Crystal structure of digadolinium tricarbomolybdate(III), $Gd_2[Mo_2C_3]$

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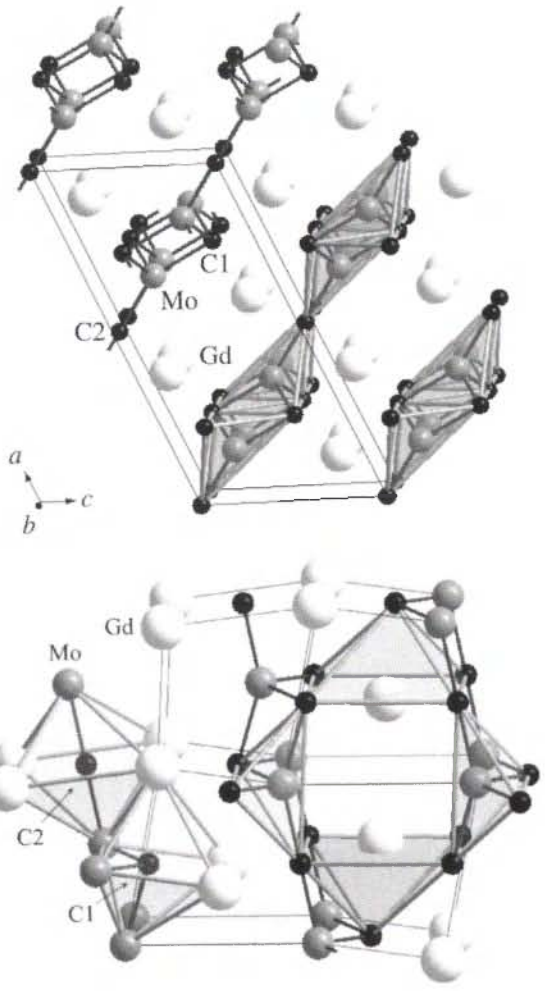

Abstract

$C_3Gd_2Mo_2$, monoclinic, $C12/m1$ (no. 12), $a = 11.870(2)$ Å, $b = 3.3575(6)$ Å, $c = 5.756(1)$ Å, $\beta = 113.11(1)°$, $V = 211.0$ Å^3, $Z = 2$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.090$, $T = 293$ K.

Source of material

Dark gray, platy single crystals of the title compound have been obtained by a two-step high temperature synthesis. Cold-pressed pellets of a mixture of the elements in stoichiometric amounts (Gd, 99.9 %; Mo, 99.9 %; graphite C, 99.9 %) were arc-melted under argon atmosphere and subsequently annealed at 1723 K for 72 h in a tube furnace (Lora 1800, HTM-Reetz GmbH) with permanent flushing of the heater room with argon. Finally, the sample was cooled down to room temperature with a rate of 150 K/h. Metallographic examination of the microstructure in combination with EDXS (1:0.93 Mo/Gd) and powder X-ray diffraction (Huber G670, with Ge monochromator, CuKα_1 radiation) reveal the title compound as the majority phase together with traces of Mo_2C (< 2 %). Since the bulk material is sensitive against air and moisture all handling was done in a glove box and the single crystal was mounted in an argon-filled Lindemann capillary.

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Experimental details

The cell parameters were determined from the least-squares refinement of the 2θ values of 24 reflections in the range $10° < 2\theta < 85°$ using LaB_6 powder SRM 660a as an internal standard.

Discussion

Recently, we have introduced criteria for carbometalates by extending the concept of complex anions from fluoro-, oxo-, nitrido- to carbometalates [1]. In case of the general formula $RE_2[T_2C_3]$ with RE = rare earth metal and T = transition metal three different crystal structure types containing polyanions $[(T_2C_3)^{6-}]$ as well as RE^{3+} cations are known: $Ho_2[Cr_2C_3]$ [2], $Er_2[Mo_2C_3]$ [3] and $Pr_2[Mo_2C_3]$ [4]. The polyanions are built from distorted TC_4-tetrahedra with the carbo-ligands covalently bonded to the transition metals of low oxidation state.

The title compound crystallizes in the $Er_2[Mo_2C_3]$ structure type [3] and consists of stacked $^2_\infty[(Mo_2C_3)^{6-}]$ layers with Gd^{3+} cations in between (figure, top). The polyanion forms infinite chains via edge (C1···C1) sharing of distorted MoC_4 tetrahedra, which are vertex-connected via the remaining two apices (C2) to form 2D layers with interatomic distances: d(Mo—C1) = 1 × 2.093(9) Å, 1 × 2.156(1) Å and d(Mo—C2) = 2 × 2.065(1) Å. The metal atoms form a distorted bcc arrangement with d(Mo—Mo) = 2.862(2) Å, d(Mo—Gd) = 3.198(1) Å, 3.213(1) Å, 3.380(1) Å and d(Gd—Gd) = 3.358(1) Å. The carbon atoms, which occupy a fraction of the octahedral voids, are connected to three (C1) and two (C2) Mo atoms, respectively (figure, bottom). The coordination polyhedron around Gd represents a GdC_5 square pyramid with Gd being slightly shifted out of the square plane. The compound is a Curie-type paramagnet with an effective moment of 8.02 μ_B per Gd atom in agreement with theoretical value of 7.94 μ_B for Gd^{3+} ion. Below 41.5 K the magnetic moments of Gd order antiferromagnetically. $Gd_2[Mo_2C_3]$ is a bad metallic conductor with a room temperature resistivity of order 1 mΩ cm.

Table 1. Data collection and handling.

Crystal:	gray, plate-like, size 0.05 × 0.06 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	366.25 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7 & Mercury70 CCD, ω/φ
$2\theta_{max}$:	59.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	791, 307
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 300
$N(param)_{refined}$:	23
Programs:	SHELXL-97 [5], DIAMOND [6]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Gd	4*i*	0.39147(6)	0	0.1806(1)	0.0179(5)	0.0150(4)	0.0179(4)	0	0.0052(3)	0
Mo	4*i*	0.1577(1)	0	0.3259(2)	0.0150(7)	0.0138(5)	0.0163(6)	0	0.0040(5)	0
C(1)	4*i*	0.251(1)	0	0.732(2)	0.010(6)	0.024(7)	0.013(6)	0	0.000(5)	0
C(2)	2*a*	0	0	0	0.03(1)	0.015(8)	0.03(1)	0	0.016(9)	0

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