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# Physico-chemical properties of ceramic pigments for high-temperature application

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**Abstract**

Heat resistant coatings are required primarily for stacks, exhaust pipes, reactors, space crafts and similar equipments that are permanently or occasionally exposed to elevated temperatures. High-temperature coatings are generally based on silicone resin with ceramic and metallic pigments. In this study, iron oxide, cobalt oxide (thermo chromic compound) and aluminum oxide are used for the preparation of four new types of coloured pigments. The thermal resistant characteristics of these ceramic pigments were studied by differential thermal analysis, thermo gravimetric analysis and differential scanning calorimetric analysis. These ceramic pigments are found to be thermally stable up to 400 °C.


*Keywords:* Ceramic pigment; Iron oxided; Differential thermal analysis

## 1. Introduction

Coloured ceramic pigments have been prepared from the chromophores of transition metal oxides into the stable host oxide by calcining operation. The important property of a ceramic pigment is its stability at high temperature and in corrosive environment. The ceramic materials with spinel structures have been studied, owing to their wide application as ceramic pigments, magnetic devices, semiconductors, refractories, etc. [1]. Iron oxide has been used in the ceramic pigment formulation because of its excellent colorant characteristics combined with thermal stability [2]. When cobalt is doped with aluminum oxide it produces blue colour due to the coordination of cobalt(IV). On the other hand, when it is combined with a magnesium matrix, it produces rosy colour due to cobalt(VI) [3]. It is highly desirable to investigate the thermal stability of aluminum oxide with doped cobalt and iron transition metal ions. Further, simultaneous doping of two or more colourants in a single matrix to get various colours was also tried. Not much study has been reported for this type of doping of more chromophores into a single host oxide. The synthesis and characterization of a new class of coloured ceramic pigments viz. $Co^{2+}$/$Fe^{3+}$-doped $Al_2O_3$ is presented here.

## 2. Experimental

$AlFeO_3$ powder was prepared from a mixture of aluminum oxide and iron oxide at the elemental ratio of 3:9 (Al:Fe) and 9:3 (Al:Fe). The mixture of powders was calcined at 1100 °C for 4 h. $AlCoFeO_4$ powder was prepared from a mixture of aluminum oxide, iron oxide and cobalt carbonate at the elemental ratio of 3:10:5 (Al:Fe:Co) and 3:5:10 (Al:Fe:Co). The ceramic powder was prepared by calcining at 1100 °C for 4 h. The colour and composition of the prepared ceramic pigments are given in Table 1.

After the synthesis, these ceramic pigments were characterized by Fourier transform-infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermo gravimetric (TG), differential thermal analysis (DTA) and differential scanning calorimetric (DSC). The proposed composition for the pigments was further analyzed by atomic absorption spectrophotometer (AAS) method.

The FTIR spectra of these ceramic pigments were taken using Paragon—500 FTIR Spectrometer. The XRD observation of the ceramic pigments was made by using X'pert PRO PAN analytical diffractometer with Syn Master 793s Software. The AAS

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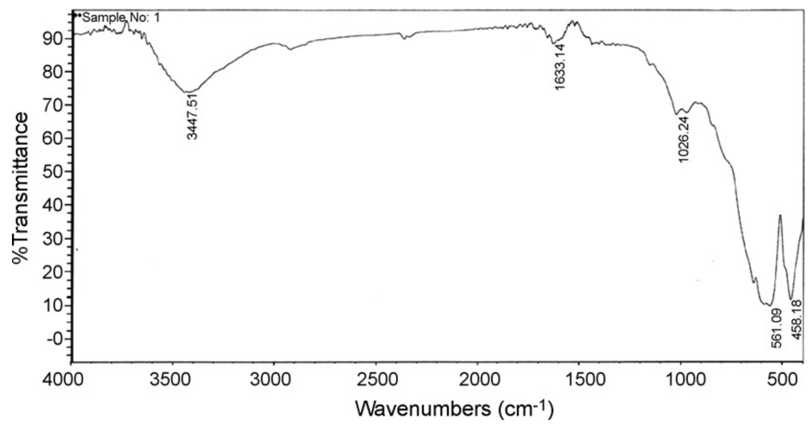


Fig. 1. FTIR spectra of ceramic pigment composition $FeAlO_3$.

