UDC 546

INTERACTION OF COBALT AND MANGANESE NITRATES WITH GRAPHITE UNDER HYDROTHERMAL CONDITIONS

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Received 12.10.2021
Accepted 04.03.2022

Abstract: *The hydrothermal reduction of cobalt and manganese nitrates with graphite in the temperature range of 250-350^{0}C has been investigated to obtain nanosized spinel structures. As a result, $Co_2Mn_3O_8$ and $(Co,Mn)(Co,Mn)_2O_4$ spinel phases with average particle sizes of 42 nm and 66 nm have been obtained depending upon reaction conditions (temperature, reaction time and ratio of reagents).*
The compounds had the following compositions in accordance with the data of energy dispersive analysis (EDA): C-graphite - 86.2%, $Co_2Mn_3O_8$ - 13.8%, and C-graphite - 93.2%; $(Co,Mn)(Co,Mn)_2O_4$ - 4.8%, Mn_3O_4 - 1.6%, Co_3O_4 - 0.5%.
Keywords*: hydrothermal synthesis, oxides, graphite, spinel structures.*
DOI: 10.32737/2221-8688-2022-1-35-39

Introduction

The hydrothermal method is a method of obtaining various chemical compounds and materials (solid-phase substances) based on chemical processes in closed systems that occur in aqueous solutions (as a solvent) at temperatures above 100°C and inder pressures above 1 atmosphere and is one of the most effective methods obtaining single crystals, porous and layered materials, various silicate materials, films and coatings, highly dispersed nanosized powders of metals, their oxides and carbonates [1-3].

The pressure, presence of various reducing agents, temperature, synthesis time, nature of the initial reagents, concentration of the solution, presence of the organic templates, and a number of other parameters [4-6] have their influence on the process of hydrothermal crystallization.

Spinel type structures with a chemical formula of AB_2O_4 (A, B = Ni, Co, Mn, etc.) are widely used in electronics, catalysis, magnetism and energy storage devices. In the crystal structure of AB2O4 spinel, oxygen anions are closely packed in a face-centered cubic configuration with 1/8 tetrahedral sites occupied by the A cation and 1/2 octahedral sites occupied by the B cation. Many types of cations can be inserted into the spinel framework by chemical modification. The cations in A and B sites can have oxidation states of +2 to +3 and +2 to +4, respectively.

Mixed transition metal oxides capable of forming spinel structures are playing an increasingly important role in various applications [7].

Metal nitrates form mixed oxide systems interacting with various reducing agents (ethylene glycol, glycerin, formic acid, etc.) under hydrothermal conditions. Cobalt and manganese oxides are able to form spinel structures.

We have previously studied reactions of cobalt and manganese nitrate with various reducing agents under hydrothermal conditions in order to obtain nanosized spinel structures [8].

It ought to be noted that hydrothermal synthesis is a very complex multifactorial process. Advantages of the hydrothermal

method in comparison with other methods are that it is a one-stage method and it is possible to carry out the reaction in aqueous solutions at temperatures from 100°C-370°C. It also allows producing metastable compounds and metastable phases, provides the possibility of controlling the morphology, particle size and phase composition of the resulting products.

The investigation of the reaction of graphite with various compounds is of interest from the obtaining intercalates standpoint which can be used as lubricants in chemically aggressive media and protectors of aggressive substances [9-12].

In this work, we studied the reaction of metal nitrates with graphite in an aqueous medium and obtained $Co_2Mn_3O_8$ and $(Co,Mn)(Co,Mn)_2O_4$ spinel phases. This system can be used in a variety of applications such as electronics, energy storage devices and medical procedures.

It should be noted that the use of graphite as a reducing agent was carried out for the first time in this work

Experimental part

Synthesis technique:

All used reagents corresponded to the analytical grade. The synthesis was carried out in an autoclave made of stainless steel into which a glass ampoule was inserted. A typical experimental technique is shown below:

Obtaining dicobalttrimanganate (IV) oxide $Co_2Mn_3O_8$:

A glass tube was loaded with 0.72 g of cobalt nitrate $Co(NO_3)_2$, 0.71g of manganese nitrate $Mn(NO_3)_2$, 4g of finely ground graphite and 6 ml of distilled water. The autoclave was placed in an oven and kept at a certain temperature from 250^0C to 350^0C (in different experiments) for 2-12 hours (in different experiments). The resulting precipitate was separated from the reaction solution, washed with water and dried at 70^0C.

