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Research Article

Highly Dispersed Re-Doped $CoAl_2O_4$ Nanopigments: Synthesis and Chromatic Properties

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Nanosized spinel $CoAl_{2-x}Re_xO_4$ complex oxides were prepared by self-propagation combustion method. The products have been characterized by XRD, SEM, and EDS. The results indicated that Al^{3+} can be partly replaced by Re^{3+} when the doped amount is less than 10%, which forms single solid solution. The NIR reflectance and chromatic properties of samples have also been investigated. The substitution of Re^{3+} for Al^{3+} in $CoAl_2O_4$ can increase the blueness of pigments. SEM results revealed that the obtained $CoAl_{2-x}Re_xO_4$ pigments consisted of highly dispersed spherical-like nanoparticles with uniform size distribution. EDS results indicated that the distribution of element was considerably uniform with no chemical segregation phenomenon.

1. Introduction

Spinel-type structure pigments with a general formula $A_2B_2O_4$ have attracted extensive attention due to their chemical and thermal stability, which have been applied in decorating porcelains, ceramics, catalysts, paints, and so forth [1–3]. Among them, $CoAl_2O_4$ is one of the most important blue pigments, which has classic spinel-type structure and superior properties, such as high resistance to acids, and chemical, color, optical, and thermal stabilities [4–6]. Particularly, for application as optical devices like color filters or pigments, the presence of highly dispersed submicrometer or nano-$CoAl_2O_4$ particles is important and indispensable [7].

Recent efforts have focused on tailoring a controllable and simple synthetic method for high-quality $CoAl_2O_4$ nanopigment. Many new synthetic technologies have been developed to synthesize $CoAl_2O_4$ nanopigment, such as organic ligand-assisted supercritical water hydrothermal method [8], polyacrylamide gel method [9], coprecipitation process [6], sol-gel method [5, 10], autoignition technique [11], molten salts method [12], and combustion method [13].

The self-propagation combustion method has been developed by our team for preparation of pyrochlore-type and spinel-type nanoparticles [14, 15]. In this paper, we study synthesis and chromatics properties of rare earth ion doped $CoAl_2O_4$ nanopigment via self-propagation combustion method, based on the fact that rare earth element as doping ion can change the crystal structure and play an important role in stabilizing the color and changing the color of pigments.

2. Experimental

2.1. Preparation of Materials. All reagents were of analytical grade and used without further purification. In this work, all pigment samples of $CoAl_{2-x}Re_xO_4$ (Re = Y, La, Nd, Sm, and Eu) were synthesized by self-propagation combustion method. $Co(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used as the precursors of Co and Al, respectively. $Re(NO_3)_3 \cdot nH_2O$ was obtained by dissolving Re_2O_3 in concentrated HNO_3. Urea was used as fuel. According to the formula $CoAl_{2-x}Re_xO_4$ (where $x = 0.05$, 0.1, 0.15, 0.2, and 0.3), stoichiometric amounts of $Co(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and $Re(NO_3)_3 \cdot nH_2O$ were added to urea aqueous solution in turn. After a series of steps of magnetic force stirring, evaporating, and self-propagating combustion, the loose precursor was obtained. The precursor was ground into powder and then submitted to calcination at 750°C

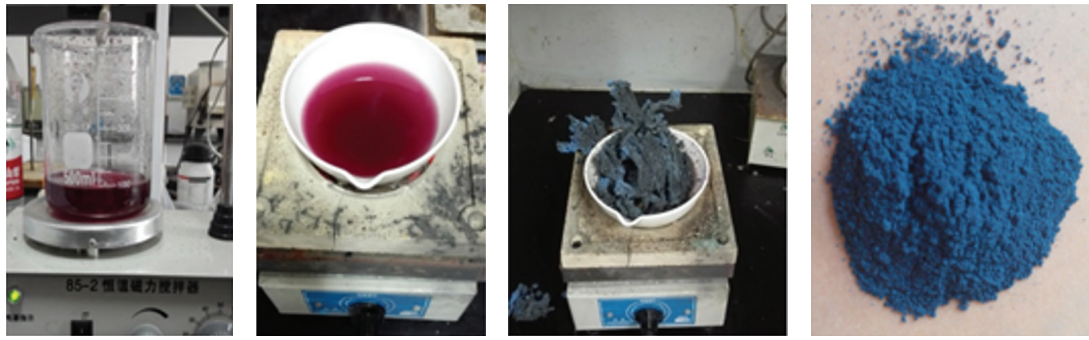


Figure 1: The synthesis procedure of $CoAl_2O_4$ nanoparticles.

