 DCMA) and zirconium vanadium yellow (1-01-4 DCMA), cadmium yellow and lead antimonite. Among them, praseodymium yellow (ZrSiO$_4$:Pr) has been known as one of the environmentally benign inorganic colorants, which can be applied to paints, inks, plastics, rubbers, ceramics, enamels and glasses because of its thermal stability [Hill and Lehman 2000; Del Nero et al. 2004]. However, this pigment requires high temperature calcinations (>1573 K) for the 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 dispersion of the pigment is essential. Other yellow pigments commonly used such as Pb$_2$Sb$_2$O$_7$, PbCrO$_4$, CdS are now being expelled from the market because of their toxicity.

Recently, many rare earth-based inorganic yellow pigments have been proposed by several researchers [Huguenin et al. 1996; Jansen et al. 2000; Sreeram et al. 2007]. Although these pigments are non-toxic, 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 [Jansen et al. 2000]. Further, their chromatic properties are not very attractive. Therefore, research needs to be performed in developing novel green and yellow inorganic pigments with various advantages over traditional pigment formulations.

Thus the present chapter is focused on the development of novel class of green and yellow pigments based on alkaline-earth metal doped Pr$_2$Mo$_2$O$_9$ system from an
environmental point of view. The new pigments of the formula $\text{Pr}_{2-x}\text{A}_x\text{Mo}_2\text{O}_{9-\delta}$ ($\text{A} = \text{Ca}^{2+}$, $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$) have been synthesized by solid-state reaction of the respective oxides and characterized for their structure and optical properties. The thermal and chemical stabilities of the pigments and their application for coloring plastics have also been investigated.

4.2. Experimental Section

4.2.1. Materials and Methodology

Several compositions based on $\text{Pr}_{2-x}\text{A}_x\text{Mo}_2\text{O}_{9-\delta}$ ($\text{A} = \text{Ca}^{2+}$, $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$ and $x$ ranges from 0 to 1.0) were prepared by corresponding oxides: $\text{Pr}_6\text{O}_{11}$ (99.9%), $\text{CaCO}_3$ (99%), $\text{SrCO}_3$ (99%), $\text{BaCO}_3$ (99%) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}$ (99.9%), supplied by Sigma Aldrich. In this method, the reactants were mixed and homogenized by wet milling with acetone media in an agate mortar for 30 min. The homogeneous mixture was calcined in platinum crucibles in an electric furnace at optimized temperatures ($1000^\circ\text{C}$ for $\text{Pr}_2\text{Mo}_2\text{O}_9$, $1050^\circ\text{C}$ for $\text{Ca}^{2+}$-doped system, $1000^\circ\text{C}$ for $\text{Sr}^{2+}$-doped system and $950^\circ\text{C}$ for $\text{Ba}^{2+}$-doped system) and time (9 h) in air atmosphere. The heating of the furnace was programmed to increase the temperature at $5^\circ\text{C}$/min. The final pigment powders were subsequently ground in an agate mortar with the aim of refining and homogenizing the particle size.

4.2.2. Methodology adopted for coloration of plastic materials

The typical pigment samples, $\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ (10%) and $\text{Pr}_{1.4}\text{Ca}_{0.6}\text{Mo}_2\text{O}_{9-\delta}$ (10%) was studied for their application in coloring of plastics and the procedure used for coloring is same as that described in chapter 3.

