Ternary Carbides from the Point of View of Carbometalates

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In the past decades, a number of investigations were focused on the syntheses, characterization and properties of ternary carbides $A_xT_yC_z$ (A = group 3 element, lanthanide, actinide; T = transition metal). Thus far, 52 different structure types for ternary carbides have been reported including 19 with monoatomic species C^{4-} as structural units. Here, we present the concept of carbometalates, which is useful for the classification of these structure types. The corresponding structure types are listed in Tab. 1 ordered by the metal to carbon atom ratio $(x + y)/z$. Representatives, the coordination number (CN) of the transition metals by carbon atoms and the bibliographical references are also given.

Two groups are clearly distinguishable and labelled as *carbometalates* and *metal-rich carbides*, respectively. The group of compounds classified as carbometalates contains complex anions

Class	Structure type	Representatives	$(x+y)/z$	CN[#] of T	Ref.
Carbometalates	$UMoC_2$[†]	$AMoC_2$, A = Y, Gd – Tm AWC_2, A = Y, Tb – Tm, Pu UTC_2, T = V – Mn, Mo, Tc, W, Re	1	4 and 5	[1]
	$U_5Re_3C_8$[†]	$U_5Re_3C_8$			[2]
	$U^{IV}[Cr_4^{III}C_4]$	$U[Cr_4C_4]$	1.25	4	[3]
	$U^{IV}[W_4^{III}C_4]$	$U[W_4C_4]$			[4]
	$Ho_2^{III}[Cr_2^{III}C_3]$	$A_2[Cr_2C_3]$, A = Y, Gd – Lu			[5]
	$Er_2^{III}[Mo_2^{III}C_3]$	$A_2[Mo_2C_3]$, A = Ce, Gd – Tm, Lu	1.33	4	[6, 7]
	$Pr_2^{III}[Mo_2^{III}C_3]$	$Pr_2[Mo_2C_3]$			[8]
	$Pr_2^{III}[Mo^{II}C_2]$	$A_2[MoC_2]$, A = Pr, Nd $A_2[WC_2]$, A = Ce, Pr		4	[9]
	$Pr_2^{III}[Re^{II}C_2]$	$A_2[ReC_2]$, A = Y, Ce – Nd, Sm, Gd – Tm, Lu $A_2[OsC_2]$, A = Y, Gd – Er	1.5	3	[10] [11]
	$U_2^{IV}[Ir^0C_2]$	$Th_2[TC_2]$, T = Ru, Os, Rh, Ir, Ni, Pt		2	[12]
	$Y^{III}[Co^{I}C]$	$A[CoC]$, A = Y, Gd – Lu	2	2	[13]
Mixed	$La_5Os_3C_{4-x}$	$A_5Os_3C_{4-x}$, A = La – Nd, Sm	2	2	[14]
Metal-rich carbides	Y_3RhC	$ThRu_3C$ and many other representatives	4	2	[15]
	$LaMn_{11}C_{2-x}$	$AMn_{11}C_{2-x}$, A = La – Nd, Th $ThFe_{11}C_{2-x}$	~6	0 and 1	[16]
	$Pr_2Mn_{17}C_{3-x}$	$A_2Mn_{17}C_{3-x}$, A = La – Nd, Sm, Th	~6.33	0 and 1	[17]
	$Tb_2Mn_{17}C_{3-x}$	$A_2Mn_{17}C_{3-x}$, A = Y, Gd – Tm, Lu $A_2Fe_{17}C_{3-x}$, A = Nd, Tb, Dy, Lu			[18]
	$Ce_2Ni_{22}C_{3-x}$	$A_2Ni_{22}C_{3-x}$, A = La – Nd, Sm, Gd – Ho	~8	0, 1 and 2	[19]
	$Tm_{11}Ni_{60}C_6$	$A_{11}Ni_{60}C_6$, A = Y, Dy – Lu	11.83	0 and 1	[20]
	$Nd_2Fe_{14}C$	$A_2Fe_{14}C$, A = Pr, Sm, Gd – Tm, Lu	16	0, 1 and 2	[21]

[†] Compounds tentatively assigned to the group of carbometalates
[#] Number of carbon atoms in the first coordination shell

Tab. 1: Classification of ternary carbides $A_xT_yC_z$ (A = group 3 element, lanthanide, actinide; T = transition metal) with monoatomic species C^{4-} as structural units.