Table 1
Colour of ceramic pigments

| Composition | Colour |
|---|---|
| Aluminum iron oxide $(Al_3Fe_9)O_3$ | Reddish brown |
| Aluminum iron oxide $(Al_9Fe_3)O_3$ | Light brown |
| Aluminum iron cobalt oxide $(Fe_{10}Al_3Co_5)O_3$ | Chocolate brown |
| Aluminum iron cobalt oxide $(Fe_5Al_3Co_{10})O_3$ | Winter grey |

elemental analysis of the ceramic pigments was done by using Spectra 220, Varian Spectra atomic absorption spectrophotometer. TG and DTA studies were carried out in nitrogen atmosphere to understand the thermal behavior of the ceramic pigments using simultaneous thermal analyzer (STA, 1500), Polymer Laboratory, Thermal Science Ltd. Universal V2.5H TA instrument was used to carry out the DSC measurements for the ceramic pigments.

## 3. Results and discussion

### 3.1. Fourier transform-infrared spectroscopy analysis

Figs. 1 and 2 show the IR spectra of $AlFeO_3$ at two different ratios. As can be seen from the figures, the iron oxide content is higher in sample 1 than in sample 2 and so the characteristic broad band of iron oxide is observed in the region of 520–600 $cm^{-1}$ and the second peak is present in the region in between 1630 $cm^{-1}$ and 1680 $cm^{-1}$. The aluminum oxide incorporated in the pigment has completely reacted with the iron oxide and so the characteristic peak of aluminum oxide is not observed in this ceramic pigment. But the presence of aluminum oxide is indicated by the appearance of a small peak at 640 $cm^{-1}$ and in between 1025 $cm^{-1}$ and 1033 $cm^{-1}$. In Fig. 2, the higher amount of aluminum oxide is observed with the characteristic broad band at 600–680 $cm^{-1}$. At the same time, the iron oxide peak present in the region of 455 $cm^{-1}$ is reduced. Thus, these two oxides seem to have completely reacted with each other to form a new ceramic pigment. In Fig. 3, the broad peak at 608 $cm^{-1}$ characteristic for $Co_3O_4$ is seen, but this peak is very broad and maximum absorption is around 655 $cm^{-1}$ (Fig. 4). This indicates that the concentration of $Co_3O_4$ in maximum in formulation 4. The characteristics absorption bands of iron oxide and aluminum oxide are also seen in Figs. 3 and 4 [4,5].

### 3.2. X-ray diffraction analysis

Figs. 5 and 6 show the XRD spectra of $(Al_3Fe_9)O_3$ and $(Al_9Fe_3)O_3$ pigments. The maximum intensities for XRD lines are seen at angles $2\theta = 33.47$, 35.92 and 43.51. These values indicate that the most probable crystal structure is $FeAlO_3$. Fig. 6 shows maximum intensity peaks at $2\theta = 35.28$, 43.47 and

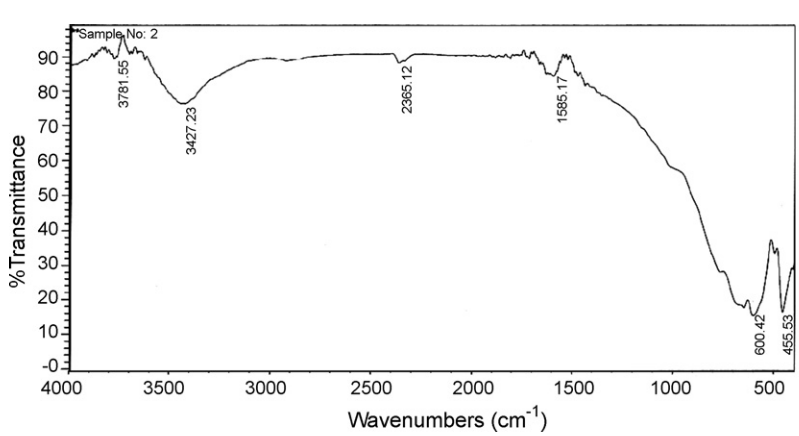


Fig. 2. FTIR spectra of ceramic pigment composition $FeAl_2O_4$.