4.2.3. Characterization Techniques

The instrumental techniques employed for the characterization of various pigments designed in the present study are the same as that described in the previous chapter 2.
4.3. Results and Discussion

4.3.1. Powder X-ray diffraction analysis

The XRD patterns of alkaline-earth metal free Pr$_2$Mo$_2$O$_9$ pigment sample calcined at various temperatures (900°C to 1000°C) for 9 h are depicted in Fig. 1. The sample calcined at 900°C exhibits poor crystallization. On the other hand, the sample calcined at 1000°C shows the characteristic reflections of the cubic structure of Pr$_2$Mo$_2$O$_9$ with a lattice constant of 0.7068 nm, which is in good agreement with the earlier report [Yamazaki et al. 2002]. The diffraction pattern of Pr$_2$Mo$_2$O$_9$ shown in the figure resembles to that of La$_2$Mo$_2$O$_9$ with a cubic structure [Lacorre et al. 2000; Subasri et al. 2004; Tealdi et al. 2004; Marrero-Lopez et al. 2007]. Thus it can be concluded from the above study that a minimum of 1000°C calcination temperature is essential to obtain the phase pure product of Pr$_2$Mo$_2$O$_9$.

![Fig. 1. XRD patterns of Pr$_2$Mo$_2$O$_9$ samples calcined at different temperatures.](image-url)
Fig. 2 shows the powder X-ray diffraction patterns for Pr$_{2-x}$Ca$_x$Mo$_2$O$_{9-\delta}$ with different doping content of Ca, where $x = 0, 0.10$ and $0.20$, respectively. The XRD pattern of the pure Pr$_2$Mo$_2$O$_9$ sample can be indexed very well as a cubic structure of $P213$ with a lattice constant of 0.7068 nm. Since Ca$^{2+}$ (ionic radius: 0.099 nm) is slightly smaller in size than Pr$^{3+}$ (0.112 nm) and in addition, the substitution of a lower valence ion in the Pr$^{3+}$ sites leads to creation of O$^{2-}$ vacancies, the cell volume lowers with increasing Ca$^{2+}$ content up to 10% as can be seen from Fig. 3 [Subasri et al. 2004]. With increase of Ca$^{2+}$-dopant content, the lattice constant decrease first, reaches to a minimum of 0.7058 nm at 10% Ca$^{2+}$ doping content and increases to a value, which is even greater than the lattice constant of Ca$^{2+}$ free specimen. This variation rule of lattice constant is resulted from the contribution of substitution of Ca$^{2+}$ for Pr$^{3+}$ and introduction of extrinsic vacancies by Ca$^{2+}$ doping, the former of which will shrink the lattice while the latter of which will expand the lattice [Wang et al. 2002].

![XRD patterns of the Pr$_{2-x}$Ca$_x$Mo$_2$O$_{9-\delta}$ (x = 0, 0.1 and 0.2) samples (Calcination temperature: 1050°C; Time duration 9 h).]
Fig. 3. Lattice constants of the Pr$_{2-x}$A$_x$Mo$_2$O$_{9-\delta}$ (A = Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$) pigment samples.

With the increase of Ca$^{2+}$-doping in Pr$_{2-x}$Ca$_x$Mo$_2$O$_{9-\delta}$ ($x = 0.4$–$1.0$) beyond 10%, structural transformation from cubic to monoclinic fergusonite-type (JCPDS No. 22-1180) has been noticed from the XRD patterns of the pigment samples given in Fig. 4 [Tkachenko and Fedorov 2003]. Further, some minor peaks appeared in the XRD patterns when the Ca$^{2+}$ concentration is greater than 10% can be indexed to CaMoO$_3$ with tetragonal phase as reported elsewhere [Subasri et al. 2004; Marrero-Lopez et al. 2007].

