

On preparation of nanocrystalline chromites by co-precipitation and autocombustion methods



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ABSTRACT

We present a comprehensive study on optimization of wet preparation routes yielding well-crystalline spinel chromite, ACr_2O_4 nanoparticles (A=Cu, Fe, Ni, Mn and Mg). The auto-combustion and co-precipitation methods in the presence of nitrate or chloride ions and under different atmospheres, followed by annealing of final products at different temperatures were tested. All samples were characterized by powder X-ray diffraction (PXRD) and vibrational spectroscopy in order to evaluate their phase composition, particle size and micro-strain. Selected samples were subjected to investigation by transmission electron microscopy (TEM). The degree of the particle crystallinity was estimated by relating the apparent crystallite size obtained from the PXRD analysis to the physical grain size observed by the TEM. Optimal conditions leading to single-phase and highly-crystalline chromite nanoparticles are proposed.

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1. Introduction

The spinel chromites attracted considerable interest due to their interesting physical and chemical properties. The chromites have been already used as smart coatings, resistant materials or functional components of various types of sensors. They were successfully utilized as high-temperature ceramics [1], high emissivity and spectrally selective paints [2,3], or coatings in light water nuclear reactors [4]. Their sensing performance has been used in high-pressure and humidity sensors [1,5] and monitoring of toxic and harmful gases [6–8]. Recently, outstanding catalytic efficiency of the transition metal chromites has been also reported [9–12]. The physical properties of the spinel chromites are strongly dependent on the cation stiffness and distribution within the tetrahedral and octahedral sites in the spinel lattice [13].

Consequently, the transition metal chromites span an enormous range of magnetic exchange strengths in competition with geometrical frustration resulting in variety of magnetic ground states and complex magnetic phase diagrams [14–20]. In CoCr_2O_4 , FeCr_2O_4 and CuCr_2O_4 compounds, the interaction between spin and lattice degrees of freedom also originates considerable magnetoelastic

effects [21] and ground state degeneracy in frustrated magnetic state [22]. On the other hand, in the highly frustrated antiferromagnets [23] the spin–spin interaction can play an essential role in the long-range magnetic order. Such a phenomenon is typical for the spinels with nonmagnetic A-site ions (Zn^{2+} , Mg^{2+}) and it is referred as the spin Jahn–Teller effect [22,24,25] – being analogous to the ordinary Jahn–Teller effect where the orbital degeneracy of an ion is lifted by the lowering of the crystal symmetry.

The competition between the single-cluster Jahn–Teller distortion and spin–orbit coupling in FeCr_2O_4 results in smaller impact on the magnetic interaction and structural transition from tetragonal to orthorhombic system [26,27]. On the other hand, the CuCr_2O_4 exhibits a tetragonally distorted spinel structure at ambient conditions and the distortion is related to the cooperative Jahn–Teller effect of Cu^{2+} at the tetrahedral sites [28]. Complex scenario of Jahn–Teller driven symmetry lowering from cubic to tetragonal and additional symmetry lowering to orthorhombic coinciding with onset of long-range ferrimagnetic order has been reported for NiCr_2O_4 [29–32]. Most of the 3d transition metal chromites exhibit ferroelectric order with coupling of the spontaneous polarization and magnetization [29,33,34].

The spinel chromites can be rather easily obtained either by solid-state or wet techniques with subsequent thermal treatment. The most widely used method for the preparation of spinels involves solid-state reactions of mechanically mixed metal oxides

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at high temperatures [35], high-temperatures solid-state reaction [36], micro-emulsion method [15], solution method [37], spray pyrolysis [38], solid-state microwave metathesis [39], air plasma spraying [2] and aerosol synthesis [40]. The Pechini method and its modifications, based on polymeric precursors, can be used to prepare spinels without requirement of high temperature calcinations and permits good stoichiometric control [3,41]. Recently, alcoxide-free sol-gel method and in situ reduction route were proposed for preparation of the Cu and Co chromites [10,42].

The motivation of our work was to develop user-friendly wet routes yielding sufficient amount of nanocrystalline powders of several spinel chromites. We focused on modification of auto-combustion and co-precipitation techniques carried out with different precursors. The obtained products were subjected to additional heat treatment, which ensured formation of well-developed crystallites of the spinel phase. The goal of the work was to find the most appropriate conditions leading to stabilization of the single chromite phase in fine powders, with regard on the high nanoparticle crystallinity as required for specific applications. Detailed investigation of the content of impurity binary phases was also carried out. The prepared samples were thoroughly analysed by powder X-ray diffraction (PXRD) considering micro-strain PXRD line broadening, particle size was determined. The obtained results were corroborated by the measurements and careful analysis of vibrational spectroscopy – Fourier transforms infrared spectroscopy and Raman spectroscopy [1,43–45]. The samples were also investigated by transmission electron microscopy (TEM), which enabled correlation of the apparent crystallite size (determined by the PXRD) to the physical size observed by the TEM.

