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Polymeric Precursor Route for the Synthesis of Nanosized $Co_x Mg_{1-x} Al_2O_4$ Blue Pigments

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Abstract: In this work, synthesis of nanocrystalline $Co_x Mg_{1-x} Al_2O_4$ (x =0, 0.1, 0.2, 0.4, 0.6, 0.8 and1) spinels by the thermal decomposition of polymeric precursors derived from metal nitrate salts and starch as a novel fuel has been systematically studied. The resulting blue pigments were characterized by the techniques X-ray diffraction (XRD), infrared (IR) and UV-Vis spectroscopy and scanning electron microscope (SEM). The XRD patterns displayed the characteristic peaks of the spinel structure and a good crystallinity. The FTIR spectra pointed out frequency bonds in range of 500-800 cm^{-1} correspond to metal oxygen bonds through vibrations for the spinel structure compounds. SEM images showed nano particles with less than 30 nm crystallite size. The color measurements of nano pigments were studied by using CIE L*a*b Parameter method which depicted the bluest color was obtained for x = 0.1. The UV-Vis spectra of the $Co_x Mg_{1-x} Al_2O_4$ pigments confirmed the presence of tetrahedrally coordinated Co^{2+}. These facts confirmed that starch can be applied as a new and environmentally benign fuel to obtain ceramic blue pigments with $Co_x Mg_{1-x} Al_2O_4$ structure in low Co content.

Key words: Oxide materials · Nano fabrications · Ceramic blue pigment · Starch

INTRODUCTION

In recent years homogeneous and highly crystalline nano-phased metal oxide spinels have been studied by several research groups around the world for their potentials in electrochemical [1-3], magnetic [4], catalytic [5,6] and ceramic [7] applications. Generally, aluminate spinels show high thermal stability, high mechanical resistance, hydrophobicity and low surface acidity[8]. One example is $CoAl_2O_4$ which is well known as Thenard's blue for its impressive optical property and widely used in the ceramics, glass, paint, industry and color TV tubes as contrast - enhancing luminescent pigment[9]. However Low Co^{+2} contents are recommended since Co^{+2} is considered toxic, scarce and expensive[10]. One of the main objectives is the preparation of quality blue pigments with minimum amount of Co^{+2} under advantageous economic conditions [11]. Therefore in this work $MgAl_2O_4$ was chosen as a host lattice for its high melting temperature and remarkable chemical stability. Then ceramic blue pigments from the $Co_x Mg_{1-x} Al_2O_4$ (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8 and1) system synthesized by means of the polymeric precursor method and applying starch as an environmentally benign fuel.

MATERIALS AND METHODS

Powder Synthesis: Merck (Darmstadt, Germany) analytical reagents were used as raw materials: cobalt nitrate $Co(NO_3)_2.6H_2O$, magnesium nitrate $Mg(NO_3)_2.6H_2O$, aluminum nitrate $Al(NO_3)_3.9H_2O$ and starch $\{(C_6H_{10}O_5)_n\}$. An aqueous solution containing Mg (II), Al (III) and Co(II) metal ions salts and fuel was heated at 60°C under continuous stirring after 1h, then the temperature was raised to 80°C and the mixture was stirred for several hours until a pink-reddish gel was formed. The used molar ratio M (II)/Al(III) {M(II)=Mg and Co} was 0.5 and M_{total}/ starch{M_{total}=M(II) and Al(III)} was 2.4. The blue mixed oxide obtained after a heat treatment of the metal-starch gel precursors at T=800°C for 1h.

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Characterization Methods: X-ray diffraction patterns were recorded using a D_4-BRUKER diffractometer by Cu Ká radiation at 20 KV and 30mA. A Philips XLΦ-30 scanning electron microscope (SEM) was used to observe the morphology of nano-particles. The Fourier transform-infrared (FT-IR) spectra of the gel precursors or powders were obtained on a Shimadzu FT-IR-8101 by employing potassium bromide (KBr) pellet technique. CIE-L* a* b* chromatic coordinates were determined using a Varian UV-VIS spectrophotometer (Cary 300 Bio, Mulgrave Victoria, Australia) under D65 illuminant and 10° standard observer angle.

