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Synthesis, Structure, Bonding, and Properties of $Sc_3Al_3O_5C_2$ and $ScAl_2ONC$—Unique Compounds with Ordered Distribution of Anions and Cations[†]

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Single crystals of the new compounds $Sc_3Al_3O_5C_2$ and $ScAl_2ONC$ were obtained by reacting Sc_2O_3 and C in an Al-melt at 1550 °C. Their crystal structures continue the row of transition metal oxide carbides with an ordered distribution of anions and cations with ScAlOC as the first representative. In the structure of $Sc_3Al_3O_5C_2$ ($P6_3/mmc$, $Z = 2$, $a = 3.2399(8)$ Å, $c = 31.501(11)$ Å, 193 refl., 23 param., $R_1(F) = 0.024$, $wR_2(I) = 0.058$) the anions form a closest packing with five layers of oxygen separated by two layers of carbon atoms. Sc is placed in octahedral voids and Al in tetrahedral voids thus forming layers of $AlOC_3$ tetrahedra and ScC_6- and ScO_6-octahedra, respectively. Surprisingly the layers of ScO_6 octahedra are connected by an additional layer of undistorted trigonal bipyramids AlO_5. The structure of $ScAl_2ONC$ (space group $R\bar{3}m$, $Z = 3$, $a = 3.2135(8)$ Å, $c = 44.636(1)$ Å, 187 refl., 21 param., $R_1(F) = 0.023$, $wR_2(F^2) = 0.043$) can directly be derived from the binary nitrides AlN (wurtzite-type) and ScN (rocksalt-type). The anions form a closest packing with alternating double layers of C and O separated by an additional layer of N. Again, Al and Sc occupy tetrahedral and octahedral voids, respectively. All compositions were confirmed by energy dispersive X-ray spectroscopy (EDXS) measurements on single crystals. According to band structure calculations $Sc_3Al_3O_5C_2$ is electron precise with a band gap of 0.3 eV. Calculations of charges and charge densities reveal that the mainly ionic bonding contains significant covalent contributions, too. As expected Sc and C show higher covalent shares than Al and O. The different coordinations of O, Al, and Sc are clearly represented in the corresponding p and d states.

Introduction

Recently[1] we have reported on ScAlOC as the first transition metal's oxide carbide with an ordered distribution of the anions. The crystal structure of ScAlOC and all structural features can easily be derived from the structures of the binary nitrides ScN (NaCl type) and AlN (Wurtzite-type) by combination of alternating layers with ScC_6 and ScO_6 octahedra and $AlOC_3$ tetrahedra. This is remarkable because usually oxides and carbides of transition metals show distinct differences. Owing to the mostly ionic interaction, the oxides are described in terms of the closest sphere packing of the oxide anions, while the cations occupy voids of matching size.[2,3] In contrast to this, the carbides are classified as interstitial compounds. According to Hägg,[4] the metal atoms form a closest packing, and the C atoms are located in voids. The interactions contain covalent, ionic, and metallic contributions as well.[5] This difference in chemical bonding is noticeable in ternary compounds, too, as ordered oxide carbides of transition metals were unknown.[6] Only elements of group 3, 4, and 5 are able to form solid solutions TMO_xC_{1-y} (TM = Sc,[7] Ti,[8] Zr,[9] Hf,[10] V,[11] Nb,[12] with NaCl type structure. For main group elements (group 13, 14, and 15) Al_4O_4C was

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[†] Dedication to the 65th birthday of Prof. Rüdiger Kniep.

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characterized as the only compound with ordered O/C sites.[13,14] Al_2OC was characterized as a solid solution with a wurtzite structure.[15]

The exceptional position of ScAlOC suggested band structure calculations. It was shown that the bonding is mainly ionic, but the charge of the Sc cations is reduced by interaction of the d orbitals with the p orbitals of O (weaker) and C (stronger). The bondings Al−C and especially Sc−C perform a significant covalent share. Furthermore the number of ionic carbides with isolated carbon anions is very limited, so ordered oxide carbides are good objects to study them. Besides Be_2C and Al_4C_3, there are only a few ionic ternary carbides like $ScAl_3C_3$ and UAl_3C_3.[16]

Moreover oxide carbides may show interesting material properties. Oxides like Al_2O_3, ZrO_2, and MgO are important ceramic materials.[17] Carbides of the "early" (i.e., group 4 to 6) transition metals like TiC, TaC, and WC belong to the hardest and highest-melting materials of all.[18]

The behavior of nitrogen is between C and O. For most of the transition metals the nitrides are very similar to the carbides.[6] Additionally, there are some nitrides like the red Ta_3N_5[19] and Nb_4N_5,[20] where the analogous carbides do not exist. In general, the tendency to form solid solutions with the corresponding carbides and oxides is much more pronounced, but ordering was never observed.[6] Some representatives are of technological importance as hard materials ($TiC_{1-x}N_x$[5]) or ceramics (Zr_2N_2O[21]). The nitrides of main group elements (Al, Ga, Si, Ge) are fundamentally different from the corresponding carbides and oxides, but solid solutions are well-known ("AlONs",[22] "SiONs",[23] "SiAlONs"[24]). The ratio O/N is varying in a way that there result electron-precise compounds. Ordered anions are only known for Si_2N_2O[25] and Ge_2N_2O.[26]

By variation of the reaction conditions we now were able to synthesize and characterize two further representatives, namely, the oxide carbide $Sc_3Al_3O_5C_2$ and the oxide nitride carbide $ScAl_2ONC$. These new compounds amend and extend the oxide carbides of transition metals as a new type of compounds. Furthermore, their crystal structures fit perfectly to the system of building block units on the basis of the corresponding binary nitrides ScN and AlN ($ScAl_2ONC$) or the trigonal bipyramids AlO_5 ($Sc_3Al_3O_5C_2$) as new features.