Obtaining cobalt manganese oxide $(Co,Mn)(Co,Mn)_2O_4$:

A glass tube was loaded with 0.72 g of cobalt nitrate $Co(NO_3)_2$, 0.71g of manganese nitrate $Mn(NO_3)_2$, 2g of finely ground graphite and 6 ml of distilled water. The autoclave was placed in an oven and kept at a temperature of 270^0 C for 6 hours (in another experiment, it was kept at a temperature of 350^0 C for 3 hours). The resulting precipitate was separated from the reaction solution, washed with water and dried at 70^0C.

The reaction solution was evaporated in vacuum and the residue studied using IR and UV spectrometry. The phase composition, size and configuration of the particles were examined using a Bruker D2 Phaser X-ray diffractometer (Germany); IR spectra and Electronic Absorption Spectra which were recorded on an FT Nicolet-AS10 Spectrometer (USA) and An Evolution 60s Spectrophotometer, respectively.

The particle size was estimated using the Debye equation:

$$D=k\lambda/\beta\cos\theta$$

where D- is the particle diameter, λ -is the wavelength of X-ray radiation, β -is the peak width at half maximum, k- is the Scherrer constant equal to 0.89.

Results and their discussion

Previously, we studied the reactions of cobalt and manganese nitrate with various reducing agents - formic acid, ethylene glycol and glycerol under hydrothermal conditions at temperatures of 180-270^0C. It was of interest to study the conversion of metal nitrates using graphite as a reducing agent.

We have studied the conversion of cobalt and manganese nitrates in the presence of graphite (as a reducing agent) at temperatures of 250-350^0C under hydrothermal conditions.

When using glycols, reductive decomposition of cobalt and manganese nitrates occur through the stages of formation of oxalates, carbonates, and, ultimately, metal oxides. It revealed that the calcination of samples obtained by hydrothermal reduction of a mixture of cobalt and manganese nitrates with

ethylene glycol leads to the formation of nanosized (20-40nm) spinel powders with the composition $(Co,Mn)(Co,Mn)_2O_4$. In most cases, the formation of the (Co,Mn) $(Co,Mn)_2O_4$ phase was observed along with other phases ($CoMn_2O_4$, MnOOH, $MnCO_3$).

The X-ray diffraction measurement of the samples obtained by the reduction of nitrates with finely ground graphite (4g) and 2-ethylene glycol (2g) at a temperature of 250^0C for 6 hours is indicative that 13.8% $Co_2Mn_3O_8$ of dicobalttrimanganese (IV) oxide was obtained. In another experiment, 4g of finely ground graphite was used as a reducing agent without changing the composition of the starting products. In this case, 2.1% $Co_2Mn_3O_8$ of dicobalttrimanganese (IV) oxide was obtained with an average particle size of 42 nm was formed.

It revealed that when the reaction was carried out without a reducing agent (graphite), no changes in the composition of the starting materials of nitrates were observed; i.e. they were not decomposed or restored. In order to obtain nanosized spinel structures, we changed the initial composition and reaction time. The highest yield of the spinel phase $(Co,Mn)(Co,Mn)_2O_4$ (4.8%) with an average particle size of 66 nm -73 nm was observed at a temperature of 270^0C and here, a reaction time of 6 hours (Fig. 1).

In the IR spectrum of graphite after the reaction with cobalt and manganese nitrates, an absorption band was observed at 1694 cm^{-1} which referred to the absorption of the C=O carbonyl group.

The characteristic absorption bands of the benzene ring were observed at ~ 208 and 255 nm in the electronic spectra of reaction solutions (Fig. 2). The band observed at 255 nm contained an electron-vibrational structure which unequivocally, together with the band at 208 nm, revealed the presence of a benzene ring.