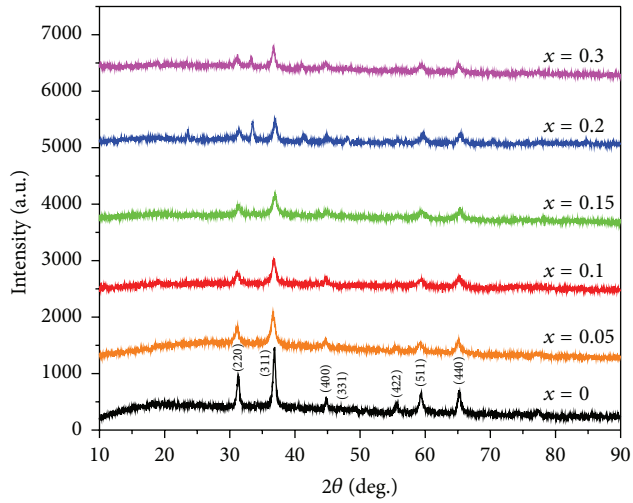


Figure 2: XRD patterns of $CoAl_{2-x}La_xO_4$ (x = 0, 0.05, 0.1, 0.2, and 0.3) precursor calcined at 750°C for 4 h.

for 4 h. The synthesis procedure and product of $CoAl_2O_4$ nanoparticles are shown in Figure 1.

2.2. Instrumentation. The crystalline phase structure was determined by Bruker D8 Advance X-ray diffractometer (XRD) using Cu Kα radiation. Scanning electron microscopy (SEM) image was recorded on a JSM-7500F scanning electron microscope, and EDS was taken on INCAPentaFET-x3 energy dispersive X-ray detector. The CIE 1976 $L^*\alpha^*b^*$ colorimetric method was used, as recommended by the Commission Internationale de l'Eclairage (CIE). In this method, L^* is the lightness axis [black (0) to white (100)], α^* is the green (−value) to red (+value) axis, and b^* is the blue (−value) to yellow (+value) axis. The parameter C^* (chroma) represents saturation of the color. For each colorimetric parameter of a sample, measurements were made in triplicate and an average value was chosen as the result. Typically, for a given sample, the standard deviation of the measured CIE-$L^*a^*b^*$ values is less than 0.10, and the relative standard deviation is not higher than 1%, indicating that the measurement error can be ignored. UV-vis-NIR reflectance of the obtained pigments was carried out by UV-vis-NIR spectrophotometer (Perkin Elmer Lambda 950), using polytetrafluoroethylene as a white standard.

3. Results and Discussions

3.1. XRD Analysis. The XRD patterns of $CoAl_{2-x}La_xO_4$ (x = 0, 0.05, 0.1, 0.2, and 0.3) nanocrystals are shown in Figure 2. From Figure 2, it is clear that all the main peaks when $x < 0.2$ are similar except for a trivial difference of 2θ value. All diffraction peaks of $CoAl_{2-x}La_xO_4$ ($x < 0.2$) are in good agreement with the reflection of spinel $CoAl_2O_4$ phase (JCPDS number 44-016) which indicates that Al ion can be replaced by La^{3+} and the crystal type remains unchanged with the structure of $CoAl_2O_4$ only with small crystal distortion. In our present investigation, we found that another phase evolution starts from that composition (x = 0.2) onwards. The diffraction peaks at $2\theta = 25.51^\circ$ and 34.03° when $x \geq 0.2$ are indexed as $LaAlO_3$, which indicates that more La cannot be accommodated in $CoAl_2O_4$. Moreover, compared with pure $CoAl_2O_4$, the diffraction peaks of doped products become low. The obtained $CoAl_2O_4$ nanocrystals at 750°C have higher crystallinity than that of products via polyacrylamide gel method at the same temperature [9].