RESULT AND DISCUSSION

The soluble starch is a low-cost, abundant, renewable, natural polysaccharide and thus fulfills environmentally aware chemistry demands [12]. Besides these facts, applying starch resulted in spinel single homogenous phase in our paper, but some other fuels like glycine leads to undesirable mixed oxides like Co_3O_4/$CoAl_2O_4$in similar routs Starch has a triple role during the synthesis as complexing, template and gelation agent [13]. The starch has already been employed as a powerful tool for controlling the particle shape and size of inorganic materials and carries a large number of functional polyol groups, thereby acting as a ligand towards divalent or trivalent metal ions [14]. Moreover, at 80-90°C, the resulting complex precursors, in the presence of an excess of starch, form gels [15]. The polysaccharide acts initially as ligand toward the metal cations and determines the formation of the metals-starch complex. The helical form of the carbohydrate plays a structure-director role on the supra molecular assembly [16]. The host magnesium aluminate lattice was not chosen randomly but, rather, because $MgAl_2O_4$ is non-toxic/non-hazardous [17].

Fig. 1. shows the XRD patterns of the Co_x Mg_{1-x} Al_2O_4 (x =0, 0.1, 0.2, 0.4, 0.6, 0.8 and1) oxides heated at 800°C. For all the samples the characteristic peaks of the spinel structure were noticed, according to the ICDD files 21-1152 and 03-0896, for $MgAl_2O_4$ and $CoAl_2O_4$, respectively. The patterns did not show the presence of secondary phase. The development of the spinel phase at a relatively low temperature indicates one advantage of this synthesis route, as compared with other methods [18].

The crystallite size of the calcined pigments Co_xMg_{1-x} Al_2O_4 (x=0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1) was determined based on the XRD patterns using the

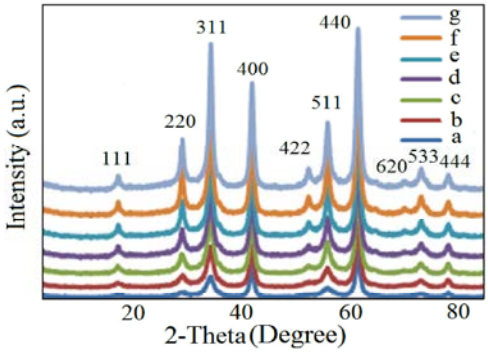

Fig. 1: Powder X-ray diffraction patterns of $Co_xMg_{1-x}Al_2O_4$ {x = 0(a), 0.1 (b), 0.2(c), 0.4(d), 0.6(e), 0.8(f) and 1(g)} calcinated for 1 h at 800°C

Table 1: Crystallite size and colorimetric analysis of the calcined samples

Sample	Crystallite size (nm)	L*	a*	b*	ΔE
$CoAl_2O_4$	15	37.56	-0.799	-1.023	37.58
$Co_{0.8}Mg_{0.2}Al_2O_4$	21	38.51	-1.399	-0.046	38.54
$Co_{0.6}Mg_{0.4}Al_2O_4$	20	39.01	-1.759	-1.211	39.07
$Co_{0.4}Mg_{0.6}Al_2O_4$	27	39.23	-0.666	-1.485	39.27
$Co_{0.2}Mg_{0.8}Al_2O_4$	15	42.50	-1.299	-3.676	42.68
$Co_{0.1}Mg_{0.9}Al_2O_4$	10	67.03	-10.399	-8.796	68.39
$MgAl_2O_4$	7	65.97	-0.168	3.455	66.06

Williamson Hall method is given in Table 1. It seems that nano pigments with mean levels of cobalt content have larger crystallite sizes while all samples have crystallite sizes bellow 30 nm. The chromatic coordinate (L*, a* and b*) of the pigments Co_x Mg_{1-x} Al_2O_4 (x =0, 0.1, 0.2, 0.4, 0.6, 0.8 and1) heat treated at 800°C, are displayed in Table 1. It can be seen that the lightness, L*, decreases with the increase of the Co content, pointing out the formation of darker pigments. The coordinate a* is kept negative for all the samples, indicating a slight green condition. The b* values shows the bluest color pigment was obtained for x = 0.1 and 0.8 and the sample with x = 0.1 is the one with the darkest blue. According to Souza *et al*. higher Co-enrichment leads to darker blue pigments but the most negative values of b* observed in medium cobalt content samples in the Co_x Zn_{1-x} Al_2O_4 system [19].

