



*Dedicated to the memory of
Professor Eugen Segal (1933-2013)*

Co-Al LAYERED DOUBLE HYDROXIDES AS PRECURSORS OF CERAMIC PIGMENT CoAl_2O_4 . PART II: MAGNETIC AND TINT PROPERTIES

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Various oxide phases have been obtained by stepwise heating of Co-Al layered double hydroxides (molar ratio of $\text{Co}^{2+}/\text{Al}^{3+} = 0.5, 1.5$ and 3.0) in the range of 200–1200°C. The effect of the Co content on the magnetic properties of the solids was studied varying the $\text{Co}^{2+}/\text{Al}^{3+}$ molar ratio and the temperature of thermal treatment. It was found that the magnetic properties of the oxide products are compatible with the crystalline phases identified by X-ray diffraction. Magnetic measurements suggest a change of Co^{2+} coordination from octahedral to tetrahedral above 200°C and appearance of octahedrally coordinated Co^{3+} ions both related to the formation of spinel-like mixed oxide $\text{Co}(\text{Co},\text{Al})_2\text{O}_4$. The sample with the lowest Co content produces intense and bright blue colored ceramic pigment CoAl_2O_4 after calcination at 1000°C due to the full reduction by oxidation of octahedrally coordinated Co^{3+} to tetrahedrally coordinated Co^{2+} cations.



INTRODUCTION

This paper continues the study about the characterization of co-precipitated Co-Al layered double hydroxides (LDHs) as basic materials for obtaining of ceramic pigment CoAl_2O_4 .¹ Part I was dealing with the examination of the effect of Co content on the structure evolution of Co-Al layered systems by varying the $\text{Co}^{2+}/\text{Al}^{3+}$ molar ratio and the temperature of thermal treatment in an air in the range of 200–1200°C. It was established that a single phase CoAl_2O_4 spinel is registered only for the solid with the lowest Co loading after

calcination at 1000°C, while the presence of solid solution $\text{CoAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ with spinel structure is observed in samples with higher Co amount after treatment at 1200°C.

The controlled thermal treatment of LDHs usually gives rise to free divalent metal oxides and stoichiometric spinels, the nature of which depends on the precise composition of the starting solids and the heating atmosphere. The presence of oxidizable transition metal cations such as Co^{2+} , Fe^{2+} , Cr^{3+} , etc. offers the potential to tailor the composition of the calcined products because of the transition metals show variable oxidation

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states, and form colored and stable compounds which often possess paramagnetic behavior due to the presence of unpaired electrons.²

CoAl₂O₄ spinel is widely used for obtaining of blue pigment, known as Thenard's blue, cobalt blue or royal blue, applied in the ceramic, glass, plastics, rubber and paint industry as a coloring agent, due to the its intense color, high mechanical, thermal, solar and atmospheric stability, resistance to alkaline and acid attacks, insolubility in glazes and stability at glaze firing temperatures.^{3, 4} The coloring performance of Co containing pigments strongly depends on the molar fraction of the Co cations, their oxidation state and the symmetry of occupied sites. It is well known that the tetrahedrally (Td) coordinated Co²⁺ cations are responsible for the pigment blue color.^{5, 6}

The aim of Part II is to elucidate the role of Co amount on the magnetic properties of the mixed metal oxides obtained from Co-Al LDHs by varying the Co²⁺/Al³⁺ molar ratio and the temperature of thermal treatment in the range of 200–1200°C. The study of magnetic behavior will allow to precise revealing the coordination symmetry and the oxidation state of Co ions as well as their effect on the coloration of the calcined products as potential materials for obtaining of ceramic pigment CoAl₂O₄.

EXPERIMENTAL

Sample preparation

The preparation procedure of Co-Al LDHs with Co²⁺/Al³⁺ molar ratios of 0.5, 1.5 and 3.0 is reported in Part I.¹ The dried layered materials were step-wise thermally treated in an air for 2 h in the temperature range 200–1200°C at a heating rate of 3°C/min. The materials were labeled as xCoAl-y, where *x* represents Co²⁺/Al³⁺ ratio and *y* – temperature of the thermal treatment, for example 3.0CoAl-200.