For $CoAl_{1.95}Re_{0.05}O_4$ nanocrystallines, we study the effect of the different doped ion on the structure of products. The XRD patterns of $CoAl_{1.95}Re_{0.05}O_4$ (Re = Y, La, Nd, Sm, and Eu) precursor calcined at 750°C for 4 h are shown in Figure 3.

Table 1: Lattice constant and crystal size of $CoAl_2O_4$ and $CoAl_{1.95}Re_{0.05}O_4$.

Sample	Lattice constant a	Crystal size/nm	Strain/%	Radius/Re^{3+}
$CoAl_2O_4$	8.09881	18.4	−0.081	$R(Al^{3+}) = 0.54$
$CoAl_{1.95}Y_{0.05}O_4$	8.09550	12.8	−0.094	1.02
$CoAl_{1.95}La_{0.05}O_4$	8.09297	10.3	−0.426	1.18
$CoAl_{1.95}Nd_{0.05}O_4$	8.09050	8.9	−0.591	N/A
$CoAl_{1.95}Sm_{0.05}O_4$	8.08787	11.6	−0.419	1.08
$CoAl_{1.95}Eu_{0.05}O_4$	8.08547	11	−0.125	1.07

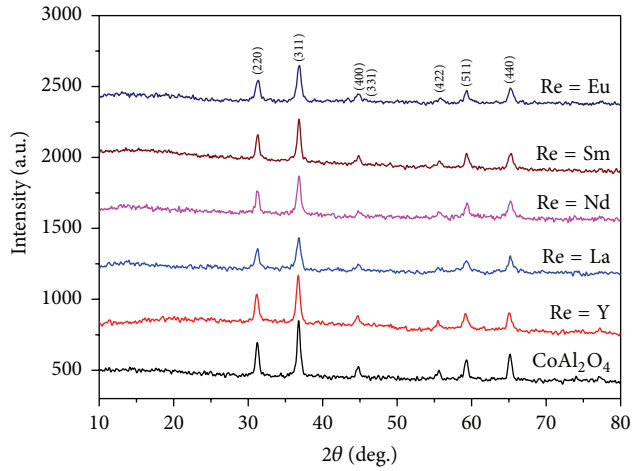


Figure 3: XRD patterns of $CoAl_2O_4$ and $CoAl_{1.95}Re_{0.05}O_4$ (Re = Y, La, Nd, Sm, and Eu).

It can be found from Figure 3 that all the main diffraction peaks are similar and belong to the standard spinel phase of $CoAl_2O_4$. The lattice constants of samples are obtained by Jade 6 program, the average crystal sizes are determined from the XRD patterns according to the Scherrer equation, and corresponding data are listed in Table 1. The average crystal size is about 8~20 nm. From the XRD patterns, it could be noted that doping of $CoAl_2O_4$ with Re^{3+} leads to a marginal shift of diffraction peaks towards lower 2θ angle side only except for the doping of La^{3+}. Due to larger radius of Y^{3+}, Eu^{3+}, Sm^{3+}, Nd^{3+}, and La^{3+}, the lattice constant value has been decreased from 8.09550 to 8.08547.

3.2. NIR Reflectance of Samples. Figure 4 shows the NIR reflectance spectra of the pigments. The sample of $CoAl_2O_4$, $CoAl_{1.95}Eu_{0.05}O_4$, $CoAl_{1.9}Eu_{0.1}O_4$, $CoAl_{1.85}Eu_{0.15}O_4$, and $CoAl_{1.8}Eu_{0.2}O_4$ processes the NIR reflectance of about 79.7%, 86.5%, 85.8%, 79.4%, and 82.8%, respectively. It can be seen that the presence of Eu in $CoAl_2O_4$ improves the NIR reflectance to some extent except for $CoAl_{1.85}Eu_{0.15}O_4$. The sample $CoAl_{1.95}Eu_{0.05}O_4$ processes the highest NIR reflectance and enhances the NIR reflectance to 86.5%. With the increasing of Eu-doped amount, the NIR reflectance decreases, which may be due to similar results to "fluorescence quenching."