Experimental Section

Synthesis and Characterization. $ScAl_2ONC$ was observed as a byproduct in several batches when screening the formation conditions of ScAlOC.[1] Typical conditions were as follows: Sc_2O_3 and C were reacted with an excess of aluminum (ratio Sc_2O_3/C/Al as 1:0.34:40). The starting materials (total mass: ca. 2 g) were mixed and heated in a corundum crucible with 300 °C/h to 1550 °C under a flow of argon. After a dwelling time of 10 h, it was cooled with 10 °C/h to 800 °C, and then the furnace was turned off. The metal excess was dissolved with 5*n* hydrochloric acid. The residue contained mostly black hexagonal platelets of ScAlOC and some thin crystal of $ScAl_2ONC$ ($Ø_{max.}$ = 0.2 mm). According to the similar color and crystal shape the distinction to ScAlOC was only possible by a single crystal investigation. In general $ScAl_2ONC$ was only observed when the maximum temperature was below 1500−1550 °C.

The synthesis of $Sc_3Al_3O_5C_2$ is very similar, but AlN as an additive is necessary for its formation: Sc_2O_3, C, and AlN with an excess of aluminum (Sc_2O_3/C/AlN/Al as 1:1.16:0.6:40) whereas the starting materials (total mass: ca. 2 g) were also heated, but with 100 °C/h to 1600 °C for 5 h and were cooled with 10 °C/h to 1200 °C. The solidified melt was treated with 5*n* hydrochloric acid. The powder X-ray pattern of the residue showed $Sc_3Al_3O_5C_2$ and $ScAl_2O_3N$ (PDF file 42-155) as the main products with small amounts of $ScAlO_3$ and Sc_2O_3. Black single crystals (hexagonal platelets and columns, $Ø_{max.}$ = 0.4 mm) were separated mechanically from the other colorless byproduct. The diffraction pattern of the selected crystals was indexed with a hexagonal unit cell of $a = 3.2495(5)$ Å and $c = 31.564(6)$ Å. The intensities calculated from the structural parameters (see below) fitted well to the observed ones.

It should be noticed that the exact ratio of the starting materials is not the determining factor for successful synthesis of either compound, but the heating program is. Higher reaction temperatures (1600 °C) and faster cooling rates (20 °C/h) favor the formation of ScAlOC. The influence of AlN is not clear. Although no significant amounts of nitrogen are found in the single crystals (energy dispersive X-ray spectroscopy (EDXS) results) the addition of AlN seems to change the reaction conditions in a way that enables the formation of $Sc_3Al_3O_5C_2$, because up to now syntheses without AlN were (not yet) successful. The nitrogen content in $ScAl_2ONC$ probably results from the atmosphere. Samples synthesized under the same conditions in welded Ta-ampules never contained $ScAl_2ONC$ but only ScAlOC.

Structure Analysis. $Sc_3Al_3O_5C_2$. A black hexagonal column (diameter 0.3 mm, length 0.2 mm) was selected under a microscope. Reflection intensities were measured using a single crystal diffractometer with image plate detector (Stoe IPDS II, MoKα). The reflections were indexed with a hexagonal unit cell. Lattice constants were refined from the data set[27] to $a = 3.2399(8)$ Å and $c = 31.501(11)$ Å. Measurement of 1495 reflections up to $2\theta = 58°$ and merging in Laue class $6/mmm$ resulted in a data set of 193 unique reflections (149 with $I > 2\sigma(I)$). According to the reflection conditions hhl: $l = 2n$ and the E-statistics the crystal structure was solved by direct methods[28] in $P6_3/mmc$ and refined without peculiarities. A check of the symmetry showed that the structure is centrosymmetric, and $P6_3/mmc$ the correct space group. The labeling of the anions resulted in a O/C ratio of 5:2 which is in good agreement to the EDXS results. The refinement

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Table 1. Structure Determination and Refinement of $Sc_3Al_3O_5C_2$ and $ScAl_2ONC$

	$Sc_3Al_3O_5C_2$	$ScAl_2ONC$
crystal shape	hexagonal column	hexagonal platelet
crystal color	black lustrous	black lustrous
crystal size	$0.3 \times 0.3 \times 0.2$ mm^3	$0.3 \times 0.3 \times 0.025$ mm^3
formula weight	639.68 g/mol	422.82 g/mol
crystal system	hexagonal	rhombohedral
space group	$P6_3/mmc$ − No. 194	$R\bar{3}m$ − No. 166
lattice constants	$a = 3.2399(8)$ Å; $c = 31.501(11)$ Å	$a = 3.2135(5)$ Å; $c = 44.639(9)$ Å
cell volume	286.36 Å^3	399.18 Å^3
formula units	2	6
density, calculated	3.71 g/cm^3	3.52 g/cm^3
radiation	MoKα, graphite monochromator	MoKα, graphite monochromator
θ-range	$-4 \leq h \leq 4$ $-4 \leq k \leq 4$ $-43 \leq l \leq 43$	$-4 \leq h \leq 4$ $-4 \leq k \leq 4$ $-60 \leq l \leq 60$
temperature	23 °C	23 °C
$2\theta_{max}$	58.3°	58.3°
diffractometer	STOE IPDS II	STOE IPDS II
mode of measurement	rotation method, $\varphi\Delta = 2°$; 120 s per frame	rotation method, $\varphi\Delta = 1°$; 720 s per frame
reflections measured	1495	1312
independent reflections	193	187
reflections $I > 2\sigma(I)$	149	147
absorption correction	numerical; program XSHAPE[27]	numerical; program XSHAPE[27]
$R_{int.}$, R_{sigma}	0.058, 0.020	0.059, 0.031
absorption coefficient	3.88 mm^{-1}	3.13 mm^{-1}
extinction coefficient[28]	0.037(10)	0.0003(12)
max./min transmission	0.281; 0.146	0.631; 0.206
structure solution	direct methods[28]	direct methods[28]
refinement	SHELXL[28]	SHELXL[28]
residual electron e$^-$/Å^3	+0.53, −0.64, 0.10	+0.57, −0.43, 0.09
min, max, σ weighting function[28]	0.0430; 0.0	0.0261; 0.0
number of parameters	23	21
R-factors	$R_1(F) = 0.0236$; $wR_2(F^2) = 0.0579$	$R_1(F) = 0.0226$; $wR_2(F^2) = 0.0432$