Sample characterization

The magnetic susceptibility per gram of the samples (χ_g) in dependence on the decomposition temperature were performed at room temperature with a Faraday Balance calibrated with HgCo(SCN)₄ salt as a standard.⁷⁻⁹ The measurements was calculated taking into account the magnetic moments (μ) of Co ions with different valences and coordination, namely, octahedrally (Oh) coordinated Co²⁺(Oh) = 5.1 μ_B ,¹⁰ tetrahedrally (Td) coordinated Co²⁺(Td) = 4.88 μ_B ¹⁰ and octahedrally (Oh) coordinated Co³⁺(Oh) = 0.4 μ_B .¹¹ The diamagnetic corrections for the compounds were estimated from Pascal constants¹² according to the recommendation of Olivier Kahn.¹³ The paramagnetic contribution of Al³⁺ for all temperatures¹⁴ as well the contributions of ferromagnetic impurities at 80°C, which become paramagnetic at higher temperatures, are taken into account.¹⁵

RESULTS AND DISCUSSION

The magnetic measurements of the studied solids show that the magnetic susceptibility per gram (χ_g) decreases, pass through minimum at different calcination temperatures, depending on the sample composition and increases with the decomposition temperature rising (Table 1).

It is observed that at the final temperature of 1200°C magnetic susceptibility increases only for 0.5CoAl sample related to the Curie–Weiss paramagnetic behavior of the system.

The highest concentration of Co³⁺(Oh) is registered for 3.0CoAl sample at 200°C (Fig. 1), followed by decrease with the temperature increase. The value passes through maximum at 250°C for 1.5CoAl and starts above 500°C for 0.5CoAl sample. The obtained results are in accordance with the phases identified by PXRD¹ suggesting collapse of Co-Al layered structure by changing the coordination symmetry of Co²⁺ cations from Oh to Td and appearance of Co³⁺(Oh) ions, both related to concomitant formation of badly organized non-stoichiometric spinel-like mixed oxide, Co²⁺(Co³⁺, Al²⁺)₂O₄. The transformation of spinel-like mixed oxide phase Co²⁺(Co³⁺, Al³⁺)₂O₄ to well defined spinel Co²⁺Al³⁺₂O₄ is complete at 1000°C only for 0.5CoAl sample due to the full reduction of Co³⁺(Oh) to Co²⁺(Td) by oxidation. The concentration Co²⁺(Td) for all samples increases with the raising of temperature of the thermal treatment (Fig. 2).

The differences in the sample behavior depending on the phase composition reflect on the Co²⁺(Td)/Co³⁺(Oh) ratio trend (Fig. 3). A sharply increase above 600°C is observed only for 0.5CoAl sample due to the of Co²⁺(Td) value augmentation. The rest of the samples demonstrate monotonically enhancement with the temperature of calcination, more salient for 1.5CoAl as a result of the lower Co content in the sample.

The magnetization measurements for the samples calcined at 1200°C were performed as a function of applied magnetic field (Fig. 4). The figure presets also data of CoO material as a reference sample. The reversible linear dependence is found up to the highest magnetic field strength pointing to the paramagnetic behavior of the solids. This finding is in strong dependence on the oxidation state of the Co ions.

Table 1

Magnetic susceptibility of the studied samples

Temperature (°C)	Magnetic susceptibility, $\chi_g \cdot 10^{-6}$ (cm ³ /g)		
	0.5CoAl	1.5CoAl	3.0CoAl
105	41.0	63.6	79.2
200	28.5	18.5	19.6
250	27.2	16.3	21.6
350	23.6	21.2	23.7
400	21.9	22.8	24.9
500	19.0	25.4	26.8
600	22.2	28.8	29.2
800	31.4	31.4	31.4
1000	31.6	34.5	36.8
1200	34.0	31.5	29.4