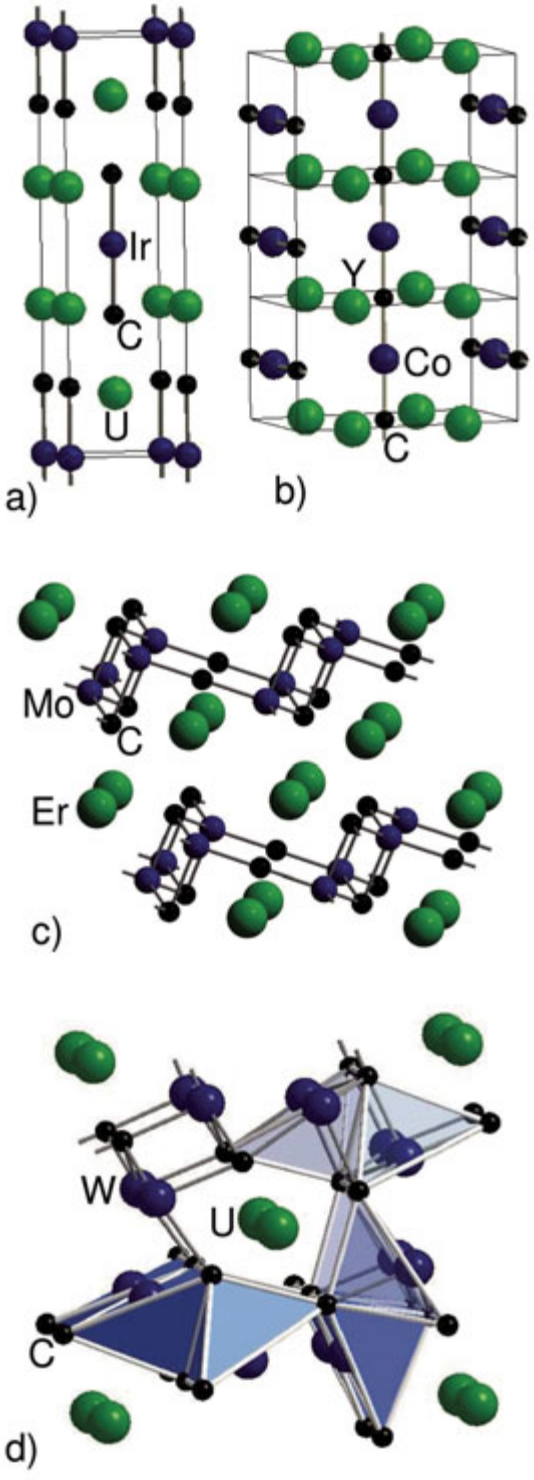

Fig. 1: Examples of carbometalates: (a) The crystal structure of $U_2[IrC_2]$ containing the discrete molecular anion $[CIr^0C]^{8-}$. (b) Linear chains of $^1_\infty[Co^IC]^{3-}$ in the crystal structure of Y[CoC]. (c) The crystal structure of $Er_2[Mo_2C_3]$ with layers $^2_\infty[Mo_2^{II}C_3]^{6-}$, composed of edge and corner sharing MoC_4 tetrahedra. d) Framework substructure of $^3_\infty[W_4C_4]^{4-}$ in the crystal structure of $U[W_4C_4]$ with triangular pyramidal coordination by C with W close to the centre of the base (blue polyhedra).

$[T_yC_z]^{n-}$ with carbon atoms covalently bonded to the transition metal. Characteristic examples of carbometalates with discrete polyanions and anionic chain-, layer- and framework-substructures are shown in Fig. 1. For carbometalates, the metal to carbon atom ratio $(x + y)/z$ ranges from 1 to 2. Both, composition and oxidation state of the transition metals are well defined and their coordination numbers (CN) are low ranging from 2 to 5. The metal atoms, *A* and *T*, form motifs of a body centred cubic structure with the carbo-ligands occupying parts of the octahedral voids in ordered arrangements. This situation closely resembles the structural chemistry of nitridometalates. However, the oxidation states of the transition metals in the carbo-compounds (e.g. Ni^0, Co^I, Re^{II}, Mo^{II}) are usually lower due to the higher polarizability and lower electronegativity of the carbo-ligand. The concept of complex anions includes the formalism of ionic charge assignment and charge balancing of the chemical formulae, a common and well accepted procedure in chemistry.

The second group with monoatomic species C^{4-} as structural units is classified as *metal-rich carbides*. Here, the metal atoms are superior in number, the ratio $(x + y)/z$ being between 4 and 16. They are best described as interstitial carbides with carbon atoms statistically occupying interstitial sites of close-packed arrangements of metal atoms. Some of the transition metal atoms are not even coordinated by any carbon atom. Due to the strong metal-metal interactions partial structures containing complex anions $[T_yC_z]^{n-}$ cannot be distinguished and the application of simple oxidation states assignment fails. The bonding situation in the metal-rich carbides is in general much more complicated compared to that of carbometalates. Usually, they exhibit homogeneity ranges and display electronic properties similar to that of intermetallic phases.

The classification of $UMoC_2$ and $U_5Re_3C_8$ as carbometalates is debatable due to the lack of precise structural data. Consequently, an assignment of oxidation states to the transition metals is difficult. However, at present, both structure types have been added to the list of carbometalates, because of their low $(x + y)/z$ ratios and their low coordination numbers. $La_5Os_3C_{4-x}$ seems to be a border-line case since its crystal structure contains complex anions as well as carbon in interstitial sites. However, a conclusive discussion of such mixed types needs more examples.

The carbometalates are bad metals with electrical resistivities ranging from 50 to 400 μΩcm at room temperature. The magnetic properties of the lanthanide-based carbometalates are usually dominated by the localized 4*f* moments of the A^{3+} ions.

The main benefit of the presented classification of ternary carbides into metal-rich carbides and carbometalates is its strategic help. Novel carbides may be synthesized in a targeted approach and structural information, e.g. the coordination type polyhedra of the transition metals and their linkages, and homogeneity ranges are anticipated.

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