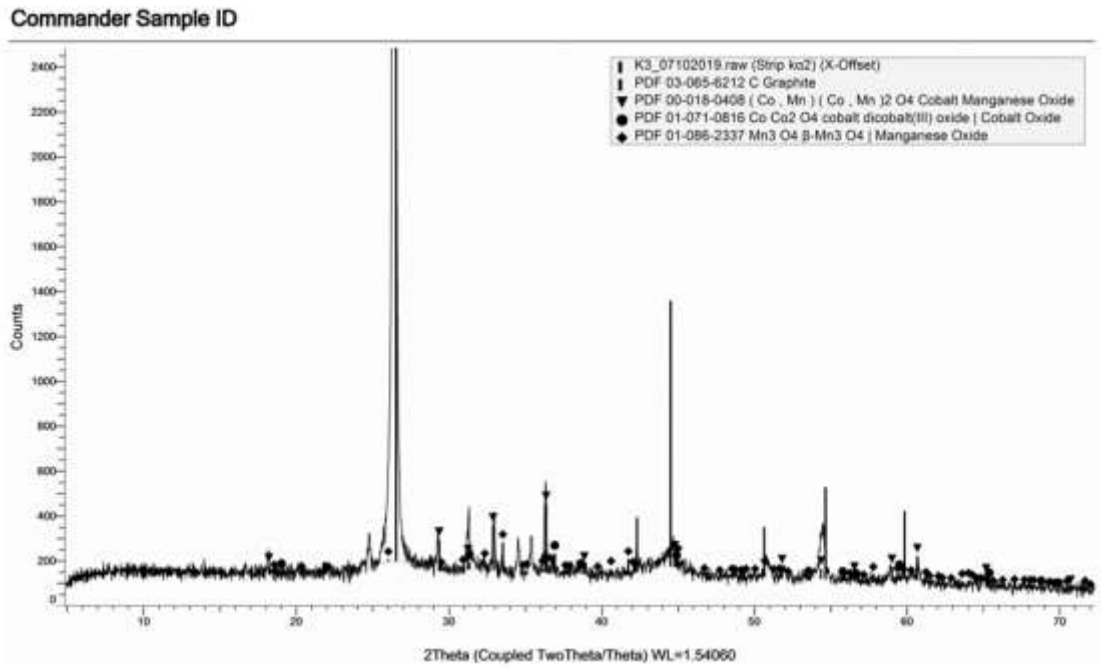

Fig. 1. Diffraction pattern of a sample obtained by hydrothermal conversion of cobalt and manganese nitrates mixture in the presence of graphite at a temperature of 270°C.

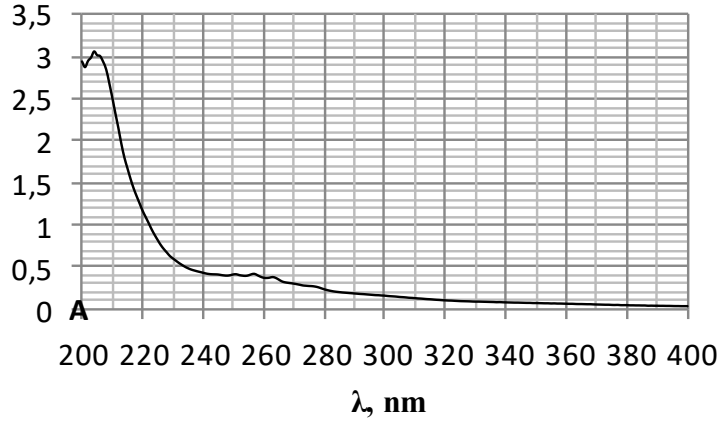

Fig. 2. UV spectrum of a sample obtained by hydrothermal conversion of a mixture of cobalt and manganese nitrates in the presence of graphite at a temperature of 270°C for 6 hours.

Thus, it found that graphite can be used as a reducing agent for cobalt and manganese nitrates under hydrothermal conditions. In this case, spinel phases are formed in the form of $Co_2Mn_3O_8$, $(Co,Mn)(Co,Mn)_2O_4$ with an average particle size of 42-66 nm.

