X-ray powder diffraction data for a new nickel zinc chromate, $(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$

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A new nickel zinc chromate with the composition of $(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$ was synthesized by hydrothermal method. The compound was characterized by XRD, TGA, and XRF. X-ray powder diffraction data show that the crystal system of the title compound is hexagonal with space group $R\text{-}3m$, $z=3$, and unit-cell parameters: $a=5.9794$ and $c=21.4875$ Å. © *2010 International Centre for Diffraction Data.* [DOI: 10.1154/1.3505334]

Key words: nickel zinc chromate, hydrothermal synthesis, XRD, XRF, TGA

I. INTRODUCTION

Chromium oxides are widely used as catalysts in industrial reactions, such as ammonia synthesis (Jennings, 1991), and have been researched as catalysts in many reactions, such as alkanes dehydrogenation (Weckhuysen and Schoonheydt, 1999), VOC elimination (Sinha and Suzuki 2007), nitric oxide reduction, and carbon monoxide oxidation (Stegenga *et al.*, 1993) among others. Chromium oxides have usually been supported in porous solids with high surface areas to improve its catalytic properties. On the other hand, NiO-ZnO catalysts have showed excellent catalytic properties because of their physical-chemical properties. Therefore, the development of new materials that include in their structure, chromium, combined with other transition metals, such as zinc and nickel, would allow obtaining catalysts with interesting properties. In this work, we report the synthesis and crystallographic details of a new trimetallic nickel zinc chromate, $(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$.

II. EXPERIMENTAL

The new material was synthesized from three aqueous solutions of CrO_3, $NiCl_2 \cdot 6H_2O$, and $Zn(NO_3)_2 \cdot 4H_2O$. These three solutions were first prepared separately; then, they were mixed to obtain a new solution containing three metallic cations and thereafter added dropwise NH_4OH. An orange gel with molar composition $CrO_3 : NH_4OH : NiCl_2 : Zn(NO_3)_2 : 170H_2O$ was formed and homogenized for 30 min with final pH=6. This gel was heated at 100 °C for 24 h in a Teflon-line autoclave. An orange solid was recovered by filtration, washed, and dried at 100 °C.

A TA Instrument, TGA 2950, was used for thermal gravimetric analysis (TGA). The analysis was carried out in nitrogen atmosphere and at a heating rate of 10°/min. An X-ray fluorescence (XRF) spectrometer, PHILIPS MAGIX PRO PW2400, was used for elemental analysis of Zn, Ni, and Cr. Powder X-ray data were collected at room temperature using a Bruker D8-Advance diffractometer equipped with a 3 kW KRISTALLOFLEX X-ray generator K 760-80F and a Göebel mirror. Other XRD experimental conditions were 40 kV, 40 mA, Cu $K\alpha_1$ ($\lambda=1.5406$ Å), 5°–90° 2θ range, 0.015° 2θ step size, and 30 s/step.

The values of 2θ of the observed diffraction peaks were determined using a subroutine incorporated in EXPO 2009 (Altomare *et al.*, 2009), subject to default conditions and individual inspection. The crystal system and unit-cell parameters were determined using the indexing program TREOR09 incorporated in EXPO 2009. The CHEKCELL program (Laugier and Bochu, 2000) was also used to check and to obtain the space group and the final calculated values of unit-cell parameters.

III. RESULTS AND DISCUSSION

The experimental results obtained by XRF and TGA confirm that the chemical formula of the orange solid is $(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$ with a formula weight of 525.97. The theoretical and experimental concentrations for the title compound are listed in Table I. The TGA curve shown in Figure 1 reveals that there are two thermal events occurred between 0 and 800 °C. The first event, which occurred between 250 and 400 °C, was caused by a combined evolution of water and ammonia with a weight loss of 16%. The second event, which occurred between 400 and 600 °C, was caused by a recrystallization process and subsequent oxide formation with a weight loss of 3.5%. The entire thermal transformation of the material can be expressed by the following chemical equation:

TABLE I. Elemental concentrations for $(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$.

Metal	Theoretical concentration (%)	Experimental concentration[a] (%)
Zn	25	27.0
Ni	11.2	13
Cr	20	23
H_2O and NH_3	15.2	16.5

[a]Values of the experimental concentration of Zn, Ni, and Cr were determined by XRF and H_2O and NH_3 by TGA.

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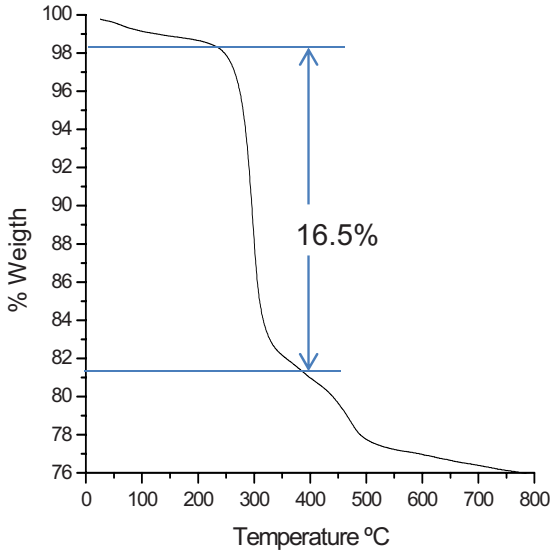