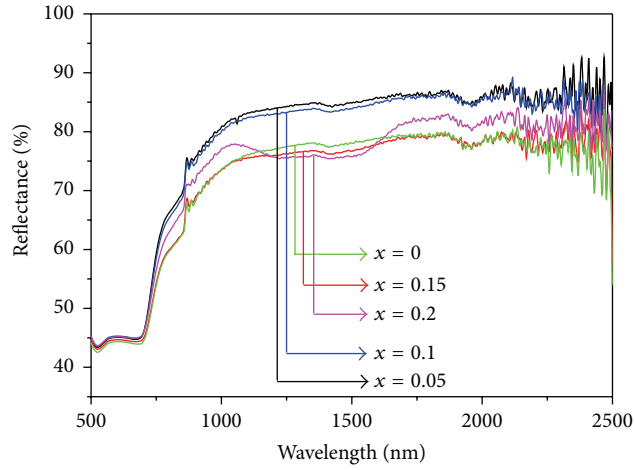


Figure 4: NIR reflectance of $CoAl_{2-x}Eu_xO_4$ samples.

3.3. Chromatic Properties of Samples. Based on the above discussion, for $CoAl_{1.95}Re_{0.05}O_4$, we study the chromatic properties of the obtained $CoAl_{1.95}Re_{0.05}O_4$ pigment samples, which can be assessed from their CIE 1976 $L^*\alpha^*b^*$ color coordinate values; the corresponding values are shown in Table 2. With the doping of Re^{3+}, the increasing of b^* value