The UV-Vis absorbance spectra of the samples Co_x Mg_{1-x} Al_2O_4 (x>0) displays a wide absorption in the range from 540 nm to 630 nm, corresponding to the absorption of the colors yellow, orange and red (especially for x=0.1) as present in Fig. 2. Thus, the reflectance occurs in the complementary colors, namely violet, blue and cyan, centered in the blue. The analysis of the UV-Vis spectra (Fig. 2) reveals that in the $Co_{0.1}$ $Mg_{0.9}$ Al_2O_4 (lowest cobalt content) three broad absorptions at approximately 540, 586 and 632 nm are well defined which are attributed to the

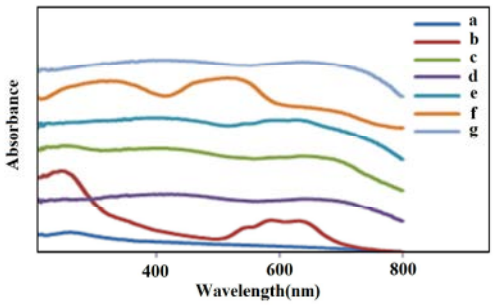

Fig. 2: UV-vis spectra of $Co_x Mg_{1-x} Al_2O_4$ {x = 0(a), 0.1 (b), 0.2(c), 0.4(d), 0.6(e), 0.8(f) and 1(g)} calcinated for 1 h at 800°C

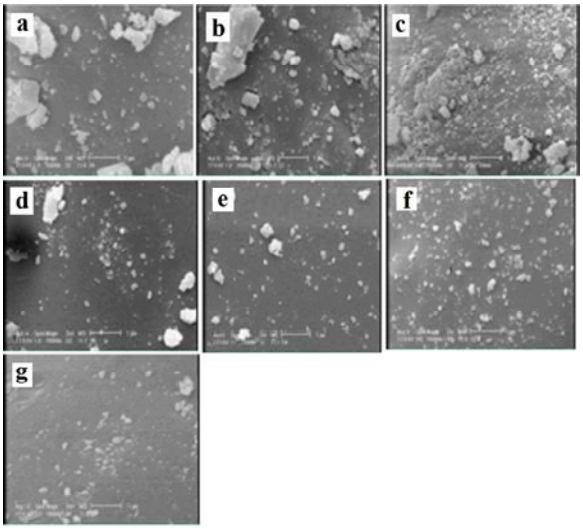

Fig. 3: SEM micrograph of the powders: $Co_x Mg_{1-x} Al_2O_4$ (x =1(a), 0.8 (b), 0.6 (c), 0.4 (d), 0.2 (e), 0.1 (f) and 0(g)

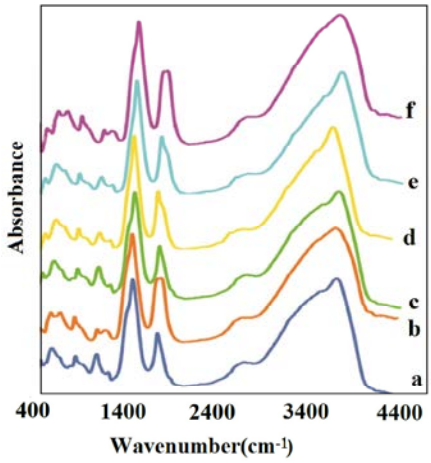

Fig. 4: FTIR spectrum for metals-starch gel precursors of $Co_x Mg_{1-x} Al_2O_4$ {x = 0.1(a), 0.2 (b), 0.4(c), 0.6(d), 0.8(e) and 1(f) } oxides

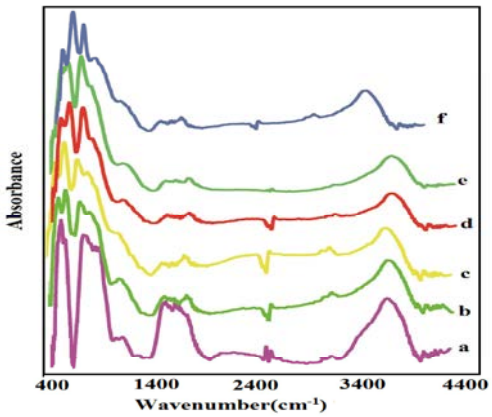

Fig. 5: FTIR spectra of $Co_x Mg_{1-x} Al_2O_4$ {x = 0.1(a), 0.2 (b), 0.4(c), 0.6(d), 0.8(e) and 1(f)} calcinated for 1 h at 800°C

spin allowed transitions ($^4A_2(F) \rightarrow {}^4T_2(F)$, $^4A_2(F) \rightarrow {}^4T_1(F)$ and $^4A_2(F) \rightarrow {}^4T_1(P)$) of the Co^{+2} ions in tetrahedral sites according to the energy levels of Orgel diagram [19]. Same results were reported in the spectroscopic characterization of $CoAl_2O_4$ coatings by Stangar *et al*. [20] and Zayat *et al*. [21].