of the site occupation factors revealed no significant deviations from full occupation. The distinction between C and O on the basis of the X-ray refinement is clear. Refinements of the site occupation factors resulted in values between 95(2)% and 101(1)%. The assignments are confirmed by displacement parameters and R-values. The higher standard deviations for O1 are caused by the site symmetry (i.e., multiplicity). Finally R-values of $R_1(F) = 0.0236$ and $wR_2(F^2) = 0.0579$ were obtained.

$ScAl_2ONC$. One of the thin black hexagonal platelet (diameter 0.3 mm, thickness 0.025 mm) was selected under a microscope. Reflection intensities were measured using a single crystal diffractometer with image plate detector (Stoe IPDS II, MoKα). The indexing routine led to a rhombohedral unit cell. Lattice constants were refined from the data set[27] to $a = 3.2135(5)$ Å and $c = 44.639(9)$ Å. Measurement of 1312 reflections up to $2\theta = 58°$ and merging in Laue class $\bar{3}m$ resulted in a data set of 187 unique reflections (147 with $I > 2\sigma(I)$). Except for the reflection conditions for the rhombohedral crystal system (hkl with $-h + k + l = 3n$), no additional extinctions were found. The crystals structure was solved by direct methods[28] in $R\bar{3}m$ and refined without peculiarities. A check of the symmetry and the following refinement showed that the structure is centrosymmetric and $R\bar{3}m$ the correct space group.

While two of the anions were clearly assigned to O and C, one of the anion's sites exhibited an electron density between O and C, that is, corresponding to N. The distances to Al were in between the Al−C and Al−O distances. EDXS measurements showed the presence of nitrogen and a nearly equal O/N/C ratio. According to the EDXS results and the observed distances to Al, we assumed the occupation by N, but a partial O/C solid solution of this site cannot be excluded ambiguously.

The refined site occupation factors were in agreement to this model. The refinement of the other site occupation factors revealed no significant deviations from full occupation. Finally R-values of $R_1(F) = 0.0226$ and $wR_2(F^2) = 0.0432$ were obtained.

Further details are listed in Tables 1−3. Measurements were performed for several crystals. Tables 1−3 contain the results with the best R-values. Details on the structure refinement (complete list of distances and angles, F_o/F_c-list) may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49)724−808−666: e-mail: crysdata@fiz-karlsruhe.de) on quoting the registry number CSD-420952 ($ScAl_2ONC$) or CSD-420953 ($Sc_3Al_3O_5C_2$).

Characterization. EDXS. High reaction temperatures and high reactivity of the melt can lead to unexpected contaminations (crucible, metallic melt, starting material). Therefore single crystals of $Sc_3Al_3O_5C_2$ and $ScAl_2ONC$ were analyzed by EDXS. ScAlOC was used as a reference. The results given in Table 4 were obtained from the single crystals which were already used for the structure refinement. Ten spots for each crystal were measured and averaged. Furthermore, several crystals were checked for each compound leading to very similar results. According to comparative measurements for compounds with known composition, the error is estimated to 2% for C/O and 1% for Al/Sc. The determination of N shows a higher uncertainty because the nitrogen K-peak overlaps with the scandium L-peak (see below).

EDXS measurements were done with a DSM 962 electron microscope (Fa. Carl Zeiss) equipped with an EDXS tool INCA Energy 300 (Fa. Oxford) at the Institut für Mikrosystemtechnik (University of Freiburg).

Powder XRD. XRD patterns were recorded with a STOE Stadi P (Cu−Kα1-radiation, Ge-monochromator, image plate detector, Debye−Scherrer geometry, transmission).

Microhardness. Microhardness was measured with a microhardness equipment MHT 10 (producer: A. Paar, Austria).

