Co and Cr – doped $ZnAl_2O_4$ NIR-reflective pigments obtained via combustion synthesis

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Introduction

54% of the solar radiation reaching the Earth is in the near-infrared (NIR) region, sustaining life. YET, the Global environmental problems caused a continuous increase of the daytime average temperature in the past years. There are serious warnings concerning the Earh heating up fast. To prevent excessive heating of buildings, cars, paved spaces and other surfaces in urban areas, the scientists are developing special coatings to reflect heat. Spinel-based materials show outstanding features in terms of physical, chemical, thermal and optical properties. Therefore they can be used in making NIR-reflecting pigments designed for a wide range of colored coatings. Co and Cr-doped $ZnAl_2O_4$ pigments were prepared via a microwave–assisted combustion synthesis. They were characterized and successfully tested in making NIR-reflective coatings.

Experimental

Pigments

Pigment A: 8/10 $Zn(NO_3)_2$ + 2/10 $Co(NO_3)_2$ + 10/9 $C_2H_5NO_2$ + 2 $Al(NO_3)_3$ + 5 CH_4N_2O =

= $Zn_{0.8}Co_{0.2}Al_2O_4$ + CO_2 + H_2O + N_2

Pigment B: 8/10 $Zn(NO_3)_2$ + 2/10 $Co(NO_3)_2$ + 10/9 $C_2H_5NO_2$ + $Al(NO_3)_3$ + $Cr(NO_3)_3$ + 5 CH_4N_2O =

= $Zn_{0.8}Co_{0.2}AlCrO_4$ + CO_2 + H_2O + N_2

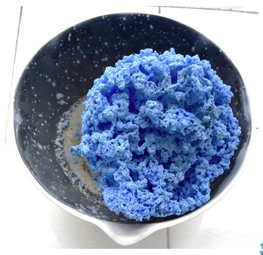

Fig 1. As-obtained pigment A.

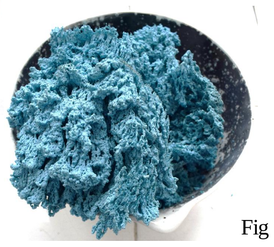

Fig 2. As-obtained pigment B.

Table 1. Samples composition.

Raw materials	Molar composition of the pigment/ Sample indicative					
	$Zn_{0.8}Co_{0.2}Al_2O_4$ / A	$Zn_{0.8}Co_{0.2}AlCrO_4$ / B	$Zn_{0.8}Co_{0.2}Al_2O_4$ / A-T10	$Zn_{0.8}Co_{0.2}Al_2O_4$ / A-T30	$Zn_{0.8}Co_{0.2}AlCrO_4$ / B-T10	$Zn_{0.8}Co_{0.2}AlCrO_4$ / B-T30
$Zn(NO_3)_2{\cdot}4H_2O$	8/10	8/10	8/10	8/10	8/10	8/10
$Co(NO_3)_2{\cdot}6H_2O$	2/10	2/10	2/10	2/10	2/10	2/10
$Al(NO_3)_3{\cdot}9H_2O$	2	1	2	2	1	1
$Cr(NO_3)_3{\cdot}9H_2O$	-	1	-	-	1	1
$C_2H_5NO_2$	10/9	10/9	10/9	10/9	10/9	10/9
CH_4N_2O	7.5	7.5	7.5	7.5	7.5	7.5
TiO_2 (wt. %)	-	-	10	30	10	30

Results and discussion

Fig 3. Pigment A.

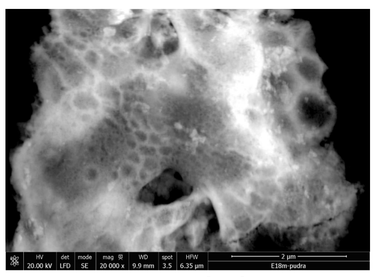

Fig 5. SEM micrograph of pigment A.