SEM images of the $Co_x Mg_{1-x} Al_2O_4$(x =0, 0.1, 0.2, 0.4, 0.6, 0.8 and1) particles prepared were showed in Fig. 3. A decrease of the agglomeration degree in lower cobalt contents (x = 0.2, 0.1 and 0) being identified in agreement with the results of Williamson Hall method for the crystallite sizes (Table 1).

Fig. 4 and 5 exhibit the IR spectrum for gel precursor samples and resultant calcined powders of $Co_x Mg_{1-x} Al_2O_4$(x =0, 0.1, 0.2, 0.4, 0.6, 0.8 and1) oxides, respectively. The FTIR spectra of the (Mg, Al, Co)-starch gel precursors are very similar. The stretching vibration assigned to the c-o and adjacent c-c bands overlap the 1000-1150 cm^{-1} region. The result revealed a broad and strong band on the 1450-1300 cm^{-1} region, which most probably results from nitrate ions. This peak disappeared in the resultant powders after calcinations at 800°C for 1h (Fig. 5). Mixed oxide spinels always display stretching bands in the 500-800 cm^{-1} range, associated with the vibrations of metal-oxygen, aluminum-oxygen and metal-oxygen-aluminum [22]. These peaks are identified in gel precursors at low intensity absorption but increased in calcined powders at T = 800°C.

In previous reports, pure and crystalline $Mg_{1-x} Co_x Al_2O_4$ powders were obtained only after annealing the as-prepared amorphous powders at high temperatures [23, 24]. Few reports on this topic show that the preparation of same ceramic pigments involves annealing

at 1400°C for 3 h [25]. Even applying new methods such as sonochemical synthesis requires heating treatment at 1000°C at least for 2 hours for the formation of pure cobalt aluminate spinel phase [26]. Generally, increasing temperature treatment increases the crystallite sizes of powders [27-29]. So preparation of single phase spinel nano particles at lower temperatures is the advantage of our liquid combustion method and makes it technically simple and cost effective.

CONCLUSIONS

Blue ceramic pigments $Co_x Mg_{1-x} Al_2O_4$ (x =0, 0.1, 0.2, 0.4, 0.6, 0.8 and1) are produced as a solid solution from two mixed phases $CoAl_2O_4$ and $MgAl_2O_4$spinels applying a starch precursor method. Powders are crystallized after calcination at 800°C and characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), UV-Vis spectroscopy, diffuse reflectance spectra(CIE L*a*b* parameters) measurements and SEM. The crystallite sizes of spinels are estimated in the range of 7-27 nm. The bluest color was obtained for x=0.1 and the lightness, L*, decreases with the increase of the Co content, pointing out the formation of darker pigments.

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REFERENCES

1. Giannakas, A.E., A.K. Ladavos and G.S. Armatas, 2007, Surface properties, textural features and catalytic performance for NO + CO abatement of spinels MAl_2O_4 (M= Mg, Co and Zn) developed by reverse and discontinuous micro emulsion method. Appl. Surf. Sci., 253: 6969-79.
2. Llusar, M., A. Fore and J.A. Badenes, 2001. Color analysis of some cobalt-based blue pigments. J. Eur. Ceram. Soc., 21: 1121-30.
3. Britto, S., A.V. Radha and N. Ravishankar, 2007. Solution decomposition of the layered double hydroxide (LDH) of Zn with Al. Solid State Sci., 9: 279-86.
4. Li, W., J. Li and J. Guo, 2003. Synthesis and characterization of nanocrystalline $CoAl_2O_4$ spinel powder by low temperature combustion. J. Eur. Cer. Soc., 23: 2289-95.
5. Ahmed, I.S., S.A. Shama and M.M. Moustafa, 2009, Synthesis and spectral characterization of $Co_xMg_{1-x}Al_2O_4$ as new nano-coloring agent of ceramic pigment. Spectrochimica Acta Part A, 74: 665-672.
6. Suzuki, T., H. Nagai and M. Nohara, 2007. Melting of antiferromagnetic ordering in spinel oxide $CoAl_2O_4$. J. Phys.: Condens Matter., 19: 145265.
7. Chen, Z., E. Shi and Y. Zheng, 2003. Hydrothermal synthesis of nano sized $CoAl_2O_4$ on $ZnAl_2O_4$ seed crystallites. J. Am. Ceram. Soc., 86(6): 1058-60.
8. Luan, C., D. Yuan, X. Duan, *et al.*, 2006. Synthesis and characterization of Co^{2+}:$MgAl_2O_4$ nano crystal, J. Sol-Gel Sci. Technol., 38: 245-249.
9. Aruna, A.T. and A.S. Mukasyan, 2008. Combustion synthesis and nano materials, Curr. Opin. Solid State Mater. Sci., 12: 44-50.
10. Ianos, R. and R. Laza, 2009. Characterization and sintering behaviour of magnesium aluminate ($MgAl_2O_4$) powders, Mater. Chem. Phys., 115: 645-648.
11. Cavalcante, P.M.T., M. Dondi and G. Guarini, 2009. Colour performance of ceramic nano-pigments, Dyes Pigments, 80: 226-232.
12. Cuiyan, W., L. Shaomin, L. Lihong and B. Xuan, 2006, Synthesis of cobalt-aluminate spinels via glycine chelated precursors, Materials Chemistry and Physics, 96: 361-370.
13. Saberi, A., F. Golestani-Fard and M. Willert-Porada, 2009. A novel approach to synthesis of nanosize $MgAl_2O_4$ spinel powder through Sol-Gel citrate technique and subsequent heat treatment. Ceram. Int., 35(3): 933-937.
14. Cui, X., M. Antonietti and S.H. Yu, 2006. Structural effects of iron oxide nanoparticles and iron ions on the hydrothermal carbonization of starch and rice carbohydrates. Small, 6(2): 756-9.
15. Vigneshwaran, N., S. Kumar, A.A. Kathe, P.V. Varadarajan and V. Prasad, 2006. Functional finishing of cotton fabrics using zinc oxide-soluble starch nanocomposites. Nanotechnol., 17: 5087-95.
16. Chowdhury, P.S., P.R. Arya and K. Raha, 2007. Green synthesis of nanoscopic iron oxide particles: a potential oxidizer in nanoenergetics. Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, 37: 447-51.
17. Nidhin, M., R. Indumathy, K.J. Sreeram and B.U. Nair, 2008. Synthesis of iron oxide nanoparticles of narrow size distribution on polysaccharide templates. Bulletin of Materials Science, 31(1): 93-6.

