Nd$_2$[MoC$_2$] and $RE_2$[WC$_2$], $RE = $ Ce, Pr, Nd: New carbometalates with Pr$_2$[MoC$_2$] structure type

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Received 13 March 2007; received in revised form 4 June 2007; accepted 6 June 2007
Available online 23 July 2007

Abstract

Four new ternary rare-earth-metal carbometalates, Nd$_2$[MoC$_2$] and $RE_2$[WC$_2$] with $RE = $ Ce, Pr, Nd, have been synthesized by argon arc melting and subsequent heat treatment at 1170 K for 30 days. They crystallize with the Pr$_2$[MoC$_2$] structure type with isolated C$_4$/C$_0$ species and are typical carbometalates with (i) low metal-to-carbon ratio, (ii) tetrahedral coordination of the transition metals ($T$) by carbon, and (iii) a polyanionic network $\frac{1}{2}[(TC)_2]^{6-}$. According to resistivity measurements the compounds are bad metals. Volume chemistry and magnetic susceptibility measurements indicate Pr$^{3+}$, Nd$^{3+}$, and Ce$^{4+}$ species, respectively. In the latter case, the additional electron is not transferred to the polyanionic network, instead it mainly populates the Ce partial structure.

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1. Introduction

Recently, it was shown that the concept of carbometalates allows the classification of ternary rare-earth-metal and actinoid carbides [1–6] containing C$_4$/C$_0$ species as structural entities. Two groups are clearly distinguishable: metal-rich carbides and carbometalates. It has been shown that carbometalates and metal-rich carbides differ in the metal to carbon ratio and in the number of carbon species in the coordination shell of transition metal atoms ($T$). Moreover, carbometalates with the general formula $RE_xT_yC_z$ ($RE =$ rare-earth element) contain polyanionic networks $[(T,C)_2]^{n-}$ of various dimensionalities, with the rare-earth-metal cations counter balancing the negative charge. For carbometalates, the metal/carbon ratio is equal to or smaller than 2, whereas metal-rich carbides usually have ratios from 4 to 16. Both classes exhibit individual covalent bonds between the transition metals and the carbon atoms, which are by far the strongest interactions. However, in case of the metal-rich carbides the metal–metal interactions outnumber all other interactions, while in case of the carbometalates the metal–metal interactions are present but not dominant. The structural chemistry of carbometalates may be viewed in analogy to the chemistry of fluoro-, oxo-, and nitridometalates [6]. However, the higher polarizibility and lower electronegativity of the carbo-ligand C$_4$/C$_0$ favor unusually low-valence states of the transition-metal atoms. Here, we present a series of new isostructural carbometalates, Nd$_2$[MoC$_2$] and $RE_2$[WC$_2$] ($RE =$ Ce, Pr, Nd). The main topic of the present work is to discuss the relationship between the volume chemistry, the oxidation state of the rare-earth metals, and the physical properties of those compounds.

2. Experimental

2.1. Preparation

The compounds under investigation were prepared by argon arc-melting of pressed pellets of the starting materials, using a non-consumable electrode on a water-cooled copper plate. The button specimens of 1 g in total mass were melted several times to improve compositional homogeneity. For
the following heat treatment at 1170 K for 30 days, the specimens were wrapped in Mo foil and encapsulated in fused silica tubes. After annealing, the samples were quenched in water. Due to the sensitivity of the products against air and moisture, all handlings were carried out under dry argon in a glove box (p(O₂, H₂O)<0.1 ppm). The Mo compound Nd₂[MoC₂] was obtained from a mixture of the elements, Nd pieces (Alfa, 3N), Mo powder (Chempur, 3N), and graphitic carbon (Chempur, 99.9%) in the molar ratio 2:1:2. In case of the carbotungstates RE₂[WC₂] (RE = Ce, Pr, Nd) powdery W₂C (Alfa, 99.9%), graphitic carbon, and pieces of the rare-earth-metals (Alfa, 3N) were used as reactants. The samples were characterized by chemical analyses and X-ray diffraction techniques.

Small single crystals of prismatic shape and silvery metallic luster could be obtained from the crushed button specimen. The metal content of selected single crystals was determined by EDXS (SEM Philips XL30 with integrated EDXS system): (1) Nd₂[MoC₂], Nd/Mo = 1.7(3); (2) Ce₂[WC₂], Ce/W = 1.94(5); (3) Pr₂[WC₂], Pr/W = 2.03(5); Nd₂[WC₂], Nd/W = 1.91(5). Analyses showed no evidence of oxygen and nitrogen.