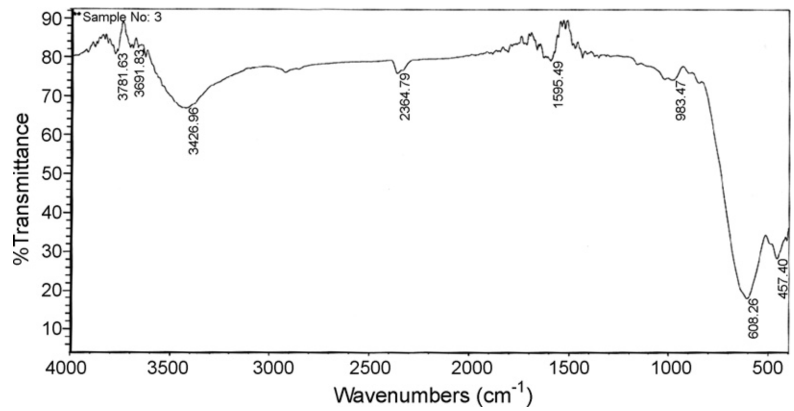


Fig. 3. FTIR spectra of ceramic pigment composition $CoFe_2O_4$.

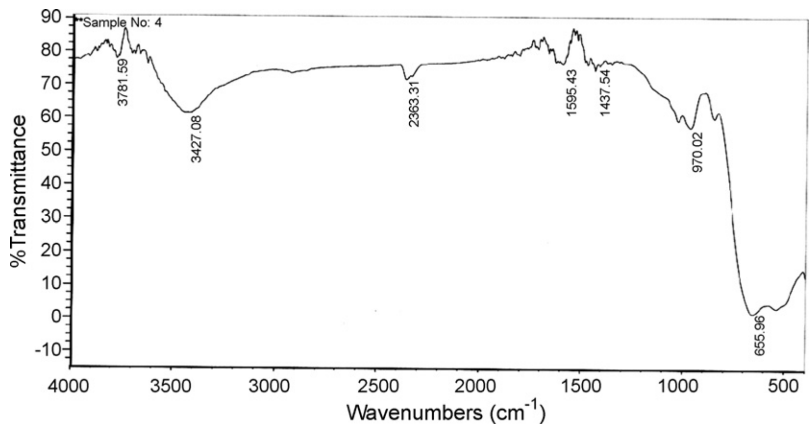


Fig. 4. FTIR spectra of ceramic pigment composition $CoAl_2O_4$.

57.61. These values represent the crystal structure of aluminum iron(II) oxide, $FeAl_2O_4$. Thus, the XRD study gives the definite crystal structure of the aluminum iron oxide new ceramic pigment.

Fig. 7 shows maximum intensity peaks at $2\theta = 35.39$, 30.49 and 57.63. These values are identical to the crystalline structure of $CoFe_2O_4$ (CAS no. 011121) and $CoAl_2O_4$ (CAS no. 440160). Fig. 8 indicates maximum intensity peaks at 35.66, 31.20 and 62.88. These values also represent similar complexes with different CAS numbers [$CoFe_2O_4$ (CAS no. 221086) and $CoAl_2O_4$ (CAS no. 100458)]. In addition to high intensity peaks, some low intensity peaks are also observed at small $2\theta$ values. This indicates that some $Co^{2+}$ ions present in the complex have entered the octahedral site in the crystal lattice [6].

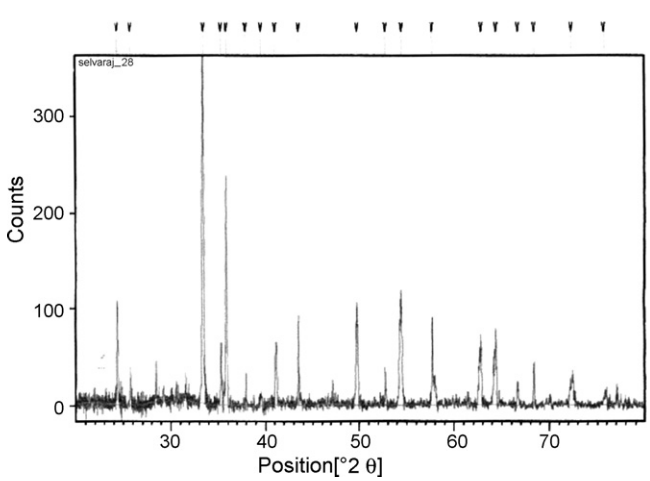


Fig. 5. XRD spectra of ceramic pigment composition $FeAlO_3$.