The XRD patterns of Sr$^{2+}$ and Ba$^{2+}$-doped into Pr$_2$Mo$_2$O$_9$ samples are summarized in Figs. 5 and 6. With the increase of Sr$^{2+}$ or Ba$^{2+}$-dopant concentration in Pr$_{2-x}$A$_x$Mo$_2$O$_{9-\delta}$ (A= Sr$^{2+}$ or Ba$^{2+}$; $x > 0.1$) beyond 2.5%, structural transformation from cubic to monoclinic fergusonite-type (JCPDS No. 22-1180) has been observed from the XRD patterns of the pigment samples [Tkachenko and Fedorov 2003]. It is also evident that there are some additional diffraction peaks (indicated with stars) for the compositions with $x > 0.1$ for Sr$^{2+}$ and Ba$^{2+}$-doped systems. The extra peaks above the solubility limit are attributed to the presence of a secondary phase (SrMoO$_3$: JCPDF No. 8-482; or BaMoO$_4$: JCPDF No. 29-193) with tetragonal phase as noted earlier by many investigators [Subasri
et al. 2004; Marrero-Lopez et al. 2007]. The variation of lattice constant with the dopant concentration is presented in Fig. 3. For Sr$^{2+}$ and Ba$^{2+}$ substitution in Pr$_2$Mo$_2$O$_9$, the cell parameter increases with the dopant content in agreement with the large ionic radii of these cations (Sr$^{2+} = 0.131$ nm and Ba$^{2+} = 0.147$ nm) compared to Pr$^{3+}$. Since Sr$^{2+}$ and Ba$^{2+}$ are also aliovalent dopant ions like Ca$^{2+}$, substitution by these ions in Pr$^{3+}$ sites also leads to formation of oxygen vacancies. As both Sr$^{2+}$ and Ba$^{2+}$ are larger than Pr$^{3+}$, they partially occupy the space created by the neighboring oxygen vacancies and can still stabilize the structure. Similar trends in cell parameter values have been reported elsewhere for the substitution of alkaline-earth metals into La$_2$Mo$_2$O$_9$ [Gao et al. 2008; Yan et al. 2010].

![XRD patterns of the Pr$_{2-x}$Ca$_x$Mo$_2$O$_9$-$\delta$ ($x = 0.4$ to $1.0$) samples (Calcination temperature: $1050^\circ$C; Time duration $9$ h).](image_url)

Fig. 4. XRD patterns of the Pr$_{2-x}$Ca$_x$Mo$_2$O$_9$-$\delta$ ($x = 0.4$ to $1.0$) samples (Calcination temperature: $1050^\circ$C; Time duration $9$ h).
Fig. 5. XRD patterns of the Pr$_{2-x}$Sr$_x$Mo$_2$O$_{9-δ}$ (x = 0 to 1.0) samples (Calcination temperature: 1000°C; Time duration 9 h).

Fig. 6. XRD patterns of the Pr$_{2-x}$Ba$_x$Mo$_2$O$_{9-δ}$ (x = 0 to 1.0) samples (Calcination temperature: 950°C; Time duration 9 h).

4.3.2. Particle size and morphological analysis

Particle size analysis of the typical pigments, Pr$_{1.4}$Ca$_{0.6}$Mo$_2$O$_{9-δ}$, Pr$_{1.4}$Sr$_{0.6}$Mo$_2$O$_{9-δ}$ and Pr$_{1.4}$Ba$_{0.6}$Mo$_2$O$_{9-δ}$ reveal a mean diameter of 28.46 µm (size of 90% particles < 54.56 µm,
50% particles < 22.43 µm and 10% particles < 0.37 µm), 27.63 µm (size of 90% particles < 61.34 µm, 50% particles < 20.50 µm and 10% particles < 7.12 µm) and 29.41 µm (size of 90% particles < 63.78 µm, 50% particles < 19.19 µm and 10% particles < 11.32 µm), respectively. The homogeneous nature of the synthesized pigment samples can be understood from the SEM images (Fig. 7) and the average grain size being less than 20 µm.

**Fig. 7.** The SEM micrographs of (a) Pr$_{1.4}$Ca$_{0.6}$Mo$_2$O$_9$–δ (b) Pr$_{1.4}$Sr$_{0.6}$Mo$_2$O$_9$–δ (c) Pr$_{1.4}$Ba$_{0.6}$Mo$_2$O$_9$–δ pigment powders.

