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Solution process for the synthesis of the "high-pressure" phase $CoMoO_4$ and X-ray single crystal resolution

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A mild solution method was developed to grow single crystals of $CoMoO_4$-II. The structure was solved by single crystal X-ray diffraction [$P2/c$, $a = 4.6598(7)$ Å, $b = 5.6862(9)$ Å, $c = 4.9159(7)$ Å, $\beta = 90.521(3)^\circ$, $V = 130.25(3)$ Å^3] from 349 unique reflections [$I \geqslant 2\sigma(I)$], $R_1 = 0.0270$ and $wR_2 = 0.066$. $CoMoO_4$-II was characterised by scanning electron microscopy and its magnetic properties investigated.

1. Introduction

Since the 1960s, a great deal of research has focussed on the preparation of divalent transition-metal molybdates because of their catalytic and magnetic properties.[1,2] $MMoO_4$ compounds from almost every first-row transition metal have been synthesised, usually using solid-state reactions at high temperature.[3–5] Cobalt molybdate oxides present two atmospheric-pressure phases: α-$CoMoO_4$ and β-$CoMoO_4$ (high temperature phase, 700 °C), and one $CoMoO_4$-II obtained by applying high pressure (50 000 bars) on pre-synthesised α-$CoMoO_4$ at 600 °C. This compound, well described by Ehrenberg *et al.*, presents some interesting antiferromagnetic properties but its synthesis requires a complicated and expensive set-up.[6,7] This paper deals with a new synthetic route to obtain $CoMoO_4$-II: a solution process without complicated apparatus that for the first time permits the isolation of single crystals. Since small structural changes and degree of crystal perfection can influence electronic properties, it was of interest to study the magnetic properties of $CoMoO_4$-II obtained under mild conditions.

2. Experimental

2.1. Materials and methods

X-Ray powder diffraction data were collected on a Siemens D5000 diffractometer with Cu-Kα radiation and X-ray single crystal data on a Siemens SMART three-circle diffractometer with Mo-Kα radiation. All the reagents were purchased from Aldrich Chemicals and used as supplied. Scanning electron micrographs (SEM) were performed on a JEOL 5800 LV.

2.2. Syntheses of $CoMO_4$

Hydrothermal reactions were carried out in 23 ml Parr acid digestion bombs under autogenous pressure (∼20 bars). A mixture of cobalt(II) chloride hexahydrate (2 mmol, 0.47 g), Na_2MoO_4 (2 mmol, 0.48 g), succinic acid (4 mmol, 0.47 g), potassium hydroxide (2 mmol, 0.15 g) and H_2O (5 ml) was sealed in the Teflon-lined autoclave and heated in a furnace at 200 °C for three days. After cooling at room temperature, the solid product was recovered by filtration, and identified by powder X-ray diffraction as the "high-pressure" phase $CoMoO_4$-II,[6] which corresponds to a unique homogeneous phase constituted of black metallic-like block-shape crystals. One single crystal was used for structure determination by X-ray diffraction. The reaction yield (based on cobalt or molybdenum) is 77%. Same quality crystals can be obtained using hydrochloric acid instead of succinic acid. An initial mixture of $CoCl_2\cdot 6H_2O$ (2 mmol, 0.47 g), Na_2MoO_4 (2 mmol, 0.48 g), HCl (6.5 mmol) and H_2O (5 ml) gives $CoMoO_4$-II with 85% reaction yield.

2.3. Single crystal structure determination

A black crystal, 0.08 × 0.04 × 0.02 mm^3, was glued to a glass fibre. Intensity data were collected at room temperature with a Siemens SMART diffractometer equipped with a CCD two-dimensional detector [λ(Mo-Kα) = 0.71073 Å]. Intensity data were collected in 1271 frames with ω scans (width of 0.30° and exposure time, 30 s per frame). A summary of crystal data is presented in Table 1. The unit-cell parameters are similar to those of the corresponding $CoMoO_4$-II synthesised in a solid-state reaction.[6] Data reduction was performed with the SAINT software and absorption corrections using SADABS program.[8] The structure was solved by direct methods and refined by full matrix least squares, based on F^2, using the SHELX-TL software package.[9] All atoms were refined anisotropically. Number of variables, 30; final $R(F) = 0.0270$, $wR(F^2) = 0.0660$; GOF 1.050; minimum and maximum peak in difference