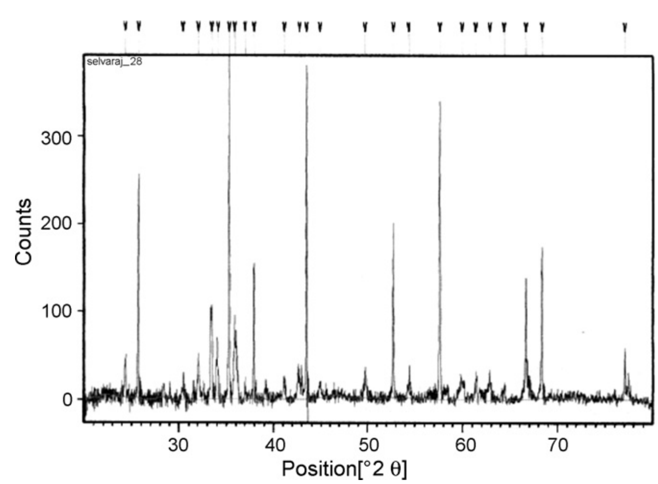


Fig. 6. XRD spectra of ceramic pigment composition $FeAl_2O_4$.

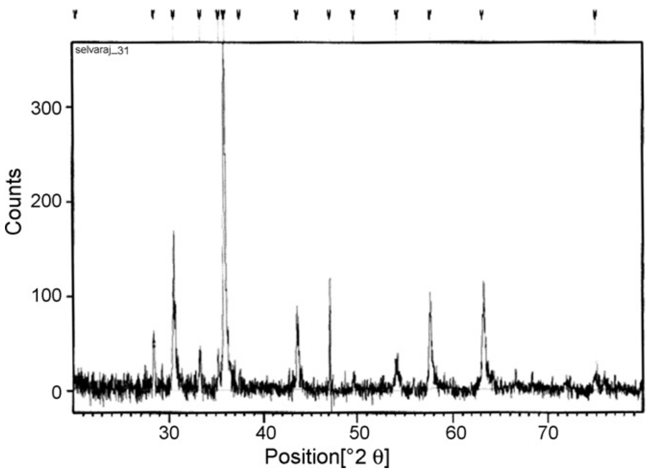


Fig. 7. XRD spectra of ceramic pigment composition $CoFe_2O_4$.

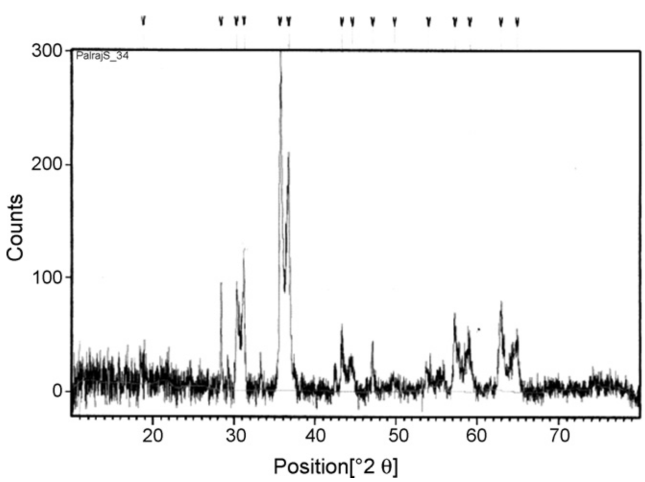


Fig. 8. XRD spectra of ceramic pigment composition $CoAl_2O_4$.