2.2. Phase analysis and crystal structure determination

X-ray powder diffraction studies were carried out for the identification of phases using a Huber Guinier camera G670 (transmission geometry, Ge monochromator, flat sample holder with vaseline-coated Mylar foil). The unit cell parameters were determined at room temperature using CuKα₁ radiation (λ = 154.059 pm) and LaB₆ as an internal standard (a = 415.692 pm) by least-squares refinement using the Bragg reflections in the range 10° < 2θ < 100°. All samples contained the respective carbometalates as the majority phase besides unreacted molybdenum or tungsten (Fig. 1).

Prismatic-shaped single crystals of each compound were sealed in Lindemann glass capillaries and then investigated on a Rigaku AFC7 diffractometer with MoKα radiation (λ = 71.073 pm). The crystal structures were refined using the program package SHELXL97 [7]. Crystallographic data and further details of the data collections and structure refinements are given in Table 1. Positional and displacement parameters are presented in Table 2.

![Fig. 1. X-ray powder diffraction diagrams for Nd₂[MoC₂] and RE₂[WC₂] (RE = Ce, Pr, and Nd).](image-url)
Table 1
Crystallographic data for Nd₂[MoC₂], Ce₂[WC₂], Pr₂[WC₂], and Nd₂[WC₂]

| Chemical formula | Nd₂[MoC₂] | Ce₂[WC₂] | Pr₂[WC₂] | Nd₂[WC₂] |
|------------------|-----------|-----------|-----------|-----------|
| Formula mass (g mol⁻¹) | 1633.76 | 1952.44 | 1958.76 | 1985.4 |
| Space group, Z | | | | P4₁/mmm (136), 4 |
| a (pm) | 580.37(2) | 570.69(6) | 579.45(6) | 578.92(4) |
| c (pm) | 1024.81(4) | 1038.81(1) | 1035.72(1) | 1027.76(9) |
| c/a | 1.766 | 1.820 | 1.787 | 1.775 |
| V (pm³) | 345.19(2) | 338.32(6) | 347.74(4) | 344.45(5) |
| \(\rho_{\text{bulk}}\) (g cm⁻³) | 7.859 | 9.583 | 9.353 | 9.571 |
| Temperature (K) | | | | 293(2) |
| \(\beta\) (Nd) | 32.94 | 60.09 | 60.30 | 62.73 |
| \(\beta_{\text{max}}\) (deg) | 34.15 | 33.34 | 34.45 | 29.98 |
| Refinement parameters | | | | 70.73 |
| Uniq./observed reflections | 397/388 | 370/351 | 403/394 | 287/286 |
| \(R_{\text{int}}\) | 0.033 | 0.035 | 0.040 | 0.036 |
| Parameters | 20 | 20 | 21 | 20 |
| \(R_{\text{wp}}\) | 0.0012(1) | 0.0025(3) | 0.0008(1) | 0.0161(9) |
| \(R_{\text{F}}\) | 0.025/0.048 | 0.033/0.067 | 0.025/0.053 | 0.023/0.069 |
| Largest diff. peak/hole (e Å⁻³) | 2.99/−1.92 | 2.24/−3.68 | 4.22/−2.99 | 2.69/−3.08 |

2.3. Magnetic susceptibility and electrical resistivity

Magnetization of the polycrystalline samples (sealed in quartz tubes under helium) was measured in a SQUID magnetometer (MPMS XL-7, Quantum Design) in the temperature range between 1.8 and 400 K with various external fields between \(\mu_0 H = 10\) mT and 7 T. The dc electrical resistance of the samples was determined either in...
2.4. Band structure calculations

We performed charge density and density of states calculations for all compounds with the self-consistent TB-LMTO-ASA method [8]. In this approach, the density functional theory is used within the local spin density approximation (LSDA). Brillouin zone integrations were performed by an improved tetrahedron method [9]. Voids were filled with empty spheres (wave function without nucleus). Both non-spin-polarized and spin-polarized calculations were performed. Chemical bonding properties were investigated by analyzing COHP [10], and fatbands of calculations were performed. The density of states of distorted tetrahedral coordination by carbon atoms. The metal atoms, Pr and Mo, form a distorted bcc arrangement with the carbon atoms occupying the octahedral voids. A detailed description of the crystal structure of Pr$_2$[MoC$_2$] was already reported in [1]. The unit cell volume of the carbometalate Pr$_2$[WC$_2$] is larger than that of Nd$_2$[WC$_2$], which is expected from the lanthanoid contraction rule (Pr$^{3+}$: 106 pm, Nd$^{3+}$: 104 pm). However, the unit cell volume of the Ce compound is smaller than that of the Pr and Nd compounds, indicating the presence of Ce$^{4+}$ species (Ce$^{3+}$: 107 pm, Ce$^{4+}$: 94 pm).