Table 1 Summary of crystal data and structure refinement for $CoMoO_4$-II

Empirical formula	$CoMoO_4$
Formula weight	218.87
Crystal system, space group	Monoclinic, $P2/c$
a/Å	4.6598(7)
b/Å	5.6862(9)
c/Å	4.9159(7)
β/°	90.521(3)
Volume/Å^3, Z	130.25(3), 2
Calculated density/g cm^{-3}	5.581
Absorption coefficient/mm^{-1}	10.964
F(000)	202
θ range for data collection degrees	3.58 to 29.85
Limiting indices	$-6 \leqslant h \leqslant 5$, $-7 \leqslant k \leqslant 6$, $-6 \leqslant l \leqslant 6$
Reflections collected	893
Independent reflections	349 [R(int) = 0.0244]
Data, restraints, parameters	349, 0, 30
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0270$, $wR2 = 0.0660$
R indices all data	$R1 = 0.0329$, $wR2 = 0.0687$
Largest diff. peak and hole/eÅ^{-3}	1.371 and −1.243

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Table 2 Atomic coordinates ($\times$ 10^4) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) for $CoMoO_4$. *U*(eq) is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

	x	*y*	*z*	*U*(eq)
Mo	0	1850(1)	2500	7(1)
Co	5000	6734(1)	2500	9(1)
O(1)	2179(6)	−1072(6)	646(6)	10(1)
O(2)	2551(6)	3772(5)	1021(6)	10(1)

Table 3 Bond lengths [Å] and angles [deg] for $CoMoO_4$

Mo–O(2)	1.775(3)	Co–O(1)^{d}	2.023(3)
Mo–O(1)^{b}	1.895(3)	Co–O(2)^{f}	2.101(3)
Mo–O(1)	2.154(3)	Co–O(2)	2.157(3)
O(1)^{b}–Mo–O(1)^{c}	153.0(2)	O(1)^{d}–Co–O(1)^{e}	103.9(2)
O(1)^{b}–Mo–O(1)^{a}	74.1(2)	O(1)^{d}–Co–O(2)^{f}	93.9(2)
O(1)^{c}–Mo–O(1)^{a}	85.1(1)	O(1)^{e}–Co–O(2)^{f}	95.7(2)
O(1)^{a}–Mo–O(1)	79.0(2)	O(2)^{f}–Co–O(2)^{g}	164.3(2)
O(2)^{a}–Mo–O(1)^{b}	99.5(2)	O(1)^{d}–Co–O(2)	166.6(2)
O(2)–Mo–O(1)^{b}	97.0(2)	O(1)^{e}–Co–O(2)	89.4(2)
O(2)–Mo–O(1)^{a}	165.5(2)	O(2)^{f}–Co–O(2)	83.2(1)
O(2)–Mo–O(1)	88.9(2)	O(2)^{g}–Co–O(2)	84.5(2)
O(2)^{a}–Mo–O(2)	104.0(2)	O(2)–Co–O(2)^{h}	77.3(2)
Mo^{c}–O(1)–Co^{i}	124.4(2)	Mo–O(2)–Co^{g}	128.6(2)
Mo^{c}–O(1)–Mo	105.9(2)	Mo–O(2)–Co	134.2(2)
Co^{i}–O(1)–Mo	126.3(2)	Co^{g}–O(2)–Co	95.4(2)

Symmetry transformations used to generate equivalent atoms: $^{a}-x,y,-z+$. $^{b}x,-y,z+$. $^{c}-x,-y,-z$. $^{d}-x+1,y+1,-z+$. $^{e}x,y+1,z$. $^{g}x,-y+1,z+$. $^{g}-x+1,-y+1,-z$. $^{h}-x+1,y,-z+$. $^{i}x,y-1,z$.

electron density map 1.37 and −1.24 eÅ^{-3}. Fractional atomic co-ordinates are given in Table 2 and selected bonds distances in Table 3.†