Table 2. Coordinates, Thermal Displacement Parameters (Å^2) and Site Occupation Factor [a]

atom	site	x	y	z	U_{eq}	sof[b]	U_{11}	U_{33}
				$Sc_3Al_3O_5C_2$				
Sc1	2a	0	0	1/2	0.0112(4)	0.996(7)	0.0108(5)	0.0120(6)
Sc2	4b	1/3	2/30	0.66069(3)	0.0174(4)	1.008(9)	0.0099(4)	0.0324(6)
Al1	2c	0	0	1/4	0.0091(5)	0.994(13)	0.0085(7)	0.0102(8)
Al2	4c	1/3	2/3	0.43020(4)	0.0101(4)	1.010(9)	0.0102(5)	0.0098(6)
C	4c	2/3	1/3	0.45377(13)	0.0111(9)	1.00(2)	0.0108(14)	0.0118(18)
O1	2c	1/3	2/3	3/4	0.0184(11)	0.95(2)	0.0133(16)	0.029(3)
O2	6c	0	0	0.80933(9)	0.0132(8)	0.99(2)	0.0143(12)	0.0109(13)
O3	6c	1/3	2/3	0.37236(9)	0.0129(7)	1.00(2)	0.0136(11)	0.0116(14)
				$ScAl_2ONC$				
Sc1	3a	0	0	0	0.0100(3)	0.989(12)	0.0076(4)	0.0149(5)
Sc2	3b	0	0	1/2	0.0202(4)	0.999(8)	0.0069(4)	0.0461(8)
Al1	6c	0	0	0.38323(3)	0.0084(3)	1.013(8)	0.0065(4)	0.0124(5)
Al2	6c	0	0	0.23040(3)	0.0090(3)	0.992(9)	0.0069(4)	0.0130(6)
C	6c	0	0	0.30083(8)	0.0091(8)	1.04(2)	0.0085(11)	0.0103(16)
N	6c	0	0	0.42636(9)	0.0126(7)	0.97(2)	0.0083(6)	0.0205(17)
O	6c	0	0	0.18933(6)	0.0131(7)	1.02(2)	0.0141(9)	0.0110(13)

[a] esd's in parentheses, $U_{11} = U_{22} = 2\,U_{12}$, $U_{23} = U_{13} = 0$. [b] To check for mixed occupations and/or vacancies site occupation factors were treated by turns as free variables at the end of the refinement.

A force of 2 N was generated within 10 s and applied for 15 s. The imprints of the indenter (Vickers hardness: square pyramid, Knoop: lozenge-based pyramid) were evaluated and converted into a value for the microhardness according to the usual procedures.[29]

Vibrational Spectroscopy. FT-IR and FT-Raman measurements were performed with a Bruker RAM II Fourier-Raman-module for a VERTEX 70 spectrometer with Nd:YAG-laser with an output of 50 to 200 mW and 1000−10000 scans to optimize Raman intensities for the black powder samples prepared in 1 mm capillary. The IR sample was made of crystalline powder pressed with KBr to pellets.

Electronic Structure Calculations. For the calculations the FP-LAPW (full potential linearized augmented plane wave) method was used. The exchange and correlation were treated within the GGA (generalized gradient approximation) using the Engel−Vosko version with the WIEN2k-program package.[30] The following muffin-tin radii R_{mt} were used for the calculations: Sc = 2.09 au (110.8 pm), Al = 1.71 au (90.6 pm), O = 1.71 au (90.6 pm), C = 1.90 au (100.7 pm). Self-consistency was achieved by demanding that convergence of the total energy to be smaller than 10^{-5} Ry/cell and a charge distance about 10^{-5}. The cutoff-energy was $R_{mt} \cdot K_{max} = 5$. The integration of the Brillouin zone to determine total and partial DOS (TDOS, PDOS) was carried out by the tetrahedron method (1000 k-points/BZ; 52/IBZ). The irreducible box for band structure plots along the k-path ΓAHKΓMK was calculated with a grid of 80 k-points. Valence charge distribution (ρ_{val}) was described with the program XCrySDen.[30]

Structure Descriptions and Discussion

$Sc_3Al_3O_5C_2$. Figure 1 shows the crystal structure of $Sc_3Al_3O_5C_2$, and Figure 2 the surroundings of the atoms. The building principle of $Sc_3Al_3O_5C_2$ is very similar to that of $ScAl_2ONC$ and ScAlOC, but $Sc_3Al_3O_5C_2$ is the first example with a different number of cations and anions. The anions form a closest packing **A***BCACB***AB***ACBCA***B** (O-layers in *italics*, C-layers in **bold**). According to Jagodzinski[2] the repeating unit of 14 layers is (**hh***cchcc*)$_2$. Similar to ScAlOC and $ScAl_2ONC$, the Sc atoms occupy the octahedral voids between the layers of equal anions while Al is in half of the tetrahedral voids between layers of unequal anions. In addition one-half of the trigonal-(bipyramidal) voids of the central O layer is occupied by Al. In total there result double layers of ScO_6 octahedra which are connected by layers of edge-sharing AlO_5 trigonal bipyramids and layers of ScC_6 octahedra which are connected to layers of ScO_6 octahedra by $AlOC_3$ tetrahedra.

The two different Sc atoms are coordinated by the anions the same way as in ScAlOC and $ScAl_2ONC$, with slight differences in bond distances (Sc−C: 2.373(3) Å; Sc−O: 2.100(2) Å, 2.148(2) Å). Also the compression in direction of the *c*-axis of ScO_6-octahedra (symmetry C_{3v}, O−Sc−O: 80.1°) and the elongation of ScC_6-octahedra (D_{3d}, C−Sc−C: 94.0°) is present. The surroundings of the two different Al atoms are formed in different ways. Al1 is coordinated by five O atoms forming a trigonal bipyramidal coordination (symmetry D_{3h}, Al1−O1$_{eq}$ = 1.873(5) Å, Al1−O2$_{ax}$ = 1.876(3) Å). In contrast Al2 forms $AlOC_3$ tetrahedra (Al2−O3 = 1.816(5) Å; Al2−C = 2.02(2) Å), with only small deviations from the ideal symmetry (C_{3v}, X−Al−X: 107°−111°).