3. Results and discussion

3.1. Crystal chemistry

The new compounds Nd$_2$[MoC$_2$] and RE$_2$[WC$_2$] (RE= Ce, Pr, Nd) are isotypic to Pr$_2$[MoC$_2$] and crystallize tetragonal in the space group P4$_2$/mmm. All crystallographic sites turned out to be fully occupied within the estimated standard deviations. The crystal structure (Fig. 2) contains polyanionic layers $\Sigma_2$[CeC$_4$]$^{6-}$ of distorted MoC$_4$-tetrahedra linked through vertices and edges and with rare-earth cations in between. The rare-earth metals are also in a distorted tetrahedral coordination by carbon atoms. The metal atoms, Pr and Mo, form a distorted bcc arrangement with the carbon atoms occupying the octahedral voids. A detailed description of the crystal structure of Pr$_2$[MoC$_2$] was already reported in [1]. The unit cell volume of the carbometalate Pr$_2$[WC$_2$] is larger than that of Nd$_2$[WC$_2$], which is expected from the lanthanoid contraction rule (Pr$^{3+}$: 106 pm, Nd$^{3+}$: 104 pm).

3.2. Magnetic susceptibility and electrical resistivity

For high external fields ($\mu_0H \geq 1$ T) and temperatures above 100 K, the temperature variation of the inverse susceptibility, $1/\chi(T)$, of the compounds Nd$_2$[MoC$_2$], Nd$_2$[WC$_2$], and Pr$_2$[WC$_2$] can be described by a Curie–Weiss law. The effective magnetic moment per mole RE atom, $\mu_{\text{eff}}$, and the Weiss temperature, $\Theta$, obtained from a non-linear least-squares fit of $\chi(T)$ are given in Table 4. The $\mu_{\text{eff}}$ are close to the values for the respective free RE$^{3+}$ ions, larger than that of Nd$_2$[WC$_2$], which is expected from the lanthanoid contraction rule (Pr$^{3+}$: 106 pm, Nd$^{3+}$: 104 pm). However, the unit cell volume of the Ce compound is smaller than that of the Pr and Nd compounds, indicating the presence of Ce$^{4+}$ species (Ce$^{3+}$: 107 pm, Ce$^{4+}$: 94 pm).

Selected interatomic distances and angles are given in Table 3. The interatomic distances $d$(T–C) vary between 208 and 214 pm; $d$(RE–C): 249–265 pm; $d$(T–T): 290–292 pm; $d$(RE–T): 329–349 pm; and $d$(RE–RE): 308–354 pm.

### Table 3

| Distances | n | Nd$_2$[MoC$_2$] | Ce$_2$[WC$_2$] | Pr$_2$[WC$_2$] | Nd$_2$[WC$_2$] |
|-----------|---|----------------|----------------|----------------|----------------|
| RE–C      | x 8 | 248.6(1) | 250.1(1) | 250.2(1) | 249.7(1) |
| RE–C      | x 8 | 259.4(8) | 257.4(2) | 262.0(8) | 259.5(9) |
| RE–C      | x 16 | 263.7(1) | 263.6(1) | 265.4(1) | 265.4(1) |
| T–C       | x 8 | 208.9(7) | 208.3(12) | 207.7(7) | 207.8(9) |
| T–C       | x 2 | 213.7(1) | 209.4(1) | 213.2(1) | 213.0(1) |
| T–C       | x 16 | 329.3(1) | 331.8(1) | 331.8(1) | 331.0(1) |
| T–T       | x 8 | 349.3(1) | 342.7(1) | 348.8(1) | 348.0(1) |
| T–T       | x 16 | 319.7(1) | 308.3(2) | 320.2(2) | 320.0(2) |
| T–T       | x 4 | 323.9(2) | 325.9(4) | 325.2(2) | 323.0(2) |
| T–T       | x 16 | 353.7(1) | 351.7(1) | 353.7(1) | 352.4(1) |
| T–T       | x 2 | 290.9(2) | 290.3(2) | 291.9(2) | 291.7(1) |