### 3.3. Atomic absorption spectrophotometer analysis

The proposed formulae for the pigments are identical with little deviation from elemental percentage (Table 2). These deviations are within the limit of acceptable values. The formulae of the four pigments are as follows:

1. Aluminum iron oxide $(Al_3Fe_9)O_3$ is $FeAlO_3$;
2. Aluminum iron oxide $(Al_9Fe_3)O_3$ is $FeAl_2O_4$;
3. Aluminum iron cobalt oxide $(Fe_{10}Al_3Co_5)O_3$ is $CoFe_2O_4$ (CAS no. 011121) and $CoAl_2O_4$ (CAS no. 440160);

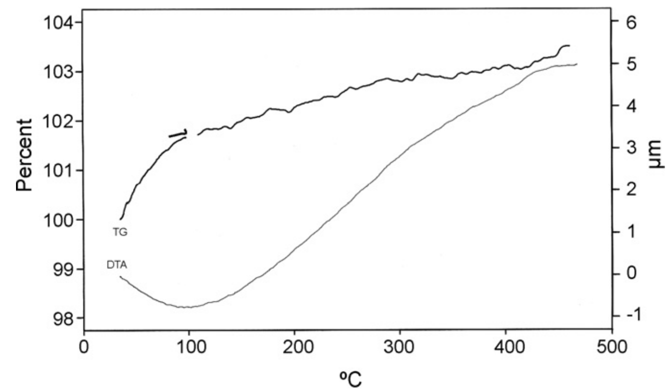


Fig. 9. TG and DTA graph of ceramic pigment composition $FeAlO_3$.

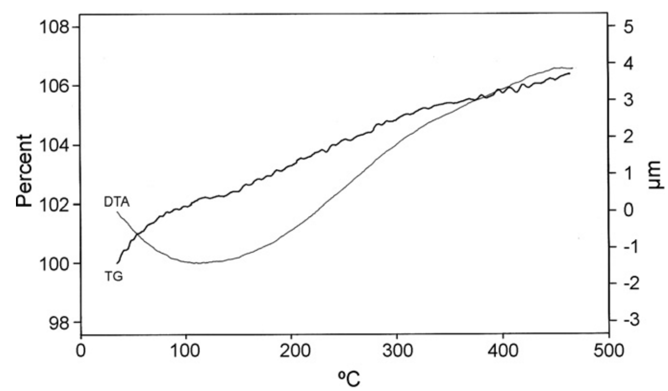


Fig. 10. TG and DTA graph of ceramic pigment composition $FeAl_2O_4$.

4. Aluminum iron cobalt oxide $(Fe_5Al_3Co_{10})O_3$ is $CoFe_2O_4$ (CAS no. 221086) and $CoAl_2O_4$ (CAS no. 100458).

### 3.4. Thermo gravimetric/differential thermal analysis

From Figs. 9–12, it is seen that the weight changes for these four pigments are quite similar. The weight values increases with temperature. This shows that the transition metals present in the formulation acquire higher oxidation state, weight and stabilize at about 400 °C. The maximum weight gain is 6% for the pigment $FeAl_2O_4$ (Fig. 10). This may be due to the excess aluminum oxide present in the formulation which reacted with nitrogen to form stable aluminum nitride particles [7]. In other three pigments (Figs. 9, 11 and 12), the weight gain is below 4%. This weight gain is due to the attainment of higher oxidation states leading to the formation of higher oxides in the composition. Thus, these ceramic pigments are stable above

Table 2
Results of elemental analysis of ceramic pigments using atomic absorption spectrophotometer (AAS) and its theoretical calculation

| Chemical formula | AAS identification (%) | | | Theoretical calculation (%) | | |
|---|---|---|---|---|---|---|
| | Fe | Al | Co | Fe | Al | Co |
| $FeAlO_3$ | 41.47 | 23.58 | – | 42.62 | 20.63 | – |
| $FeAl_2$ $O_4$ | 34.82 | 32.57 | – | 32.09 | 31.06 | – |
| $CoFe_2O_4$(CAS no. 011121) and $CoAl_2O_4$(CAS no. 440160) | 29.73 | 12.43 | 28.32 | 27.93 | 13.11 | 28.42 |
| $CoFe_2O_4$ (CAS no. 221086) and $CoAl_2O_4$ (CAS no. 100458) | 26.12 | 13.62 | 32.48 | 27.93 | 13.11 | 28.42 |