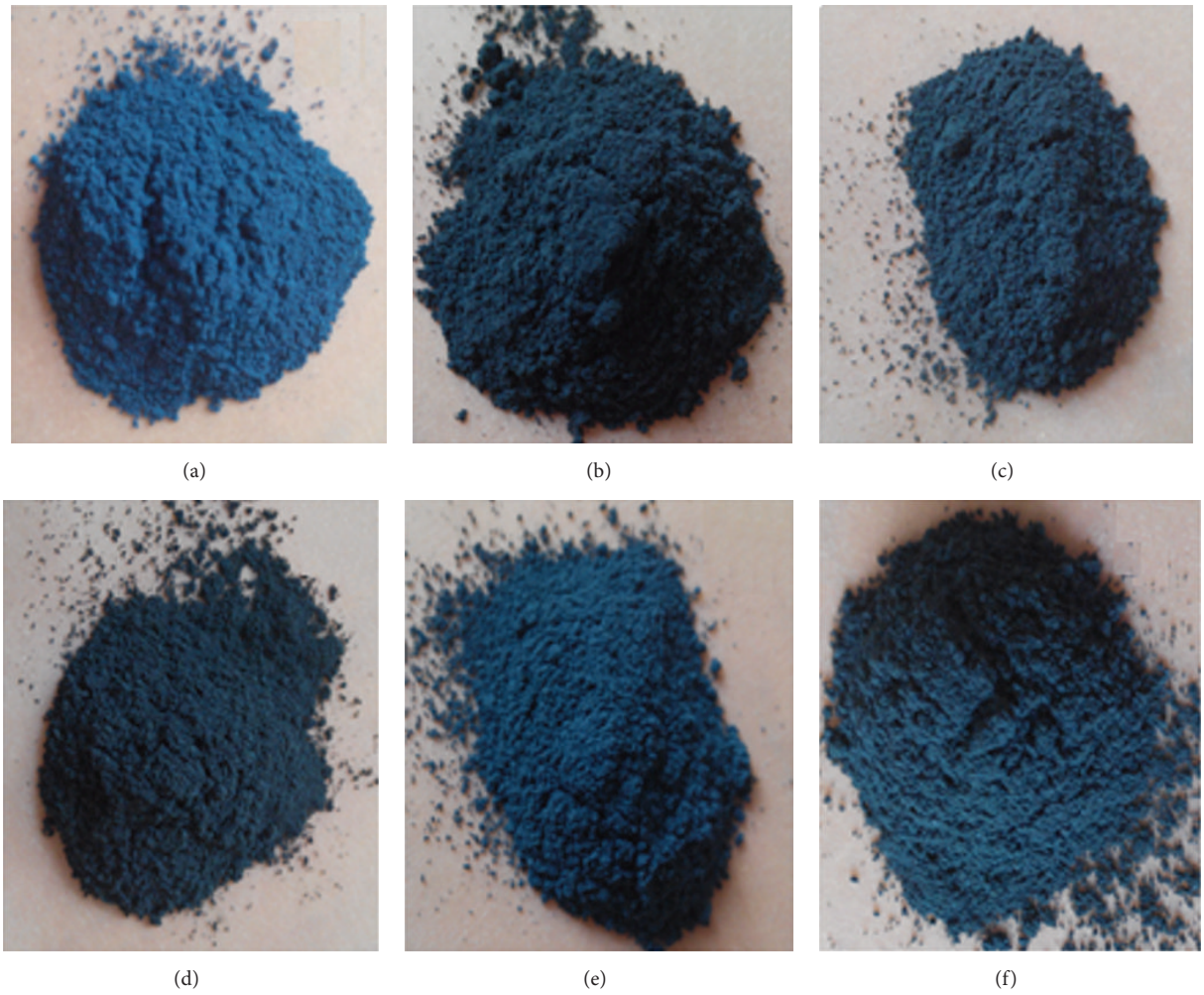


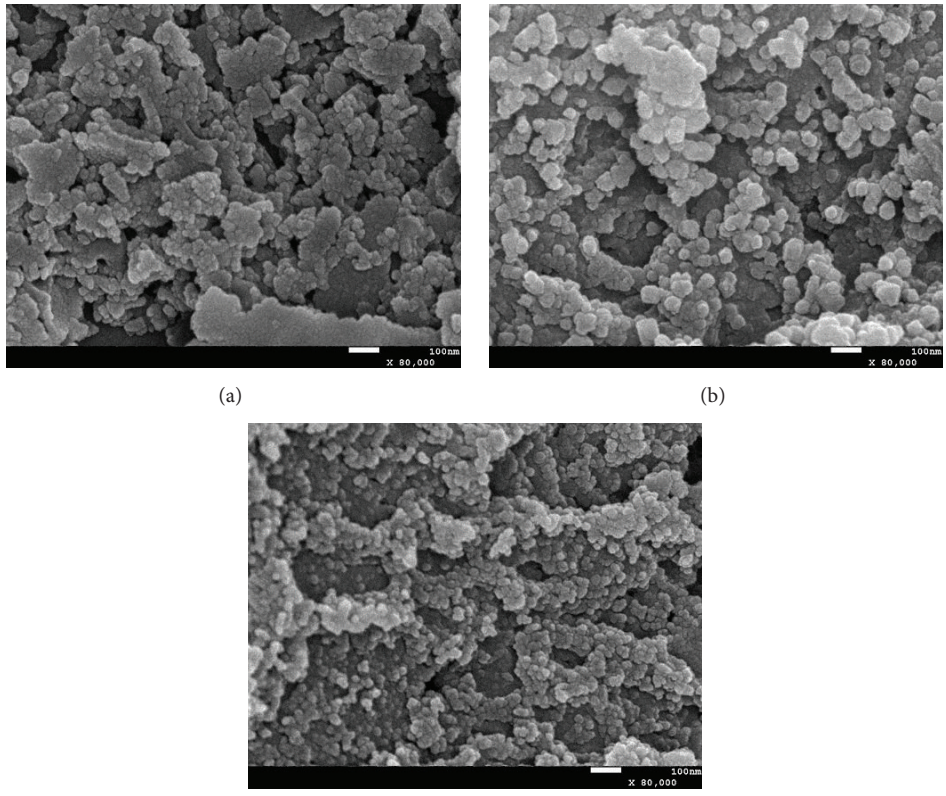
Figure 5: Photographs of $CoAl_2O_4$ and $CoAl_{1.95}Re_{0.05}O_4$ (Re = Y, La, Nd, Sm, and Eu) pigments.