3. Discussion

Solution processes such as sol–gel methods or hydrothermal techniques are nowadays an unavoidable alternative in metal oxide syntheses. This is for three major reasons: it permits a better chemical homogeneity, it is less energy consuming and it often allows control of morphology and of the size of crystallites. What is particularly noteworthy for us about soft solution processes, is the possible co-existence of organic and inorganic reactants that allows formation of hybrids derived from dense metal oxide phases.[10] We began to study cobalt–molybdate phases from solution, with the initial aim of preparing organic–inorganic hybrids.[11,12] Heating at 200 °C an aqueous solution of cobalt(II), molybdate and succinic acid (deprotonated by potassium hydroxide) doesn't lead to the formation of a hybrid phase but to the dense metal oxide compound $CoMoO_4$-II. Black single crystals were isolated as a single phase after three days under hydrothermal conditions. $CoMoO_4$-II is traditionally produced from α-$CoMoO_4$ (previously obtained at 1200 °C) in a gold container and heated at 600 °C at high pressure (50 000 bars). Therefore, it was of interest to optimise the mild synthetic procedure in order to obtain a perfectly pure and well-crystallised product. Good quality crystals were obtained with a molar ratio of 1 : 1 : 2 : 1 : 60 for cobalt, molybdate, succinic acid, potassium hydroxide and water. However, either hydrochloric acid or succinic acid can be used, the important parameters being a 1 : 1 metallic ratio (Co–Mo), and the pH of the initial mixture (pH $\approx$ 3; Co–acid ratio of 1 : 6.5). In agreement with the XRD powder, the SEM observation (Fig. 1) of the product shows a single phase. Crystallites have a regular plate-like morphology with an average size of approximately 80 × 40 × 15 μm. By decreasing the reaction temperature to 180 °C, the same phase is obtained but black crystallites are a bit smaller and present a spearhead morphology. At 150 °C, an unidentified compound with a 1 : 1 cobalt : molybdenum ratio is obtained that could correspond to a hydrated $CoMoO_4$ phase.[2]

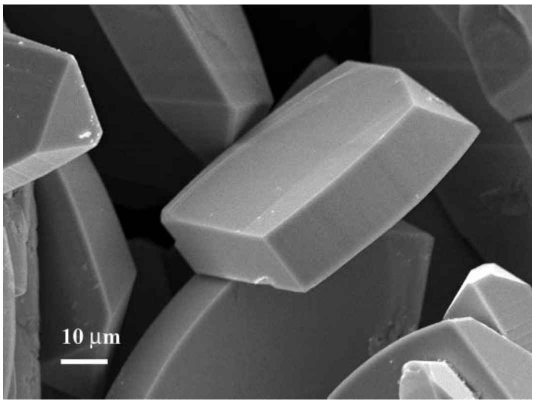

Fig. 1 SEM photographs of $CoMoO_4$-II.

Structure solution was successfully performed by single-crystal X-ray diffraction and confirms the topology previously described by Ehrenberg *et al.* from powder diffraction. The structure derives from the wolframite structure, $NiWO_4$. Both molybdenum and cobalt atoms are located on a two-fold axis and the two oxygens in general positions (Table 2). The two metal atoms are octahedrally co-ordinated: molybdenum with a slightly distorted environment (Mo–O bonds from 1.775(3) to 2.154(3) Å) and cobalt with a regular one (Co–O bonds from 2.023(3) to 2.157(3) Å) (Table 3). Fig. 2 shows a view of the structure along the *a* axis, and illustrates how the solid is constructed from chains of edge-sharing $\{CoO_6\}$ and $\{MoO_6\}$ octahedra. Valence sum calculations, based on the bond-valence method,[13] give values of 5.94, 2.05, 1.84 and 2.04 for molybdenum, cobalt, O(1) and O(2) atoms respectively. Those values are in agreement with the presence of diamagnetic Mo(VI) and magnetic d^7 Co(II). Therefore, the structure may be described as an alternation of magnetic zigzag chains with diamagnetic ones (Fig. 2).

Magnetic properties of $CoMoO_4$-II are known. Previous work, on powders synthesised at high pressure and high temperature, reports an antiferromagnetic behaviour.[6] We studied the magnetic characteristics of our sample in order to see if differences in synthetic conditions [200 °C instead of 600 °C and few bars ($\sim$20 bars) instead of 50000 bars] have an influence on macroscopic magnetic properties. Magnetisation