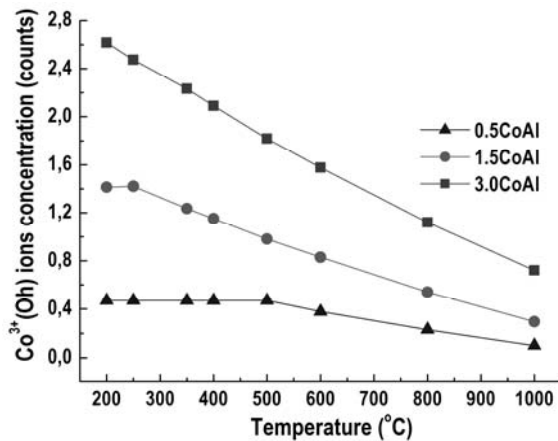
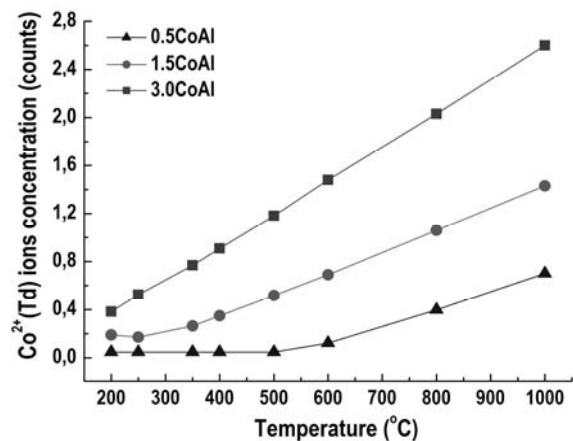
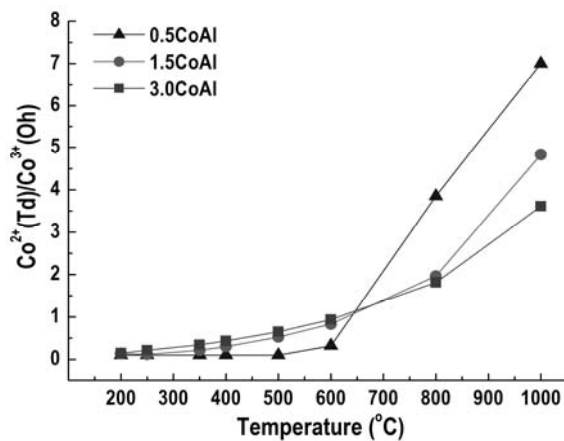
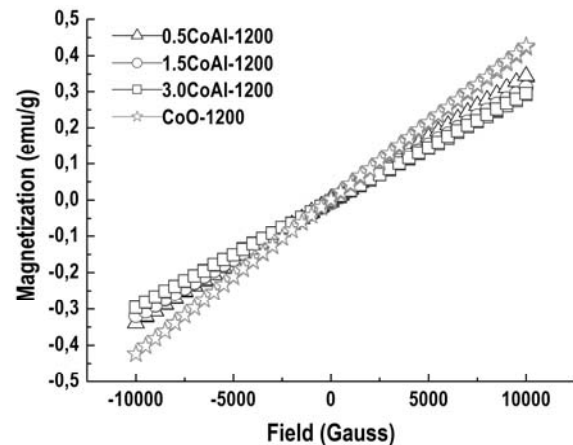
Fig. 1 – Concentration of Co³⁺(Oh) ions.Fig. 2 – Concentration of Co²⁺(Td) ions .Fig. 3 – Co²⁺(Td)/Co³⁺(Oh) ratio.

Fig. 4 – Magnetization vs magnetic field strength.

Magnetic moment is often used to gain information about the oxidation state and stereochemistry of the metal ion. The calculated magnetic moment (μ) induced by the applied field (Table 2) is linear in the field strength and reveals Td coordination of Co²⁺ ions for both CoO-1200 and 0.5CoAl-1200 samples with values lower than reported for Co²⁺(Td).¹⁰ The deviations may be ascribed to non-quenched orbital angular momentum in degenerate ground states and spin-orbit effect

which both can affect simultaneously thus contributing to the magnetic moment value. Contrariwise, the magnetic moments for 1.5CoAl-1200 and 3.0CoAl-1200 solids demonstrate higher values than published previously.^{10,11} This finding may be attributed to the cation disordering and combination of Co²⁺ and Co³⁺ ions between Td and Oh sites in the formed solid solutions with a spinel structure: $3\text{CoAl}_2\text{O}_4 + 2\text{Co}_3\text{O}_4$ for 1.5CoAl-1200 solid and $\text{CoAl}_2\text{O}_4 + 5/3\text{Co}_3\text{O}_4$ for 3.0CoAl-1200,

respectively (Table 2). Consequently, the data suggest the coexistence of Co^{2+} and Co^{3+} ions in both Td and Oh symmetry, because of it has been revealed that Al^{3+} cation has very strong preference for Oh sites.¹⁶ The amounts of Co^{2+} and Co^{3+} ions of calcined samples sustain the obtained results as well as are consistent with the crystalline phases identified in the PXRD patterns.¹

The different tints exhibited by the studied solids demonstrate the role of the oxidation state and coordination symmetry of the Co ions. It is known that the color of the transition metal ions usually arises from charge transfer processes, electron transfer between energy bands or d–d transitions. It

should consider that the pink color of 0.5CoAl-HT and 1.5CoAl-HT samples (Fig. 5) is assigned to d–d transition of Co^{2+} ions (d^7) in high spin (weak field) Oh coordination of OH^- (O^{2-}) ions.¹⁷ The beige color of 3.0CoAl-HT sample arises from d–d transitions of Co^{3+} ions (d^6) in low spin Oh surrounding suggesting the thermodynamically favored partial oxidation of Co^{2+} to Co^{3+} cations during the synthesis procedure. Green and Turquoise colors should be attributed to the concomitant Co^{2+} (Td) and Co^{3+} (Oh) presence respectively, in the spinel-like mixed oxide $\text{Co}^{2+}(\text{Co}^{3+}, \text{Al}^{3+})_2\text{O}_4$. The distinctive blue color is undoubtedly ascribed to d–d transitions of the Co^{2+} ions in Td sites of the CoAl_2O_4 spinel structure.¹⁸⁻²¹