### Table 4

| Compound | Range (K) | $\mu_{\text{eff}}$(RE-atom) ($\mu_0$) | $\Theta$ (K) | $T_N$ (K) |
|----------|-----------|------------------------------------|--------------|-----------|
| Nd$_2$[MoC$_2$] | 150–400 | 3.76 | –8.6 | 20 | 4f$^3$ |
| Pr$_2$[WC$_2$] | 150–400 | $\approx$ 3.6 | –15 | 22 | 4f$^2$ |
| Nd$_2$[WC$_2$] | 150–400 | $\approx$ 3.6 | +25 | 21 | 4f$^3$ |
| Ce$_2$[WC$_2$] | See text | | | 4f$^0$ |
with exception of the Ce compound. In contrast, Ce$_2$[WC$_2$] displays a negligible magnetic moment, which indicates the 4$f^0$ configuration of Ce$^{4+}$. The susceptibility of Ce$_2$[WC$_2$] shows a constant term $\chi_0 = 0.65 \times 10^{-3}$ emu/mol and a very small Curie-type contribution on top of it, which we attribute to some Ce$^{3+}$ species (4$f^1$ configuration, $\approx 2\%$) from impurities. There are no indications for a valence instability of Ce in Ce$_2$[WC$_2$].

All samples contain small amounts of ferromagnetic impurities, since in low-field measurements spurious ordering transitions were recognizable as steps in $1/\chi(T)$ at relatively high temperatures. Magnetic ordering transitions of antiferromagnetic character at lower temperatures (for transition temperatures see Table 4) can be assigned to the main phases. The Nd$_2$[WC$_2$] sample contained a larger amount of a ferromagnetic impurity with $T_C \approx 80$ K. Therefore, the character of the long-range order as well as the paramagnetic properties require further investigations.

All compounds have a metal-like temperature dependence of the resistivity (Fig. 3): $\rho_0 = 180 \mu\Omega\cdot$cm and $\rho_{300} = 900 \mu\Omega\cdot$cm for the Nd$_2$[MoC$_2$] powder sample, $\rho_0 = 50 \mu\Omega\cdot$cm and $\rho_{300} = 300 \mu\Omega\cdot$cm for the Ce$_2$[WC$_2$] bulk sample, $\rho_0 = 90 \mu\Omega\cdot$cm and $\rho_{300} = 390 \mu\Omega\cdot$cm for the Pr$_2$[WC$_2$] bulk sample, $\rho_0 = 250 \mu\Omega\cdot$cm and $\rho_{300} = 560 \mu\Omega\cdot$cm for the Nd$_2$[WC$_2$] bulk sample, and $\rho_0 = 500 \mu\Omega\cdot$cm and $\rho_{300} = 1100 \mu\Omega\cdot$cm for the Pr$_2$[MoC$_2$] powder sample [1]. Resistivity $\rho(T)$ of Nd$_2$[MoC$_2$] and Nd$_2$[WC$_2$] shows typical drops at 20 and 21 K, respectively, further confirming the bulk character of the antiferromagnetic ordering. Around the Néel temperature of Pr$_2$[WC$_2$] only a flat broad hump is visible in $\rho(T)$, which might be explained by the smaller deGennes factor of Pr$^{3+}$ with respect to that of Nd$^{3+}$.

### 3.3. Electronic structure

Since f states are typically found too itinerant in a LSDA calculation, an analysis of the chemical bonding with consideration of the f-electrons for such species yields no realistic picture. To reach an appropriate description for the chemical bonding of species with strongly localized f-electrons only the minority ($\beta$)-spin channel should be analyzed. Comparable results to this can be obtained in a hypothetical, isostructural lanthanum compound, so we will discuss the results for La$_2$[MoC$_2$] and La$_2$[WC$_2$], as well as fatband analyses of Ce$_2$[WC$_2$], in order to assign the oxidation state of Ce. Consistent with the magnetic
susceptibility measurements the spin-polarized calculations converge to localized Nd(4$f^{3}$) and Pr(4$f^{2}$) states for Nd$_2$[MoC$_2$], Nd$_2$[WC$_2$], Pr$_2$[WC$_2$], and a Ce(4$f^{0}$) state without unpaired electrons for Ce$_2$[WC$_2$]. The densities of states (DOS) of all compounds indicate metallic conductivity, in agreement with the experiments. In Fig. 4, the partial DOS and COHP curves of averaged individual interactions only for La$_2$[WC$_2$] are shown, since the band structures of these La compounds are quite similar and the electronic band structure of La$_2$[MoC$_2$] was discussed before in detail [1]. In the range from $-6eV$ up to $E_F$ C p and W d states occur in the DOS. These states lead to pronouncedly strong W–C covalent bonds in the energy window $-6$ to $-2eV$ on COHP. In contrast, the COHP diagrams for the La–C interactions display weak and non-exhausted covalent bonding interactions. The all metal–metal interactions (M–M; M = La, T) are small but important. However, for the relative importance of each kind of interaction in the whole crystal structure they were weighted by bond multiplicities and corresponding ICOHP values with the ratios ICOHP$_{(M-C)}/ICOHP_{(M-M)}$ given in Table 5. A clear difference is observed in transition-metal carbon bonds; due to the more disperse W d bands, W–C bonds in La$_2$[WC$_2$] are around 30% stronger than Mo–C in La$_2$[MoC$_2$] but with very similar distances. In total, the other bond energies do not differ significantly. Generally, the dominating strong Mo–C and W–C covalent bonds as well as the ratio of ICOHP$_{M-C}/ICOHP_{M-M}$ being 4.5 and 5.0, respectively, justify their description as carbometalates.