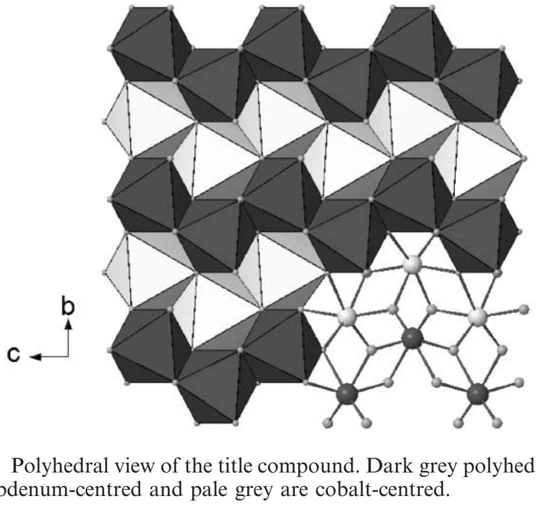

Fig. 2 Polyhedral view of the title compound. Dark grey polyhedra are molybdenum-centred and pale grey are cobalt-centred.

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†CCDC reference number 175187. See http://www.rsc.org/suppdata/jm/b1/b110760g/ for crystallographic files in .cif or other electronic format.

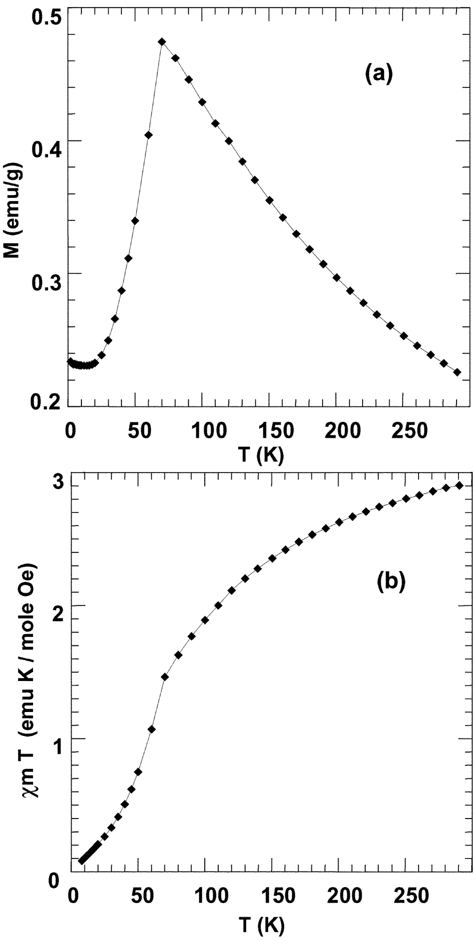

Fig. 3 Fitting of (a) the temperature dependence of magnetisation and (b) $\chi_{\mathrm{m}}T$ *vs.* T for crushed crystals of $CoMoO_4$-II.

was measured in the temperature range between 4 K and 290 K using a SQUID (Quantum Design) magnetometer with a 5 kG field strength. Temperature dependencies of the magnetisation and the $\chi_{\mathrm{m}}T$ product are shown in Fig. 3. As previously described by Wiesmann *et al.*,[6] antiferromagnetic ordering is observed below 68 K. At higher temperatures $CoMoO_4$-II began to follow the Curie–Weiss law. The curve fit between 180 and 290 K gives $C = 3.7$ emu mol^{-1} and $\theta = -87$ K. These values lead to an effective magnetic moment of $\mu(\mathrm{Co}^{2+}) = 5.4\mu_{\mathrm{B}}$, which corresponds to the previously observed value. However, as is noticeable on the $\chi_{\mathrm{m}}T = \mathrm{f}(T)$ curve, it would be necessary to perform magnetisation measurements above ambient temperature ($T > 300$ °C) to have a perfect linear fit of the Curie–Weiss law. The main difference with previous work occurs at low temperature: for our measurements on crushed crystals, magnetisation between 4 and 20 K is more or less constant whereas for powder an important increase appears below 20 K. No structural explanation is given for this increase, and it has therefore to be attributed to the presence of either impurities or defects in the powder particles.

4. Conclusion

In summary, a hydrothermal method for growing single crystals of $CoMoO_4$-II under mild conditions is presented. The product is a single phase constituted of homogeneously shaped crystals. Compared to conventional high temperature (and pressure) processing, solution synthesis circumvents many of the problems associated with diffusion in solids (defects), since it offers a homogeneous composition of the reactants. This leads to the formation of multi-component oxides at lower temperatures and the possible growth of pure single crystals due to the slow crystallisation process. This technique can certainly be adapted for other mixed metal oxides.[4]

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