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Combustion synthesis of $Zn_{1-x}Co_xAl_2O_4$ near-infrared reflective pigments

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1. Introduction

Over the last few years, the global warming led to the alarming heat island effect in urban areas manifested by temperatures up to 5.6 °C higher, as compared with the surrounding areas. This in turn increased the energy consumption used for cooling the buildings, which *accelerates* the global warming.

The World Meteorological Organization confirmed 2015 being the hottest year on record and this critical situation represents a serious concern for policymakers and society. Scientists assumed the task of finding solutions to reduce the heat island effect and smart materials are involved. Among these, pigments with high NIR reflectivity, also known as cold pigments, represent a spearhead in solar reflective coatings technology. White TiO_2 is such a pigment, but it doesn't cope with the market's demand for more appealing and diverse colors. Therefore, our approach relies for the first time on blue $Zn_{1-x}Co_xAl_2O_4$ near-infrared reflective pigments obtained by an energy efficient method, namely the combustion synthesis.

2. Experimental

2.1. Sample preparation

Table 1. Molar composition of the samples designed to obtain $Zn_{1-x}Co_xAl_2O_4$.

No.	x	Molar composition of the raw materials mixtures				
		$Zn(NO_3)_2{\cdot}4H_2O$ (Merck)	$Co(NO_3)_2{\cdot}6H_2O$ (Reactivul)	$Al(NO_3)_3{\cdot}9H_2O$ (Fluka)	$C_2H_5NO_2$ (Fluka)	CH_4N_2O (Merck)
1.	0.1	8.1	0.9	18.0	10.0	67.5
2.	0.2	7.2	1.8	18.0	10.0	67.5
3.	0.3	6.3	2.7	18.0	10.0	67.5

Equation of the combustion reaction:

$$9(1-x)\ Zn(NO_3)_2 + 9x\ Co(NO_3)_2 + 10\ C_2H_5NO_2 + 18\ Al(NO_3)_3 + 67.5\ CH_4N_2O + 46.25\ O_2 = 9\ Zn_{1-x}Co_xAl_2O_4(c) + 87.5\ CO_2(g) + 185\ H_2O(g) + 108.5\ N_2(g)$$

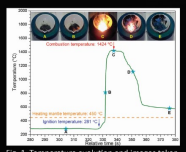

Fig. 1. Temperature evolution and images taken during the combustion reaction (sample 3).

2.2. Sample characterization and testing

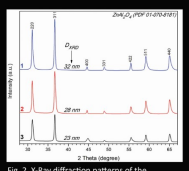

Fig. 2. X-Ray diffraction patterns of the combustion-synthesized samples.

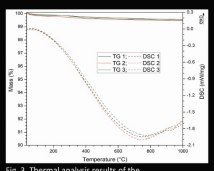

Fig. 3. Thermal analysis results of the combustion-synthesized samples.

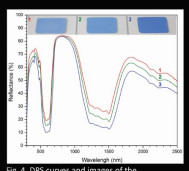

Fig. 4. DRS curves and images of the as-obtained pigments.

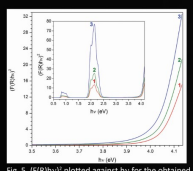

Fig. 5. $(F(R)h\nu)^2$ plotted against hν for the obtained $Zn_{1-x}Co_xAl_2O_4$ samples.

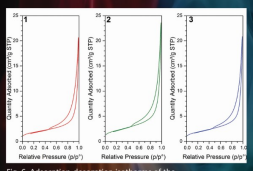

Fig. 6. Adsorption-desorption isotherms of the combustion-synthesized samples.

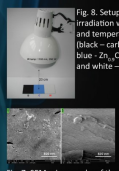

Fig. 8. Setup used for samples irradiation with an IR lamp and temperature measurement (black – carbon black, blue – $Zn_{1-x}Co_xAl_2O_4$ and white – TiO_2).

Fig. 7. SEM micrographs of the samples 1 and 3 obtained from combustion reaction.

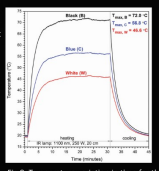

Fig.9. Temperature variation in time for three samples coated with carbon black, $Zn_{1-x}Co_xAl_2O_4$ and TiO_2.

3. Results and discussion

Table 2. Features of the $Zn_{1-x}Co_xAl_2O_4$ powders obtained via combustion synthesis.

No.	x	D_{XRD} (nm)	S_{BET} (m^2/g)	L*	a*	b*	TSR (%)	Eg (eV)
1.	0.1	32	6.5	67.9	-3.7	-39.0	63.2	4.04
2.	0.2	28	7.8	59.3	-1.9	-43.5	53.9	4.03
3.	0.3	23	6.8	53.0	3.7	-49.4	48.0	4.02
Coating (1)				64.5	-1.7	-45.3	59.4	

4. Conclusions

- Combustion synthesis was successfully used to obtain blue $Zn_{1-x}Co_xAl_2O_4$ pigments with different shades.
- TSR decreases with the increase of Co content and blue shade of the pigments.
- TSR of the coating is lower than in the case of the as-obtained pigment.
- The tested pigment shows an intermediate behaviour compared with the two extremes – TiO_2 white and carbon black.

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