For the examination of the valence state of Ce in Ce$_2$[WC$_2$] we analyzed Ce 5$d$ and 4$f$ fatband plots, the partial DOS of Ce 4$f$ and 5$d$, and the COHP curves for the Ce–C and Ce–Ce interactions. The spin-polarized calculations converge always to a non-spin-polarized state suggesting Ce$^{4+}$, which is consistent with structural and magnetization data.

The fatband plots of Ce 4$f$ and 5$d$ bands reveal that 4$f$ states primarily lie above $E_F$ and there is no large contribution of 5$d$ bands to the occupied bands below $E_F$.

Table 5
Integrated crystal orbital Hamilton populations (–ICOHP) for M–M and M–C (M = La, T) interactions and distances for hypothetical La$_2$[MoC$_2$] and La$_2$[WC$_2$]

| Bonding | n   | La$_2$[MoC$_2$] | La$_2$[WC$_2$] |
|---------|-----|----------------|----------------|
|         |      | Distances [pm] | –ICOHP$_{av.}$ | –ICOHP$_{w.}$ | Distances [pm] | –ICOHP$_{av.}$ | –ICOHP$_{w.}$ |
| T–C1    | × 4 | 209–214        | 3.86           | 15.44         | 208–213        | 4.83           | 19.3          |
| La–C1   | × 8 | 249–264        | 1.54           | 12.32         | 250–265        | 1.47           | 11.77         |
| La–T    | × 10| 330–355        | 0.39           | 3.90          | 332–356        | 0.40           | 4.03          |
| La–La   | × 6 | 322–355        | 0.29           | 1.74          | 307–351        | 0.27           | 1.62          |
| T–T     | × 0.5| 290            | 0.75           | 0.38          | 290            | 1.10           | 0.55          |

ICOHP$_{M-C}/ICOHP_{M-M} = 4.6/1$

ICOHP$_{M-C}/ICOHP_{M-M} = 5.01/1$

–ICOHP are listed as averaged values and also as weighted by the respective bond frequencies per formula unit.

Fig. 5. Total, projected Ce 4$f$- and Ce 5$d$-DOS and COHP curves for Ce–Ce and Ce–C interactions of Ce$_2$[WC$_2$].
The hybrid orbitals Ce 4f–5d just below $E_F$ are involved in weak Ce–Ce interactions and only very little in the Ce–C bonds as shown in Fig. 5. These results are comparable to Ce$_3$[MnN$_3$] rather than to CeN [11]. We therefore conclude that the description (Ce$^{4+}$·e$^-$)$_2$[W$^{2+}$(C$_4$-)] is suitable, where the remaining electron is delocalized.

4. Conclusion and summary

Four new compounds, Nd$_2$[MoC$_2$] and $RE_2$[WC$_2$] with $RE$ = Ce, Pr, Nd, were synthesized and classified as carbometalates by bonding analyses using the COHP method. The compounds crystallize with the Pr$_2$[MoC$_2$] structure type. They are bad metals, with resistivities ranging from 300 to 1100 $\mu\Omega$cm at room temperature. A comparison of the unit cell volumes and the magnetic susceptibility measurements indicate the presence of Pr$^{3+}$, Nd$^{3+}$, and Ce$^{4+}$ species. However, electronic band structure calculations reveal for the Ce compound that the additional electron (Ce$^{3+}$ → Ce$^{4+}$ + e$^-$) mainly populates the Ce partial structure, i.e., the electron is not transferred to the polyanionic network, which is in agreement with the concept of carbometalates. Therefore we can assign the following idealized ionic formulæ $RE_2^{3+}$[T$^{2+}$(C$_4$–)]$_3$ ($RE$ = Pr, Nd and T = Mo, W) and (Ce$^{4+}$·e$^-$)$_2$[W$^{2+}$(C$_4$–)]$_2$.

Supporting information

The crystallographic data are available in CIF format (see Table 1).

Acknowledgments

We thank Steffen Hückmann for the X-ray investigations and Dr. Ulrich Burkhardt for the EDXS analyses.

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