2. Materials and methods

2.1. Methods of preparation

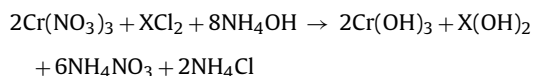
The nanocrystalline chromite powders were prepared by two different methods – co-precipitation and auto-combustion. Different precursors (nitrates or chlorides) were used in both methods. The final products were annealed at several temperatures ranging from 600 to 1000 °C in order to find the optimum conditions for preparation of single-phase samples. The temperature treatment also served for adjusting the particle size and improving the degree of crystallinity.

2.1.1. Co-precipitation method

Two variants of the co-precipitation methods were used; based either on mixture of chlorides and nitrates or chlorides only. The aqueous solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, 99%) in the case of nitrate-chloride method or $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, p.a.) in the case of chloride method were mixed together with the XCl_2 (Penta, p.a.) where X = Mg, Fe, Mn in molar ratio of 2:1.

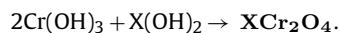
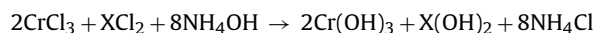
The ammonium hydroxide (Penta, p.a., aqueous solution 25–29%) was dropped slowly into the prepared solution kept under continuous stirring. The precipitate was created according to given reaction schemes:

(a) Nitrate-chloride co-precipitation method:



(where X = Mg, Fe, Mn)

(b) Chloride co-precipitation method:

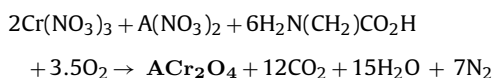


The obtained precipitate was washed by distilled water for several times, separated by centrifugation and dried in the evaporator. In the case of MgCr_2O_4 , the powder was annealed at 600–900 °C in air for 2 h. The powders of FeCr_2O_4 and MnCr_2O_4 were first preheated at 800 °C in air for 2 h. Thereafter, they were calcinated at 800 °C and 900 °C (10 °C/min up to 800 °C and then 1 °C/min up to 900 °C) and kept at these temperatures under reducing atmosphere (7.5% H_2 :92.5% Ar or 10% H_2 :90% N_2) for additional 2 h.

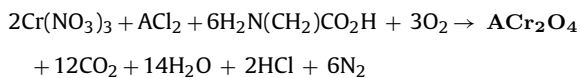
2.1.2. Auto-combustion method

Three different reaction precursors were used in the auto-combustion method.

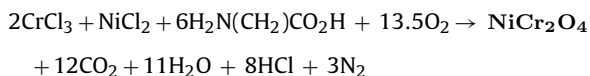
(a) Nitrate auto-combustion method – The aqueous solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, 99%) was mixed together with the $\text{A}(\text{NO}_3)_2$ (Penta, p.a.) where A = Cu, Ni in molar ratio of 2:1 together with glycine (Lach-Ner, p.a.):



(b) Nitrate-chloride auto-combustion method – The aqueous solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, 99%) was mixed together with the $\text{A}(\text{NO}_3)_2$ (Penta, p.a.) where A = Mn, Fe in molar ratio of 2:1, together with glycine (Lach-Ner, p.a.):



(c) Chloride auto-combustion method – The aqueous solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, p.a.) was mixed together with the NiCl_2 (Sigma-Aldrich, 98%) in molar ratio of 2:1, together with glycine (Lach-Ner, p.a.):



The molar ratio of glycine to the metal cations was fixed as 1:2 in all processes.

The resulting solutions were ignited by rapid heating up to 200 °C under continuous stirring. The vigorous fumes of CO_2 and nitrogen formed during the ignition. Resulting products consisted of mixture of oxide phases, therefore; further calcination was necessary to reach the target ternary products. The powders of FeCr_2O_4 and MnCr_2O_4 were preheated at 800 °C with step of 1 °C/min under air atmosphere for 2 h. Afterwards, the samples were calcinated at 800 and 900 °C (10 °C/min up to 800 °C and then 1 °C/min up to 900 °C) and kept at these temperatures for 2 h under reducing atmosphere (7.5% H_2 :92.5% Ar or 10% H_2 :90% N_2).

The samples were labelled according to the preparation method as **A.m.T.pa**, containing the abbreviations of the metal (**A**), method of preparation (**m**), annealing temperature (**T**), precursor (**p**) and annealing atmosphere (**a**) (listed in Table 1). Then **A** = Cu, Fe, Ni, Mn or Mg, **m** represents either the shortcut for auto-combustion, A or co-precipitation, C method. **T** is the annealing temperature in °C (600, 700, 800, 900 or 1000). **p** and **a** are enumerated with numbers and letters as: 1 – nitrate/nitrate (NO_3/NO_3) precursor, 2

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