Although the structure of $Sc_3Al_3O_5C_2$ is closely related to ScAlOC and $ScAl_2ONC$ it cannot be derived by a simple addition of layers as they are present in the corresponding nitrides because of the AlO_5-polyhedra. Nevertheless there are similarities to the carbides $ScAl_3C_3$,[16] Al_4C_3,[31] Al_3BC,[32] and Al_3BC_3[33] with trigonal bipyramids CAl_5 and a trigonal planar coordination of Al. Formally $Sc_3Al_3O_5C_2$ can be generated by the insertion of one additional oxygen layer or the addition of one formula unit $ScAlO_3$ into the unit cell of ScAlOC. But the relations of coordinations are very different in $ScAlO_3$ (AlO_6 octahedra, ScO_8 polyhedra).[34]

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Table 3. Selected Distances (Å) and Angles (deg) in $Sc_3Al_3O_5C_2$ and $ScAl_2ONC$[a]

$Sc_3Al_3O_5C_2$			
Sc1−C	2.371(2) 6×	C−Sc1−C	86.21(11)°
Sc1−Al2	2.887(1) 6×	C−Sc1−C′	93.79(11)°
Sc1−Sc1	3.2399(8) 6×		
Sc2−O2	2.095(1) 3×	O2−Sc2−O2	101.26(9)°
Sc2−O3	2.141(1) 3×	O3−Sc2−O3	98.36(9)°
Sc2−Sc2	3.2399(8) 6×	O2−Sc2−O3	80.16(6)/177.69(11)
Sc2−Al1	3.383(1) 3×		
Sc2−Al2	3.421(1) 3×		
Al1−O2	1.869(3) 2×	O2−Al1−O2	180°
Al1−O1	1.871(1) 3×	O1−Al1−O1	120°
Al1−Sc2	3.383(1) 6×	O1−Al1−O2	90°
Al1−Al1	3.2399(8) 6×		
Al2−O3	1.822(3)	O3−Al2−C	111.7(1)°
Al2−C	2.013(2) 3×	C−Al2−	107.2(1)°
Al2−Sc1	2.887(1) 3×		
Al2−Sc2	3.421(1) 3×		
Al2−Al2	3.2399(8) 6×		
O1−Al1	1.871(1) 3×	Al1−O1−Al1	120
O1−Sc2	2.813(1) 2×	Al1−O1−Sc2	90
O2−Al1	1.869(3)	Al1−O2−Sc2	116.79(8)
O2−Sc2	2.095(1) 3×	Sc2−O2−Sc2	101.26(9)
O3−Al2	1.822(3)	Al2−O3−Sc2	119.09(7)
O3−Sc2	2.141(1) 3×	Sc2−O3−Sc2	98.36(9)
C−Sc1	2.371(2) 3×	Sc1−C−Sc1	86.21(11)°
C−Al2	2.013(2) 3×	Sc1−C−Al2	81.95(4)°/163.7(2)°
		Al2−C−Al2	107.20(12)
$ScAl_2ONC$			
Sc1−C	2.355(2) 6×	C−Sc1−C	86.03(11)°
Sc1−Al1	2.899(1) 6×	C−Sc1−C′	93.97(11)°
Sc1−Sc1	3.2135(8) 6×		
Sc2−O	2.113(1) 6×	O−Sc2−O	99.90(9)°
Sc2−Al2	3.382(1) 6×	O−Sc2−O′	80.10(9)°
Sc2−Sc2	3.2135(8) 6×		
Al1−N	1.924(4)	N−Al1−C	112.7(1)°
Al1−C	2.016(1) 3×	C−Al1−C	106.0(1)°
Al1−Sc1	2.899(1) 3×		
Al1−Al2	2.998(1) 3×		
Al1−Al1	3.2135(8) 6×		
Al2−O	1.834(3)	O−Al1−N	103.4(1)°
Al2−N	1.907(1) 3×	N−Al2−N	114.8(1)°
Al2−Sc2	3.382(1) 3×		
Al2−Al1	2.998(1) 3×		
Al2−Al2	3.2135(8) 6×		
O−Sc2	2.113(2) 3×	Al2−O−Sc2	118.60(7)°
O−Al2	1.834(3)	Sc2−O−Sc2	98.99(9)°
N−Al2	1.907(1) 3×	Al2−N−Al2	114.8(1)°
N−Al1	1.924(4)	Al2−N−Al1	103.4(1)°
C−Sc1	2.355(2) 3×	Sc1−C−Sc1	86.03(11)°
C−Al1	2.011(2) 3×	Sc1−C−Al1	82.79(4)°/164.7(2)°
		Al1−C−Al1	106.04(12)

[a] esd's in parentheses.

The very rare 5-fold coordination of Al1 is not the kind of 4 + 1 coordination similar to that of Al in carbide layers of $ScAl_3C_3$ and of C2 in Al_4C_3 or the 3 + 2 coordinations in Al_3BC and Al_3BC_3 but more similar to the structural units AlO_5 in some silicates,[35] borates,[36] and phosphates (AlPO-21 family).[37] Interestingly, CN5 as a tetragonal pyramid was recently found for the high pressure modification of P_3N_5.[38]