### 4.3.3. The optical properties of Pr$_2$Mo$_2$O$_9$ pigment

The absorption spectrum of Pr$_2$Mo$_2$O$_9$ compound is shown in Fig 8. Several bands in the visible region have been observed, which can be assigned to the electronic transitions between 4f$^2$ → 4f$^3$5d$^1$ states of Pr$^{3+}$. The bands in the region 440–490 (blue) and 590–625
nm (red), can be assigned based on the energy levels $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{H}_4 \rightarrow ^3\text{P}_1$, $^3\text{H}_4 \rightarrow ^3\text{P}_0$ (upper) and $^3\text{H}_4 \rightarrow ^1\text{D}_2$ and $^3\text{H}_6 \rightarrow ^3\text{P}_0$ (lower), respectively [Sivakumar and Varadaraju 2005; Logvinovich et al. 2010]. Weak absorptions in the blue region and strong absorptions in the red region can be noted from the absorption spectrum of the alkaline-earth metal free Pr$_2$Mo$_2$O$_9$. Thus, the pigment exhibits green color, since red is complementary color to green (Fig. 15).

![Absorption spectra of Pr$_2$Mo$_2$O$_9$ pigment.](image)

**Fig. 8.** Absorption spectra of Pr$_2$Mo$_2$O$_9$ pigment.

### 4.3.4. The optical properties of alkaline-earth metal doped Pr$_2$Mo$_2$O$_9$ pigments

The effect of alkaline-earth metal ions (Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$) doping on the optical properties of Pr$_2$Mo$_2$O$_9$ based pigments was analyzed from the diffuse reflectance and absorption spectra and the results are displayed in Figs. 9 to 14, respectively. With the progressive doping of Ca$^{2+}$ or Sr$^{2+}$ into the matrix of Pr$_2$Mo$_2$O$_9$, strong absorptions in the blue region can be noticed with simultaneous weakening of the absorptions in the red region. The doping of Ca$^{2+}$ or Sr$^{2+}$ for Pr$^{3+}$ in Pr$_2$Mo$_2$O$_9$ creates oxygen vacancies, which in turn may impart strong optical absorptions at a wavelength below 500 nm. Thus, the color of the pigment gently changes from green to greenish-yellow with increasing Ca$^{2+}$ or
Sr\(^{2+}\) concentration, since blue is complementary color to yellow (Fig. 15). The systematic doping of Ca\(^{2+}\) for Pr\(^{3+}\) in Pr\(_2\)Mo\(_2\)O\(_9\) matrix decreases the band gap of the resultant pigments significantly from 2.44 eV to 2.24 eV. However, in the case of Sr\(^{2+}\)-doped systems, the band gap of the pigments gently changes from 2.44 eV to 2.35 eV as compared to Ca\(^{2+}\)-doped systems.

Fig. 9. Reflectance spectra of the Pr\(_{2-x}\)Ca\(_x\)Mo\(_2\)O\(_9\)-\(\delta\) (\(x = 0\) to 1.0) samples.

Fig. 10. Absorption spectra of the Pr\(_{2-x}\)Ca\(_x\)Mo\(_2\)O\(_9\)-\(\delta\) (\(x = 0\) to 1.0) samples.
Fig. 11. Reflectance spectra of the Pr$_{2-x}$Sr$_x$Mo$_2$O$_9$ (x = 0 to 1.0) samples.

Fig. 12. Absorption spectra of the Pr$_{2-x}$Sr$_x$Mo$_2$O$_9$ (x = 0 to 1.0) samples.

It is evident from the UV–vis diffuse reflectance spectra of the Ba$^{2+}$-doped Pr$_2$Mo$_2$O$_9$ pigment samples shown in Fig. 14 that the increase of dopant concentration results in the simultaneous weakening of absorptions in both blue and red regions, which is contrary to Ca$^{2+}$ or Sr$^{2+}$-doped systems. Thus minor variations in the band gap of the resultant pigment samples is noticed (2.44 eV to 2.40 eV) and consequently, no significant change in the color of the Ba$^{2+}$-doped pigment samples has been observed.
Fig. 13. Reflectance spectra of the Pr$_{2-x}$Ba$_x$Mo$_2$O$_9-\delta$ ($x = 0$ to 1.0) samples.