References

1. Hydrothermal processes. Chemical encyclopedia. Vol. 1. Moscow: Soviet encyclopedia Publ., 1988. p. 567.
2. Komarneni S., Li Q., Stefansson K.M., Roy R. Microwave-Hydrothermal Processing for Synthesis of Electroceramic Powders. *J. Mater. Res*. 1993, vol. 8, no. 12, pp. 3176–3183.
3. Meskin P.E., Ivanov V.K., Baranchikov A.E., Churagulov B.R., Tretyakov Yu.D. Ultrasonically assisted hydrothermal synthesis of nanocrystalline ZrO_2, TiO_2, $NiFe_2O_4$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders. *Ultrasonics-Sonochemistry*. 2006, vol. 13, pp. 47–53.
4. Sergev G.B. Nanochemistry. Moscow: Publishing house of Moscow State University, 2003. -288p.
5. Gusev A.I. Nanomaterials, nanostructures, nanotechnologies. Moscow: Fizmtlit Publ., 2005, -416.p.
6. Kolen'ko Yu.V., Burukhin A.A., Churagulov B.R., Olejnikov N.N., Mukhanov V.A. Hydrothermal synthesis of nanocrystalline powders of various crystalline phases of ZrO_2 and TiO_2. *Russian Journal of Inorganic Chemistry* . 2002, vol. 47, no. 11, pp. 1755-1762.
7. Han H., Lee J.S., Ryu J.H., Kim K.M., Jones J.L., Lee J., Guillemet-Fritsch S., Lee H.C., Mhin S. Effect of high cobalt concentration on hopping motion in cobalt manganese spinel oxide (Co_x Mn3– x O_4, x ≥ 2.3). *J. Phys. Chem. C*. 2016, vol. 120, pp. 13667–13674.
8. Javad-zade (Mammadova) A.A., Medzhidov A.A., Yalchyn B., Agaeva S.A., Fatullaeva P.A., Abbasov M.G. Hydrothermal redox synthesis of cobalt-manganese oxide spinels $(Co,Mn)(Co,Mn)_2O_4$. *Chemical problems journal*. 2017, no.1, pp. 59-67.
9. Dyadin Yu.A. Supramolecular Chemistry: Clathrate Compounds. *Soros Educational Journal*. 1998, no. 2, pp. 79–88. (In Russian).
10. Okino F., Touhara H. Graphite and Fullerene Intercalation Compounds. Comprehensive Supramolecular Chemistry / Ed. by J.L. Atwood et al. Oxford: PergamonPress, 1996, vol. 7, pp. 25–76.

11. Serezhkin V.N., Blatov V.A. Coordination numbers of atoms and structure of metals. *Soros Educational Journal*. 1999, no. 8, pp. 35–39. (In Russian).

12. Dyadin Yu.A. Chemistry: Graphite and its inclusion compounds. *Soros Educational Journal.* 2000, vol. 6, no. 10, pp. 43-49.(In Russian).

KOBALT VƏ MANQAN NİTRATLARIN QRAFİTLƏ HİDROTERMAL ŞƏRAİTDƏ REDUKSİYASI

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Xülasə: *Nanoölçülü şpinel quruluşların alınması məqsədi ilə 250-350^{0}C temperatur intervalında kobalt və manqan nitratların qrafitlə hidrotermal reduksiyası araşdırılmışdır. Nəticə olaraq, reaksiyanın aparılma şəraitindən asılı olaraq (temperatur, zaman və reaktivlərin nisbətindən) hissəciyin orta olçüsü 42 – 66 nm olan $Co_2Mn_3O_8$ və $(Co,Mn)(Co,Mn)_2O_4$ şpinel fazaları alınmışdır. Birləşmələr enerji dispersiya analizinin nəticələrinə uyğun olaraq aşağıdakı tərkiblərə malikdir: C-qrafit– 86.2%, $Co_2Mn_3O_8$ – 13,8% və C-qrafit – 93.2% ; $(Co,Mn)(Co,Mn)_2O_4$ – 4.8%, Mn_3O_4- 1.6%, Co_3O_4- 0.5% .*

Açar sözlər: *hidrotermal sintez, oksidlər, qrafit, şpinel quruluşlar.*

ВЗАИМОДЕЙСТВИЕ НИТРАТОВ КОБАЛЬТА И МАРГАНЦА С ГРАФИТОМ В ГИДРОТЕРМАЛЬНЫХ УСЛОВИАХ

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Аннотация: *Исследовано гидротермальное восстановление нитратов кобальта и марганца графитом в интервале температур 250-350^{0}C с целью получения наноразмерных шпинельных структур. В результате, в зависимости от условий проведения реакции (температура, времени и соотношения реагентов) были получены $Co_2Mn_3O_8$ и $(Co,Mn)(Co,Mn)_2O_4$ шпинельные фазы со средними размерами частиц 42нм и 66нм. Соединения в соответствии с данными энергодисперсионного анализа (ЭДА) имели следующие составы: С-графит–86.2%, $Co_2Mn_3O_8$ –13,8% и С-графит – 93.2%; $(Co,Mn)(Co,Mn)_2O_4$– 4.8%, Mn_3O_4- 1.6%, Co_3O_4- 0.5% .*

Ключевые слова: *гидротермальный синтез, оксиды, графит, шпинельные структуры.*