Table 2

Magnetic data of the samples calcined at 1200°C

Sample	PXRD data	^b μ (μ_B)	^c $r\mu$ (μ_B)	Co^{2+} and Co^{3+} (mass %)
CoO-1200	CoO	2.72789	-	100 % Co^{2+}
0.5CoAl-1200	only CoAl_2O_4	3.75599	-	100 % Co^{2+}
1.5CoAl-1200	^a $3\text{CoAl}_2\text{O}_4 + 2\text{Co}_3\text{O}_4$	8.66094	76.93717	55.56 % Co^{2+} and 44.44 % Co^{3+}
3.0CoAl-1200	^a $\text{CoAl}_2\text{O}_4 + 5/3\text{Co}_3\text{O}_4$	6.31559	42.9666	44.45 % Co^{2+} and 55.55 % Co^{3+}

^a Solid solution with a spinel structure; ^b magnetic moment; ^c resultant magnetic moment

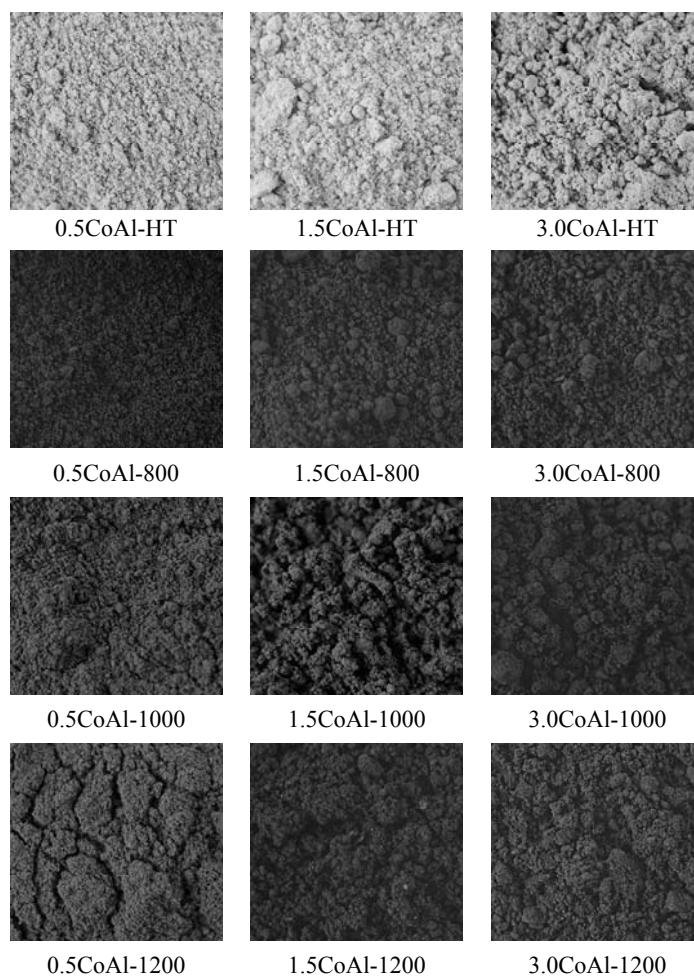


Fig. 5 – The tint of the thermally treated samples at different temperatures.

It may be summarized that the calcination temperature of 1000 or 1200°C and processing time of 2 h used for obtaining of CoAl₂O₄ spinel are significantly lower in comparison to the solid-state reaction method which requires a number of stages, including homogenization of the powder precursors, compaction of the reactants, and finally prolonged heat treatment at considerably elevated temperatures (≥ 24 h and $> 1200^\circ\text{C}$, respectively).⁶ The advantage of the proposed preparation procedures (co-precipitation and calcination of the as-synthesized Co-Al LDH) is that CoAl₂O₄ spinel may be obtained in one step from a single solid precursor rather than a mixture of two or more precursors.

CONCLUSIONS

Three series of Co-Al solids, aimed to be used as ceramic pigments, have been prepared by a controlled thermal treatment of Co-Al layered double hydroxides, synthesized with different molar Co²⁺/Al³⁺ ratios.