Fig. 14. Absorption spectra of the Pr$_{2-x}$Ba$_x$Mo$_2$O$_9-\delta$ ($x = 0$ to 1.0) samples.
The CIE 1976 color coordinates of the alkaline-earth metal doped Pr$_2$Mo$_2$O$_9$ pigments are summarized in Table 1. The increase of $b^*$ and $C^*$ values and decrease of $-a^*$ with the increase of dopant concentration of Ca$^{2+}$ or Sr$^{2+}$ from $x = 0$ to 0.6 in Pr$_{2-x}$A$_x$Mo$_2$O$_9$–δ clearly indicates that color of the pigment gently changes from green to greenish-yellow. Further, at higher Ca$^{2+}$ or Sr$^{2+}$ concentrations, the yellow hue of the pigment decreases may be due to the formation of dominant phase of CaMoO$_4$ or SrMoO$_4$. In the case of Ba$^{2+}$-doped pigments, the $b^*$ value which represents the yellowness of the pigment decreases with increasing the dopant concentration. This may be due to the formation of more stable BaMoO$_4$ phase even at smaller dopant amounts of Ba$^{2+}$ as compared to Ca$^{2+}$ or Sr$^{2+}$. On the other hand, the change in the $-a^*$ value, which represents the green hue of the pigment is not significant. Thus the green color of the Pr$_2$Mo$_2$O$_9$ resultant pigment has not been affected with the doping of Ba$^{2+}$. The observed hue angle of the designed pigments are found to be in the greenish-yellow region of the cylindrical color space ($h^\circ = 70–105$ for yellow, $h^\circ = 105–140$ for green). The color coordinates of the typical Ca$^{2+}$-doped
pigment, Pr$_{1.4}$Ca$_{0.6}$Mo$_2$O$_9$–δ ($L^* = 81.53$, $a^* = -9.01$, $b^* = 59.95$), especially yellow hue was found to be higher than that of the commercially available pigment ($L^* = 89.93$, $a^* = -3.49$, $b^* = 43.34$) Zircon Yellow (Zircon 1561: (Zr, Pr)SiO$_4$ of M/s Kawamura Chemicals, Japan).

**Table 1.** The color coordinates (±0.1) of the Pr$_{2-x}$A$_x$Mo$_2$O$_9$–δ ($x$ ranges from 0 to 1.0) powder pigments and band gap values.