18. Mumalo-Djokic, D., W.B. Stern and A. Taubert, 2008. Zinc oxide/carbohydrate hybrid materials via mineralization of starch and cellulose in the strongly hydrated ionic liquid tetrabutylammonium hydroxide. Crystal Growth and Design, 8(1): 330-5.
19. Souza, L.K.C., J.R. Zamian and G.N.R. Filho, 2009, Blue pigments based on $Co_xZn_{1-x}Al_2O_4$ spinels synthesized by the polymeric precursor method, Dyes Pigments, 81: 187-192.
20. Stangar, U.L., B. Orel and M. Krajnc, 2003. Preparation and spectroscopic characterization of blue $CoAl_2O_4$ coatings. J. Sol-Gel Sci. Technol., 26: 771-5.
21. Zayat, M. and D. Levy, 2000. Blue $CoAl_2O_4$ particles prepared by the sol-gel and citrate-gel methods. Chem. Mater., 12: 2763-9.
22. Llusar, M., A. Forés and J.A. Badenes, 2001. Colour analysis of some cobalt-based blue pigments, J. Eur. Ceram. Soc., 21: 1121-1130.
23. Ianos, R., R. Laza and P. Barvinschi, 2011. Synthesis of $Mg_{1-x}Co_xAl_2O_4$ blue pigments via combustion route. Adv. Powder Technol., 22: 396-400.
24. Koroleva, L.F., (Chekhomova), 2004. Synthesis of spinel-based ceramic pigments from hydroxycarbonates, Glass Ceram., 61: 299-302.
25. Luan, C., D. Yuan and X. Duan, 2006. Synthesis and characterization of Co^{2+}:$MgAl_2O_4$ nanocrystal, J. Sol-Gel Sci. Technol., 38: 245-249.
26. Lv, W., Q. Qiu and F. Wang, 2010. Sonochemical synthesis of cobalt aluminate nano particles under various preparation parameters, Ultrason. Sonochem., 17: 793-801.
27. Singh, R.C., M.P. Singh and O. Singh, 2009. Influence of synthesis and calcination temperatures on particle size and ethanol sensing behavior of chemically synthesized SnO_2 nanostructures. Sensors and Actuators B: Chemical, 143(1): 226-232.
28. Torkian, L., M. Amini and E. Amereh, 2012. Synthesis and Characterization of Ag/TiO Nano Composite and its Application in Photo-Degradation of Methylene Blue, Middle-East Journal of Scientific Research, 12(6): 783-788.
29. Torkian, L., M.M. Amini and Z. Bahrami, 2011. Synthesis of nano crystalline $MgAl_2O_4$ spinel powder by microwave assisted combustion, Journal of Inorganic Chemistry, 26(5): 550-554.