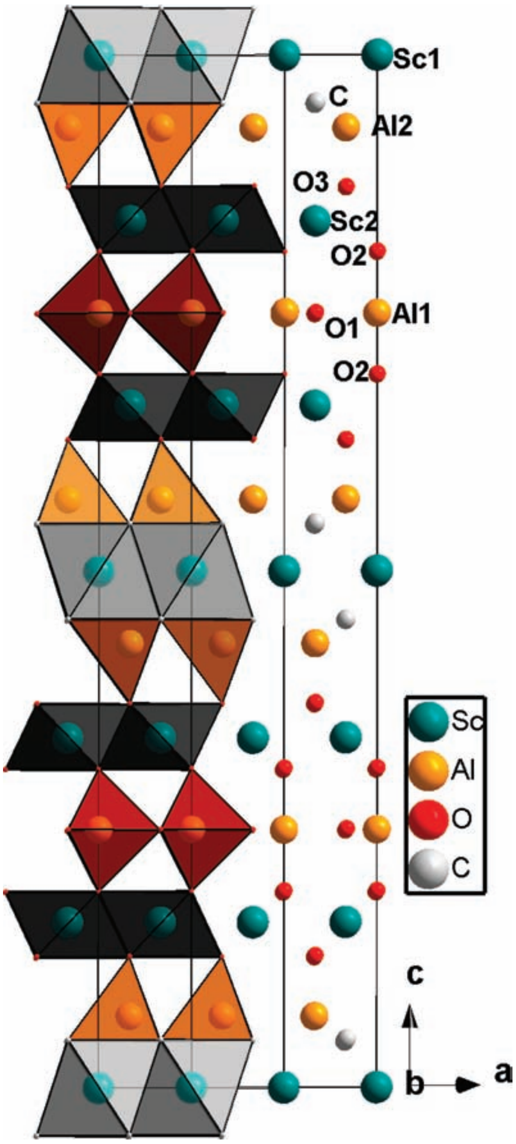

Figure 1. Crystal structure of $Sc_3Al_3O_5C_2$.

$ScAl_2ONC$. Similar to ScAlOC the crystal structure of $ScAl_2ONC$ (Figure 3) bases on a closest packing of the anions with Sc in octahedral and Al in tetrahedral voids. The coordination polyhedra are shown in Figure 4. Two consecutive layers are in each case formed by oxygen and carbon which are separated by one layer of nitrogen. The layer sequence in the direction [001] is

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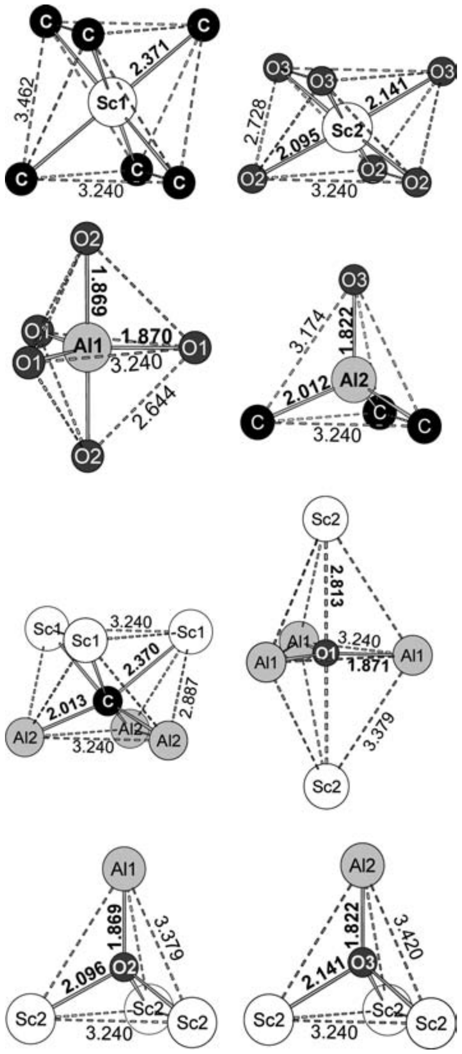

Figure 2. Coordination polyhedra in $Sc_3Al_3O_5C_2$.

*A*B**AB**A*BC*A**CA**C*AB*C**BC**B*C* (O-layers in *italics*, C-layers in **bold**, N-layers normal). According to Jagodzinski[2] the repeating unit of 18 layers is (h**hh**h*cc*)$_3$. Sc atoms occupy the octahedral voids between the layers of equal anions (OO or CC), while Al is in half of the tetrahedral voids next to the N-layers (ON or CN). Because of electrostatic reasons, the connection of the AlX_4 tetrahedra via a common face is avoided. In total there result alternating layers of ScO_6 octahedra and ScC_6 octahedra which are connected by double layers of edge-sharing tetrahedra AlC_3N and $AlON_3$.

Two different Sc atoms result from this pattern. The one is octahedrally coordinated by carbon (Sc−C: 2.357(3) Å), and the other by oxygen (Sc−O: 2.112(2) Å). While the ScO_6-octahedra are considerably compressed in the direction of the c-axis (symmetry D_{3d}, O−Sc−O: 81.0°), the ScC_6-octahedra are less distorted but elongated (C−Sc−C: 94.0°). The tetrahedral surroundings of the two Al atoms are different. While Al1 is coordinated by three C atoms (2.011(2) Å) and one N atom (1.919(6) Å), the neighbors of Al2 are one O atom (1.834(5) Å) and three N atoms (1.907(1) Å). The AlC_3N and $AlON_3$ tetrahedra (symmetry C_{3v}) show small deviations from the ideal symmetry (N−Al−N: 103.4°−114.8°). All these distances reflect the different atom sizes and the assumption of ordered anion sites.