<table>
<thead>
<tr>
<th>Pr$_{2-x}$A$_x$Mo$_2$O$_9$–δ (M= Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$)</th>
<th>Color coordinates</th>
<th>$C^*$</th>
<th>$h^\circ$</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L^*$</td>
<td>$a^*$</td>
<td>$b^*$</td>
<td></td>
</tr>
<tr>
<td>$x = 0$</td>
<td>87.8</td>
<td>-21.6</td>
<td>37.3</td>
<td>43.1</td>
</tr>
<tr>
<td>Ca$^{2+}$ $x = 0.1$</td>
<td>87.5</td>
<td>-22.8</td>
<td>39.6</td>
<td>45.6</td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>86.3</td>
<td>-15.6</td>
<td>56.4</td>
<td>56.4</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>81.5</td>
<td>-9.0</td>
<td>59.9</td>
<td>60.6</td>
</tr>
<tr>
<td>$x = 0.8$</td>
<td>79.2</td>
<td>-6.7</td>
<td>52.0</td>
<td>52.3</td>
</tr>
<tr>
<td>$x = 1$</td>
<td>83.3</td>
<td>-7.6</td>
<td>54.2</td>
<td>54.8</td>
</tr>
<tr>
<td>Sr$^{2+}$ $x = 0.1$</td>
<td>84.2</td>
<td>-23.5</td>
<td>45.5</td>
<td>51.2</td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>80.8</td>
<td>-11.7</td>
<td>51.9</td>
<td>53.2</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>83.1</td>
<td>-7.6</td>
<td>54.7</td>
<td>55.2</td>
</tr>
<tr>
<td>$x = 0.8$</td>
<td>82.6</td>
<td>-7.0</td>
<td>52.4</td>
<td>52.9</td>
</tr>
<tr>
<td>$x = 1$</td>
<td>83.9</td>
<td>-7.1</td>
<td>49.9</td>
<td>50.4</td>
</tr>
<tr>
<td>Ba$^{2+}$ $x = 0.1$</td>
<td>84.1</td>
<td>-25.5</td>
<td>46.1</td>
<td>52.7</td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>85.8</td>
<td>-22.7</td>
<td>42.6</td>
<td>48.3</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>89.4</td>
<td>-21.6</td>
<td>40.5</td>
<td>45.9</td>
</tr>
<tr>
<td>$x = 0.8$</td>
<td>83.7</td>
<td>-12.5</td>
<td>43.5</td>
<td>45.3</td>
</tr>
<tr>
<td>$x = 1$</td>
<td>85.1</td>
<td>-19.6</td>
<td>36.0</td>
<td>41.0</td>
</tr>
</tbody>
</table>

$C^* = [(a^*)^2 + (b^*)^2]^{1/2}$; $h^\circ = \tan^{-1}(b^*/a^*)$

**4.3.5. Thermal and chemical stability studies of the pigments**

The thermal analysis (TG/DTA) of the typical pigment powder Pr$_2$Mo$_2$O$_9$ has been investigated and the results are given in Fig. 16. It is clear from the TG/DTA analysis of
the solid solution Pr$_2$Mo$_2$O$_9$, that there is no loss in weight and no phase transformation in
the temperature range of 50–1000°C. This fact is in agreement with the results shown in
XRD patterns in Fig. 1.

![Graph](image-url)

**Fig. 16.** TG/DTA of powdered Pr$_2$Mo$_2$O$_9$ pigment.

The acid/alkali and water resistance of the typical pigment powders
Pr$_{1.4}$Ca$_{0.6}$Mo$_2$O$_9$–δ and Pr$_{1.4}$Sr$_{0.6}$Mo$_2$O$_9$–δ were investigated with 5% of
HCl/H$_2$SO$_4$/HNO$_3$/NaOH and H$_2$O. A pre-weighed amount of the pigment powder was
treated with acid/alkali and soaked for half an hour with constant stirring using a magnetic
stirrer. The pigment powder was then filtered, washed with water, dried and weighed.
Negligible weight loss of pigment was noticed for all the acids, alkali and water tested.
The color coordinates of the pigments were measured after acid/alkali and water treatment
and the total color difference, ΔE$_{ab}$ of the pigments are found to be negligible as evident
from the data reported in Table 2. The above studies highlight that the pigment powders
are chemically and thermally stable.
Table 2. The color coordinates (±0.1) of the Pr$_{1.4}$A$_{0.6}$Mo$_2$O$_{9−δ}$ (A= Sr and Ba) powder pigments after acid/alkali resistance tests.

<table>
<thead>
<tr>
<th>Acid/Alkali</th>
<th>Pr$<em>{1.4}$Ca$</em>{0.6}$Mo$<em>2$O$</em>{9−δ}$</th>
<th>Pr$<em>{1.4}$Sr$</em>{0.6}$Mo$<em>2$O$</em>{9−δ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>a*</td>
<td>b*</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>81.2</td>
<td>−8.9</td>
</tr>
<tr>
<td>NaOH</td>
<td>80.9</td>
<td>−10.1</td>
</tr>
<tr>
<td>HCl</td>
<td>81.9</td>
<td>−9.4</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>81.8</td>
<td>−9.6</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>82.6</td>
<td>−9.9</td>
</tr>
</tbody>
</table>