The magnetic properties of the calcined solids confirm the phase composition of the samples identified by X-ray diffraction technique. Magnetic measurements prove change the Co²⁺ ions coordination from Oh to Td after calcination above 200°C which is associated with formation of spinel-like mixed oxide Co(Co,Al)₂O₄. Its transformation to the well defined spinel CoAl₂O₄ is complete after calcination at 1000°C as a result of the full reduction by oxidation of the Co³⁺(Oh) ions to Co²⁺(Td) ones.

The color tuning (green, dark green, dark blue, blue or grey) can be controlled by the change of the precursor composition and the temperature of thermal treatment. The precursor sample with the lowest Co content (Co²⁺/Al³⁺ = 0.5) produces intense and bright blue colored CoAl₂O₄ spinel in comparison with the rest of the materials due to the presence only of Co²⁺(Td) ions.

Finally, the Co-Al LDHs represent promising materials for the preparation of nano-sized pre-spinel mixed oxides and well-defined CoAl₂O₄ spinel with wide applications as pigments in ceramic, glass, plastics, rubber and paint industry.

Note: This study is realized in the frame of inter-academic collaboration between Institute of Catalysis, Bulgarian Academy of Sciences, and “Ilie Murgulescu” Institute of Physical Chemistry, Roumanian Academy: “*Nano-sized oxide materials with catalytic and applied character*”.

REFERENCES

1. M. Gabrovska, D. Crişan, N. Stanica, D. Nikolova, L. Bilyarska and R. Edreva-Kardjieva, *Rev. Roum. Chim.*, in press.
2. V. Rives, *Mater. Chem. Phys.*, **2002**, *75*, 19-25.
3. W. Cho and M. Kakihana, *J. Alloys Compd.*, **1999**, *287*, 87-90.
4. W. Lv, Q. Qiu, F. Wang, S. Wei, B. Liu and Z. Luo, *Ultrason. Sonochem.*, **2010**, *17*, 793-801.
5. N. Srisawad, W. Chaitree, O. Mekasuwandumrong, P. Praserttham and J. Panpranot, *J. Nanomat.*, **2012**, Article ID 108369, 8 pages.
6. C. Wang, S. Liu, L. Liu and X. Bai, *Mater. Chem. Phys.*, **2006**, *96*, 361-370.
7. B. Figgis and R. Nyholm, *J. Chem. Soc.*, **1958**, 4190-4216.
8. C. O'Connor, E. Cucauskas, B. Deaver and E. Sinn, *Inorg. Chim. Acta*, **1970**, *32*, 29-32.
9. J.-C. Bünzli, *Inorg. Chim. Acta*, **1979**, *36*, L413-L414.
10. K. Petrov, L. Markov and P. Rachev, *React. Solids*, **1987**, *3*, 67-74.
11. L. Markov, K. Petrov and V. Petkov, *Thermochim. Acta*, **1986**, *106*, 283-292.
12. P. W. Selwood, “Magnetochemistry”, Second Edition, Interscience Publishers, LTD., London, 1956, p. 91.
13. O. Kahn, “Molecular Magnetism”, VCH New York, 1993, p. 355.
14. P. Weiss and W. Klemm, *Z. Anorg. U. Allgem. Chem.*, **1940**, *245*, 288-294.
15. H. Auer, *Z. Physik*, **1934**, *92*, 283-290.
16. A. Walsh, S.-H. Wei, Y. Yan, M. Al-Jassim, J. Turner, M. Woodhouse and B. Parkinson, *Phys. Rev. B*, **2007**, *76*, 165-119.
17. M. Gabrovska, R. Edreva-Kardjieva, K. Tenchev, P. Tzvetkov, A. Spojakina and L. Petrov, *Appl. Catal. A-Gen.*, **2011**, *399*, 242-251.
18. M. Ulibarri, J. Fernández, F. Labajos and V. Rives, *Chem. Mater.*, **1991**, *3*, 626-630.
19. J. Pérez-Ramírez, G. Mul, F. Kapteijn and J. Moulijn, *Mater. Res. Bull.*, **2001**, *36*, 1767-1775.
20. F. Leroux, El Moujahid, C. Taviot-Guého and J.-P. Besse, *Solid State Sci.*, **2001**, *3*, 81-92.
21. M. Taguchi, T. Nakane, K. Hashi, S. Ohki, T. Shimizu, Y. Sakka, A. Matsushita, H. Abe, T. Funazukuri and T. Naka, *Dalton Trans.*, **2013**, *42*, 7167-7176.