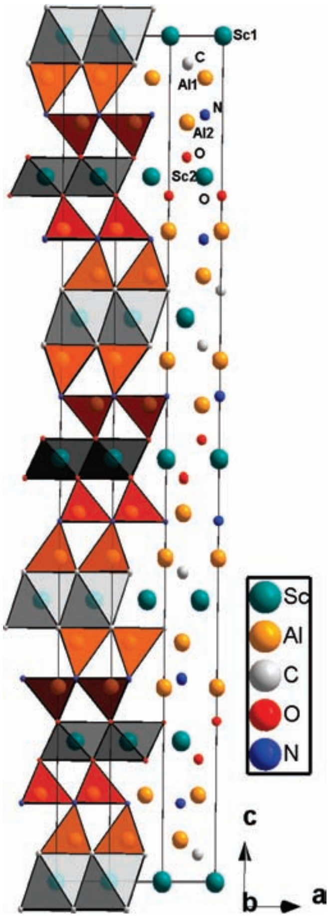

Figure 3. Crystal structure of $ScAl_2ONC$.

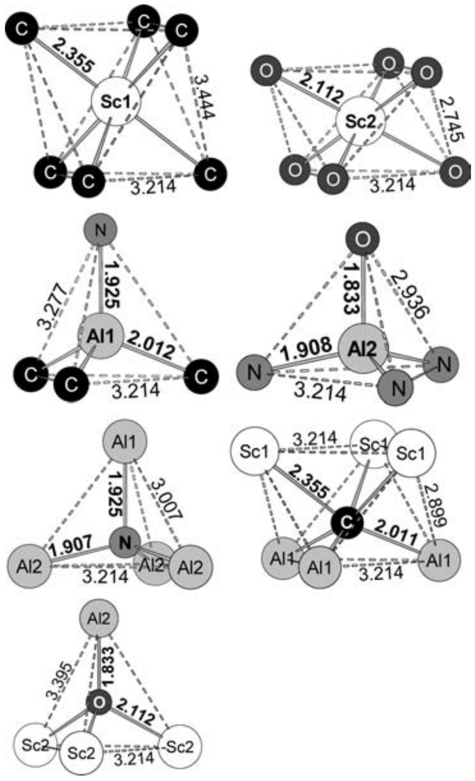

Figure 4. Coordination polyhedra in $ScAl_2ONC$.

The relation of $ScAl_2ONC$ to ScAlOC is quite simple because the structure of $ScAl_2ONC$ is obtained from ScAlOC by additional layers of a composition AlN (ScAlOC + AlN = $ScAl_2ONC$). The orientation of the Al tetrahedra corresponds to the hexagonal stacking of the wurtzite-type.

Regarding $ScAl_2ONC$ as an interstitial compound as usually done for transition metal carbides[4,5] the structure can also be described in terms of the closest packing of metal atoms. Then the metal atoms form a closest packing with the sequence A**B**CB**A**BC**A**BA**C**AB**C**AC**B**C (Jagodzinski: (c**c**ch**c**h)$_3$, Sc in **bold**).

Although $ScAl_2ONC$ shows a very simple and "plausible" structure it is surprising that an ordered structure with three different anion sites is realized despite that solid solutions are known for all combinations. Obviously the structure is optimized for the different interactions. This is suggested by the bond orders. Brown[39] has developed a method to calculate bond orders from the interatomic distances. According to this the following values are obtained for $ScAl_2ONC$: Sc1: 2.89, Sc2: 2.95, Al1: 2.99, Al2: 2.89, O: 2.03, N: 3.07, C: 3.66.

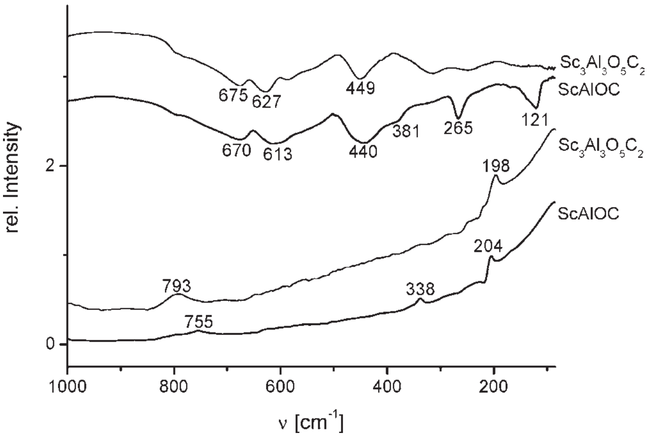

Figure 5. IR (top) and Raman spectra (bottom) of ScAlOC and $Sc_3Al_3O_5C_2$.

Chemical Stability. Similar to ScAlOC the chemical stability of $ScAl_2ONC$ and $Sc_3Al_3O_5C_2$ is remarkably high. As the single crystals can be isolated from the excess metallic melt by treatment with 5*n* hydrochloric acid over a time of several days, there is a quite high resistance against concentrated acids. This is in contrast to closely related compounds like Al_4C_3, $ScAl_3C_3$, or the very sensitive binary scandium carbides.[40] Obviously the formation of oxide carbides enhances the chemical stability of ionic carbides.