$^a$ΔE$_{ab}$ = [($ΔL^*$)$^2+(Δa^*)^2+(Δb^*)^2$]$^{1/2}$

4.3.6. Applications in coloring of plastics

The coloring performance of the typically synthesized pigments (Pr$_{1.9}$Ca$_{0.1}$Mo$_2$O$_{9−δ}$ and Pr$_{1.4}$Ca$_{0.6}$Mo$_2$O$_{9−δ}$) was tested for its coloring application in a substrate material like PMMA. Typically, 10wt.% pigment sample was dispersed in PMMA and compressed to a cylindrical disc (Fig. 17). The color coordinates of the test pieces were measured at different locations and an average value is depicted in Table 3. The $L^*$a*b* values obtained were more or less the same indicating the uniform distribution of pigment particles in the polymer matrix. The TG analysis of the pigmented polymer sample indicates that the colored polymer is thermally stable up to 236°C (Fig. 18).

Fig. 17. Photograph of (a) Pr$_{1.9}$Ca$_{0.1}$Mo$_2$O$_{9−δ}$(10%) + PMMA and (b) Pr$_{1.4}$Ca$_{0.6}$Mo$_2$O$_{9−δ}$(10%) + PMMA.
Fig. 18. TG of 10% Pr$_{1.9}$Ca$_{0.1}$Mo$_2$O$_{9-\delta}$ + PMMA.

Table 3. The color coordinates ($\pm 0.1$) of the Pr$_{1.6}$Ca$_{0.4}$Mo$_2$O$_{9-\delta}$ powder pigments after applied on polymer.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Color coordinates</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L^*$</td>
<td>$a^*$</td>
</tr>
<tr>
<td>Pr$<em>{1.9}$Ca$</em>{0.1}$Mo$<em>2$O$</em>{9-\delta}$</td>
<td>87.5</td>
<td>-22.8</td>
</tr>
<tr>
<td>$x = 0.1$ (10%) + PMMA</td>
<td>79.08</td>
<td>-13.9</td>
</tr>
<tr>
<td>Pr$<em>{1.6}$Ca$</em>{0.4}$Mo$<em>2$O$</em>{9-\delta}$</td>
<td>81.5</td>
<td>-9.0</td>
</tr>
<tr>
<td>$x = 0.6$ (10%) + PMMA</td>
<td>75.0</td>
<td>-5.52</td>
</tr>
</tbody>
</table>
4.4. Conclusions

- The effect of alkaline-earth metal ions doping on the optical properties of Pr₂Mo₂O₉ based pigment powder was systematically investigated.

- The results demonstrated that the progressive doping of Ca²⁺ for Pr³⁺ in Pr₂Mo₂O₉ matrix, having smaller ionic radii than Pr³⁺; impart strong optical absorptions in the blue region with simultaneous weakening of the absorptions in the red region. Thus, the color of the pigment powder changes from green to greenish-yellow with increasing Ca²⁺ concentration, since blue is a complementary color to yellow.

- On the other hand, the doping of Sr²⁺ for Pr³⁺, having an ionic radii moderately higher than Pr³⁺, impart weak absorptions in the blue region as compared to Ca²⁺ system, with simultaneous decreasing of absorptions in the red region. Consequently, the color of the pigment powder gently changes from green to greenish-yellow.

- However, contrary to the above observations, the doping of Ba²⁺ for Pr³⁺, having higher ionic radii than Pr³⁺, no significant changes in the absorption bands in both blue and red regions are noted and hence no change in the color of the Pr₂Mo₂O₉ pigment powder.

- The newly developed pigment powders are found to be thermally and chemically stable and also do not contain toxic metals. Thus, the present pigment powders may find potential alternative to the classical toxic yellow inorganic pigments for coloring plastics.