from −23.9 to −76.5 also presents the enhancement of the blueness of pigments, comparing with undoped samples. At the same time, L^* value decreases from 34.8 to 20.3 in the presence of Re^{3+}, which indicates that the darkness increases. This result is in agreement with the change of color of the pigments from bright blue to dark blue and then to light blue (Figure 5). It can be concluded that the doping of Re^{3+} can improve the blueness of pigments. To the best of our knowledge, for cobalt-based pigments, the Co^{2+} ions can be incorporated as coloring in all kinds of ceramics and enamels where they adopt the tetrahedral coordination. When Al^{3+} is replaced by Re^{3+} with larger radius, crystal lattice distortion appears, which may result in the shift of Co^{2+} from tetrahedral coordination to octahedral one and then cause the change of color. Combining NIR reflectance results with chromatic data, $CoAl_{1.95}Eu_{0.05}O_4$ should be a good candidate as a "colored cool pigment" for use in the surface coating application.

3.4. SEM and EDS Analysis. The representative SEM images of the obtained pigments are shown in Figure 6. As can be seen, the $CoAl_2O_4$ powders (Figure 6(a)) have sphere-like structure with the size of 20 nm, but to some extent, the particles are a bit aggregated. However, the dispersibility of samples is still better than that of samples obtained by sol-gel precursor. Many researchers reported quasi-spheric or platy or irregular shapes for $CoAl_2O_4$ powders prepared by soft-chemical methods, and so forth [5, 9]. By La doped into $CoAl_2O_4$ (Figure 6(b)), it can be seen that the products are

Table 2: Color coordinates of the $CoAl_2O_4$ and $CoAl_{1.95}Re_{0.05}O_4$ powder pigments.

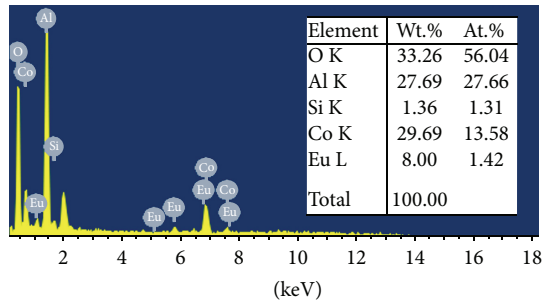
Pigment composition	Color coordinates		
	L^*	a^*	b^*
$CoAl_2O_4$	34.8	14.7	−23.9
$CoAl_{1.95}Y_{0.05}O_4$	20.8	41.3	−76.5
$CoAl_{1.95}La_{0.05}O_4$	21.9	−4.42	−7.64
$CoAl_{1.95}Nd_{0.05}O_4$	26.1	27.3	−74.2
$CoAl_{1.95}Sm_{0.05}O_4$	20.3	21.6	−75.3
$CoAl_{1.95}Eu_{0.05}O_4$	24.2	25.8	−58.6



(a) (b)

(c)

FIGURE 6: SEM images of samples: (a) $CoAl_2O_4$, (b) $CoAl_{1.85}La_{0.15}O_4$, and (c) $CoAl_{1.9}Eu_{0.1}O_4$.



Element	Wt.%	At.%
O K	33.26	56.04
Al K	27.69	27.66
Si K	1.36	1.31
Co K	29.69	13.58
Eu L	8.00	1.42
Total	100.00	

FIGURE 7: EDS results of $CoAl_{1.9}Eu_{0.1}O_4$ nanocrystals.

composed of highly dispersed nanoparticles with the size of 30 nm. Figure 6(c) shows that the $CoAl_{1.85}Eu_{0.15}O_4$ samples also consist of well-dispersed uniform nanoparticles. The results reveal that Re-doped $CoAl_2O_4$ samples have good dispersibility and uniform size distribution.