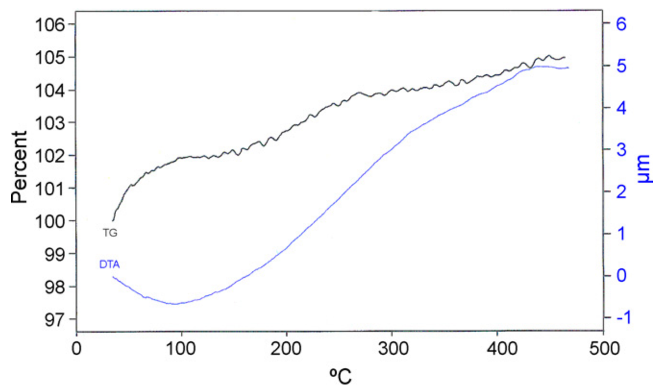


Fig. 11. TG and DTA graph of ceramic pigment composition $CoFe_2O_4$.

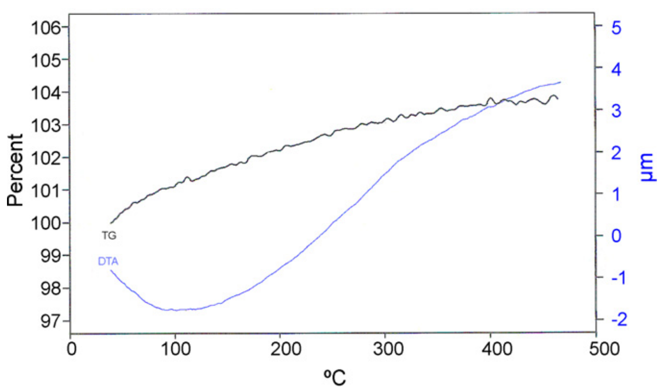


Fig. 12. TG and DTA graph of ceramic pigment composition $CoAl_2O_4$.

400 °C. It is seen from these figures that the DTA behaviors of these pigments are more or less the same. The DTA curves (Figs. 9–12) show initially an endothermic peak with a maximum at 373 K (100 °C) followed an exotherm trend up to 673 K (400 °C). Afterwards there is no change in behavior of these pigments with temperature. Thus, these pigments become thermally stable above 400 °C. This result indicates that the crystalline ceramic pigments are highly stable at high temperature [8].

### 3.5. Differential scanning calorimetric studies

The DSC studies [9] of these four pigments indicate that all the pigments have a small endothermic phase change reaction in the temperature range of 80–100 °C. This is due to the formation of higher oxidation states of the transition metals. This endothermic reaction is also observed in DTA study. Further, the DSC studies indicate that all the pigments are thermally stable above 640 °C with small exothermic phase change reaction occuring in the temperature ranges of 210–240 °C, 300–350 °C and 380–410 °C. The enthalpy change of this exothermic reaction is the highest in the range of 380–410 °C (2.508 J/g), for the pigment with excess aluminum oxide, $FeAl_2O_4$. This enthalpy change is very small for all other pigments. Thus, the DSC study reveals that these pigments are inert and useful for high-temperature resistant protective coatings.

The TG/DTA data are comparable to the DSC analysis. The TG is increased with temperature for all the systems up to 400 °C and thereafter stabilizes to a constant value. Similar results are observed in the DSC measurement of the exothermic reaction in the range of 380–410 °C. Thereafter the pigments are not affected by temperature. The DTA analysis also shows an endothermic reaction at 100 °C and thereafter the pigment is thermally stable.

## 4. Conclusions

Four different types of coloured ceramic pigments have been prepared by using suitable combinations of red iron oxide, cobalt carbonate and aluminum oxide. The thermal resistance behavior of these pigments was studied by TG/DTA and DSC analysis and found that these ceramic pigments are thermally stable above 400 °C. The TG analysis has shown that these pigments are gaining weight with temperature due to the attainment of higher oxidation state of the element present in the composition. DTA analysis indicates that the pigments are not affected by temperature above 400 °C. The DSC studies also confirm TG/DTA measurements with small exothermic reaction. The FTIR and XRD measurements show that the probable compositions of these coloured ceramic pigments are $FeAlO_3$ and $FeAl_2O_4$. The formula is further confirmed by AAS elemental analysis.

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