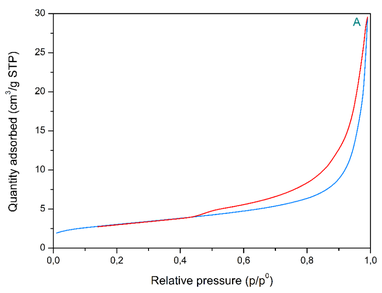

Fig 6. Adsorption-desorption isotherm of pigment A.

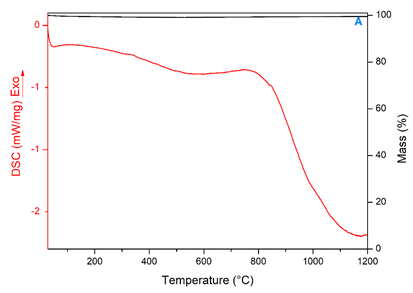

Fig 7. TG-DSC curves of the as-obtained pigment A.

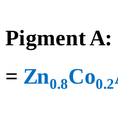

Fig 9. Pigment B.

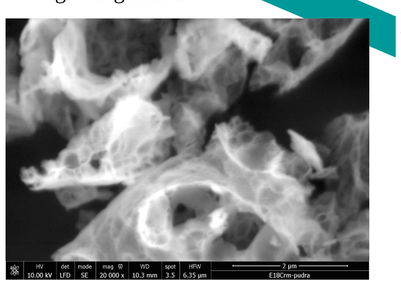

Fig 10. SEM micrograph of pigment B.

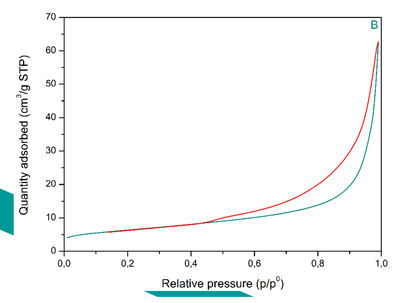

Fig 11. Adsorption-desorption isotherm of pigment B.

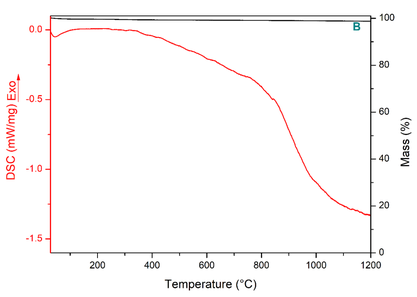

Fig 12. TG-DSC curves of the as-obtained pigment B.

Table 2. CIE L*a*b, TSR and S_{BET} of the obtained pigments.

Sample No.	Pigment stoichiometry	L* / a* / b*	TSR (%)	S_{BET} (m^2/g)
A	$Zn_{0.8}Co_{0.2}Al_2O_4$	59.3 / -1.9 / -43.5	52.9	10.8
B	$Zn_{0.8}Co_{0.2}AlCrO_4$	69.2 /-19.4 /-14.0	48.0	22.6
A-T10	$Zn_{0.8}Co_{0.2}Al_2O_4$ + 10% TiO_2	72.6 / -7.0 / -28.5	55.4	8.8
A-T30	$Zn_{0.8}Co_{0.2}Al_2O_4$ + 30% TiO_2	76.2 / -8.6 / -21.3	56.4	10.5
B-T10	$Zn_{0.8}Co_{0.2}AlCrO_4$ + 10% TiO_2	68.0 / -16.1 / -0.8	40.8	23.1
B-T30	$Zn_{0.8}Co_{0.2}AlCrO_4$ + 30% TiO_2	73.7 / -15.1 / 5.6	49.8	21.4

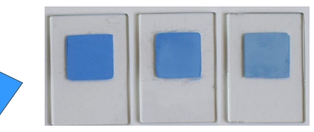

Fig 4. Pigments A, A-T10 and A-T30.

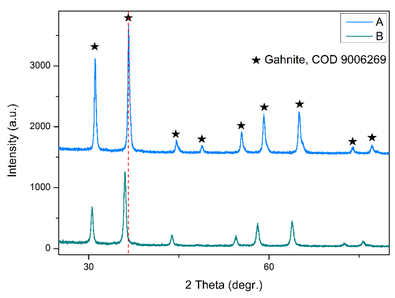

Fig 8. XRD patterns of pigments A and B.