Figure 1. (Color online) Thermogravimetrical results for $(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$.

$$(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O \rightarrow 0.5NiCr_2O_4 + 0.5ZnCr_2O_4 + 0.5NiO + 1.5ZnO + 1.5NH_3 + 3.5H_2O + 1.5O_2.$$

After several cycles of calculation in EXPO 2009, the powder diffraction pattern was successfully indexed with a hexagonal lattice with the space group R-3m. The final unit-cell parameters are a=5.9794 and c=21.4876 Å. The experimental density (D_{exp}) was measured in laboratory using the procedure used to measure the properties of crystals (Stout and Jensen, 1989). Crystallographic and XRD data are reported in Table II. Figure 2 shows the observed and calculated patterns as well as the difference curve obtained from EXPO 2009.

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TABLE II. XRD data for $(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$.

$(NH_4O_H)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$ Radiation: Cu $K\alpha_1$ Hexagonal system a=5.9794 and c=21.4876 Å D_{exp}=3.62				H 11.5, O 12.5, N 1.5, Ni 1, Zn 2, Cr 2 Wavelength: 1.5406 Å Space group: R-3m Z=3 D_{cal}=3.9			
$2\theta_{obs}$	d_{obs}	$2\theta_{cal}$	d_{cal}	I	h	k	l
12.3495	7.1615	12.3477	7.1625	100.000	0	0	3
17.5860	5.0391	17.6032	5.0342	2.920	1	0	1
23.8396	3.7295	23.8482	3.7282	12.353	1	0	4
24.8305	3.5829	24.8418	3.5813	1.269	0	0	6
26.9294	3.3082	26.9392	3.3070	23.160	0	1	5
29.8552	2.9903	29.8615	2.9897	3.453	1	1	0
32.4182	2.7595	32.4244	2.7590	3.828	1	1	3
33.9180	2.6408	33.9216	2.6406	7.538	1	0	7
34.8912	2.5694	34.8746	2.5706	5.396	0	2	1
35.6562	2.5160	35.6400	2.5171	1.544	2	0	2
37.6838	2.3851	37.6977	2.3843	5.345	0	1	8
38.5681	2.3325	38.5696	2.3324	3.410	0	2	4
39.2416	2.2940	39.2219	2.2951	2.069	1	1	6
40.6670	2.2168	40.6486	2.2177	0.563	2	0	5
45.7818	1.9803	45.8105	1.9791	3.995	0	2	7
48.7563	1.8662	48.7732	1.8656	2.654	1	1	9
49.5175	1.8393	49.5275	1.8390	1.717	2	1	4
49.8463	1.8279	49.8535	1.8277	0.931	0	1	11
50.9135	1.7921	50.9584	1.7906	8.975	0	0	12
51.2252	1.7819	51.2480	1.7812	0.634	1	2	5
55.5180	1.6539	55.5317	1.6535	4.087	0	2	10
58.5727	1.5747	58.5757	1.5746	1.201	1	0	13
59.1784	1.5600	59.2045	1.5594	5.946	2	0	11
62.0713	1.4941	62.0353	1.4948	2.684	2	2	0
63.5705	1.4624	63.5258	1.4633	1.059	2	2	3
67.1553	1.3928	67.1324	1.3932	1.663	0	2	13
68.8826	1.3620	68.8743	1.3621	1.180	3	1	5
71.3559	1.3208	71.3850	1.3203	1.539	2	0	14
72.6008	1.3011	72.6187	1.3009	1.058	1	3	7
72.7663	1.2986	72.6769	1.3000	0.604	1	0	16
73.1564	1.2926	73.1820	1.2922	2.613	4	0	1

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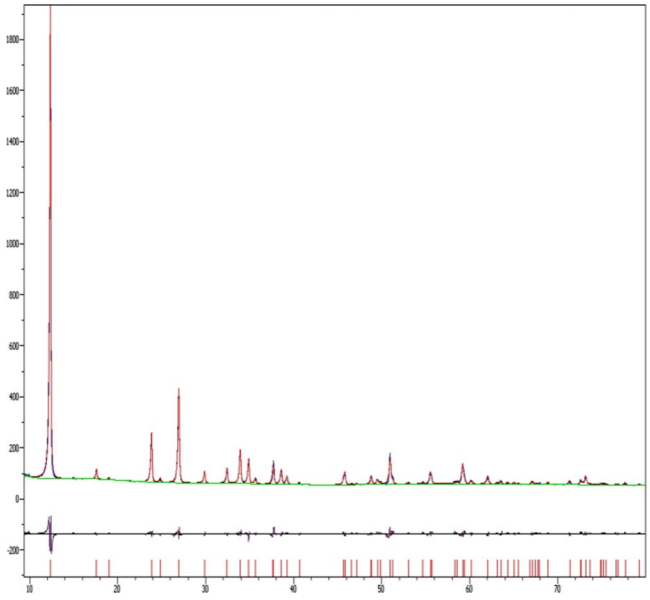

Figure 2. (Color online) X-ray powder diffraction patterns for $(NH_4OH)_{3/2}NiZn_2Cr_2O_9 \cdot 2H_2O$.

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