Figure 7 gives the EDS results of $CoAl_{1.9}Eu_{0.1}O_4$ samples. It is clear that $CoAl_{1.9}Eu_{0.1}O_4$ nanocrystals are made up of O, Al, Co, Eu, and Si. The ratio Co : (Al + Eu) is approximately equal to 1 : 2, and Al : Eu $\approx$ 19 : 1, which gives stoichiometric formula of the as-obtained product $CoAl_{1.9}Eu_{0.1}O_4$ with no chemical segregation phenomenon. The Si peak in the spectrum is from the silicon chip for making the sample. From the surface scanning results (Figure 8), it can be seen that the distribution of O, Al, Co, and Eu element is considerably uniform.

4. Conclusions

A series of Re-doped $CoAl_2O_4$ nanosized blue pigments have been synthesized. XRD results indicated that $CoAl_2O_4$ had limited accommodation for Re^{3+} only when $x < 0.2$. When $x \geq 0.2$ in $CoAl_{2-x}Re_xO_4$, the impurity phase will be formed. It can be concluded from the chromatic data that the doping of Re^{3+} can improve the blueness of pigments. SEM images revealed that the doped samples had good dispersibility and uniform size distribution. Combining NIR reflectance results

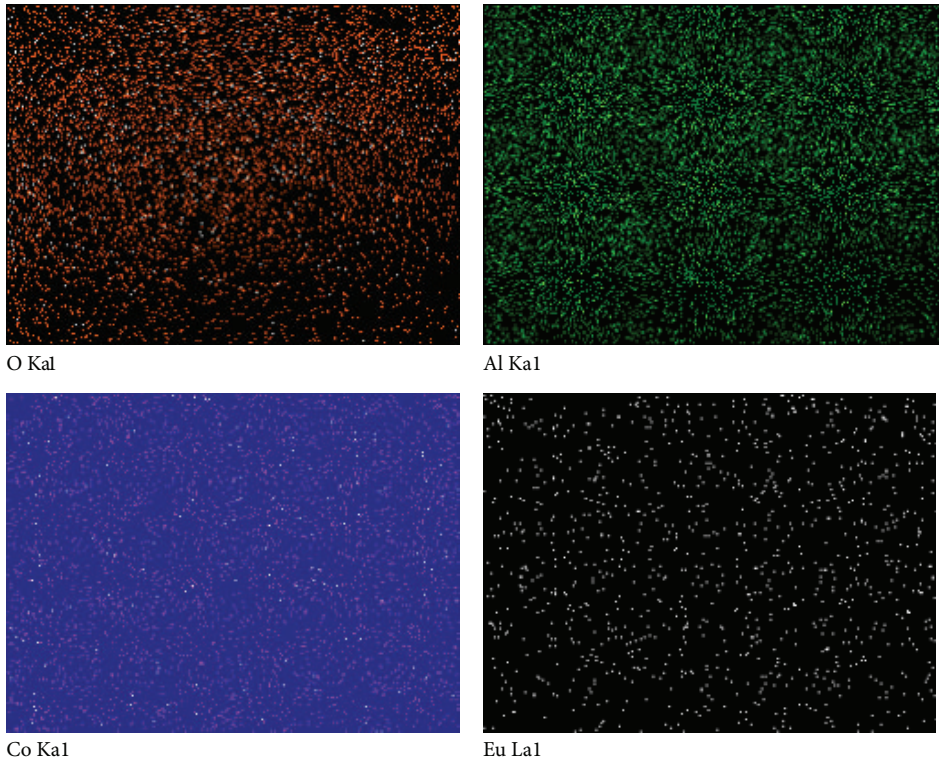


Figure 8: Surface scanning images of $CoAl_{1.9}Eu_{0.1}O_4$ nanocrystals.

with chromatic data, $CoAl_{1.95}Eu_{0.05}O_4$ can be considered as a good "colored cool pigment" candidate for use in the surface coating application.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

Acknowledgments

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