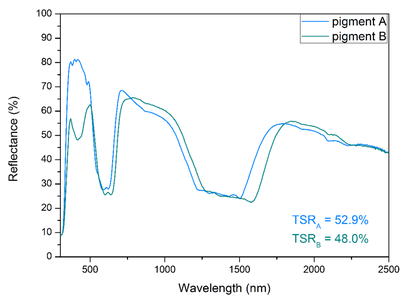

Fig 13. DRS of pigments A and B.

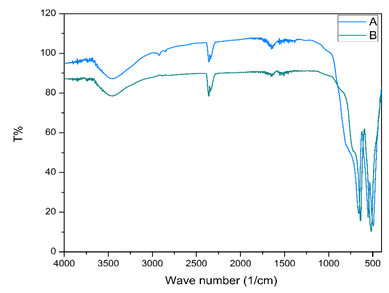

Fig 14. IR spectra of pigments A and B.

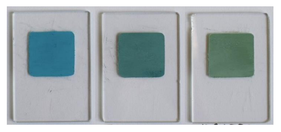

Fig 15. Pigments B, B-T10 and B-T30.

Coatings

Paint recipe:
44.2 % acrylic copolymer
20.0 % pigment
34.3% water
1.5 additives

Coating parameters:
block applicator 300 µm gap, two layers

Dry thickness: 160 µm

Dry thickness: 187 µm

Fig 16. Coatings prepared with pigments A and B.

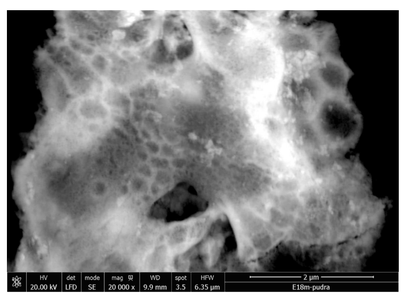

Fig 17. SEM micrograph of the coating prepared with pigment A.

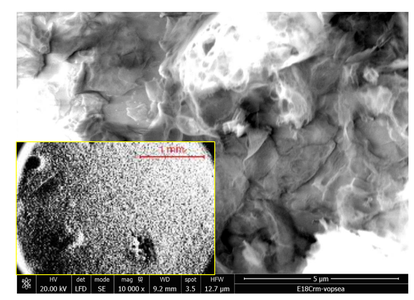

Fig 18. SEM micrographs of the coating prepared with pigment B.

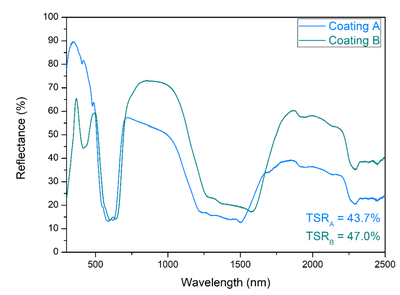

Fig 19. DRS of the coatings prepared with pigments A and B.

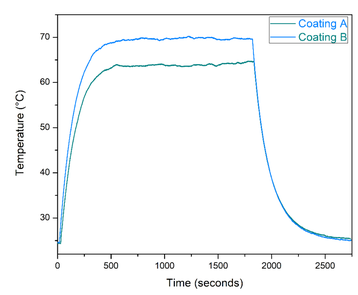

Fig 20. Temperature variation of the coatings prepared with pigments A and B, during IR irradiation.

Conclusions

- Co and Cr-doped $ZnAl_2O_4$ NIR-reflective pigments with TiO_2addition were prepared via single-step, microwave-assisted solution combustion synthesis.
- The Co and Cr co-doped pigment shows lower TSR compared to the single-chromophore pigment.
- TiO_2 addition led to no significant improvement in terms of TSR of the pigments, although it is traditionally known to have NIR-reflective properties itself.
- Both TiO_2-free pigments were tested in preparing water-based acrylic coatings showing promising NIR reflective properties.
- The coating colored with Co and Cr co-doped pigment shows higher TSR, due to the insulating, porous texture of the dried coating, caused by higher surface area of the pigment and trapped air.

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