Microhardness. Because of the potentially interesting material properties of $Sc_3Al_3O_5C_2$, the microhardness was measured (see Experimental Section). The first observation was the pronounced brittleness of the crystals, similar to ScAlOC. The measurement following the Vickers method provides a value for H_V = 9.0 GPa, the Knoop method was

Table 4. Observed and Calculated Composition (mol %) from EDXS Measurements, Observed Values Averaged from 10 spots, Standard Deviations in Parentheses

	ScAlOC		$Sc_3Al_3O_5C_2$		$ScAl_2ONC$	
	calc.	obs.	calc.	obs.	calc.	obs.
Sc	25.0	25.7(4)	23.1	22.6(5)	16.7	16.3(8)
Al	25.0	26.3(5)	23.1	22.0(4)	33.3	32.1(6)
O	25.0	23.9(4)	38.5	40.6(6)	16.7	20.9(13)
N	not detected		not detected		16.7	11.0(8)
C	25.0	24.1(5)	15.4	14.9(8)	16.7	19.6(12)

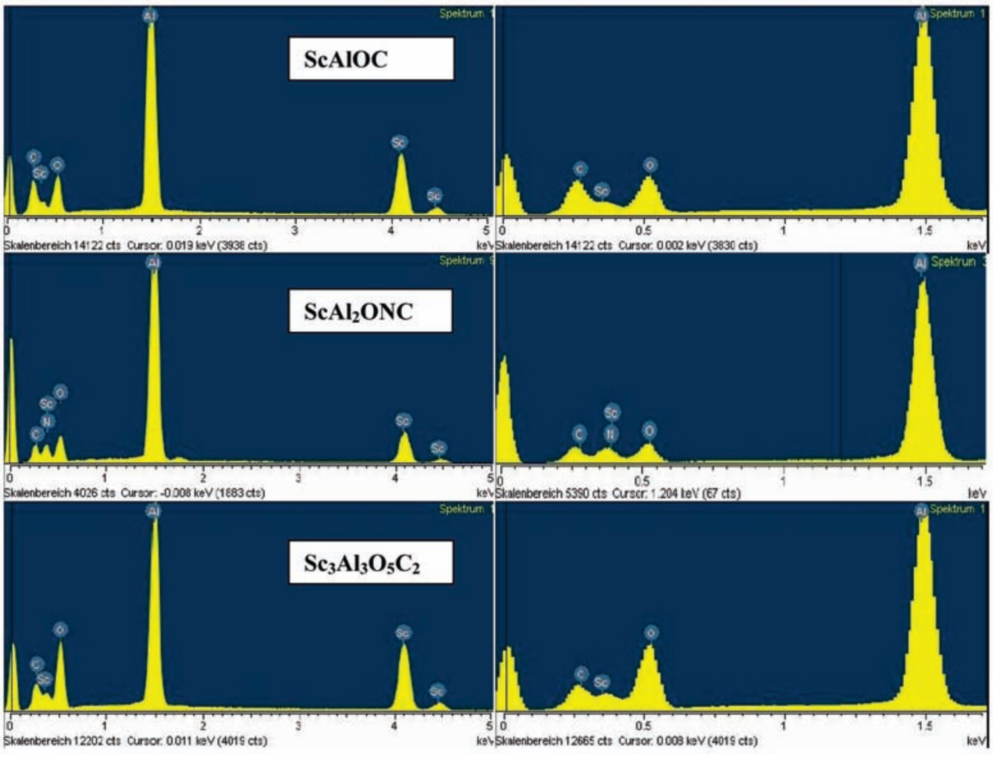

Figure 6. EDXS of ScAlOC, $Sc_3Al_3O_5C_2$, and $ScAl_2ONC$ (from top to bottom); U = 15 kV.

also successful and yielded a hardness of $H_K = 11.0$ GPa. These values are slightly higher than for ScAlOC ($H_K = 9.0$ GPa)[1] indicating more oxide-bonding in $Sc_3Al_3O_5C_2$, but the hardness is still clearly below Al_2O_3 (21 GPa[41]).

$ScAl_2ONC$ single crystals were too thin for microhardness measurement.

Vibrational Spectra. Figure 5 shows the vibrational spectra of $Sc_3Al_3O_5C_2$ in comparison to those of ScAlOC. According to the black color of the samples they were diluted with KBr and the power of the laser reduced. Therefore the quality of the spectra is reduced but Raman modes at 755, 338, 204 cm^{-1} as well as 675, 627, 449 cm^{-1} for $Sc_3Al_3O_5C_2$ and IR-modes at 670, 613, 440, 381, 265, and 121 cm^{-1} as well as 793 and 198 cm^{-1} for $Sc_3Al_3O_5C_2$ were clearly detected. Again, the similarity of the spectra and their small differences are in line with the close structural relationship.

The possibility to record vibrational spectra of $Sc_3Al_3O_5C_2$ is in agreement to the description of the bonding situation as an electron precise compound (band gap: 0.3 eV) where the ionic interaction contains significant covalent amounts.

Vibrational spectra of $ScAl_2ONC$ are not yet available because of the lack of a sufficient amount of single phase sample.

EDXS Measurements. The small difference of the electron numbers of carbon and oxygen requires an independent determination of the O- and C-content despite the very good *R*-factors of the refinement. Furthermore the close similarity to the (up to now) hypothetical nitrides asks for a clear statement on the nitrogen content which is difficult by X-ray means. Finally the crystal growth from a metallic melt at very high temperatures might result in a contamination of the crystal by another metal or nitrogen from the atmosphere or the educts. Therefore the same crystals which were already used for the structure determination were subsequently used for an analysis by EDXS. The crystal shape of well-shaped platelets with plane faces enabled a reliable analysis even for the light elements. Measurements by EDXS confirmed for ScAlOC and $Sc_3Al_3O_5C_2$ the absence of any other element except Sc, Al, O, and C. The ratios observed (Table 4) were in excellent agreement to the expected values for stoichiometric and electron precise scandium aluminum oxide carbides according to the crystal structures derived from the X-ray investigations.

Clear statements on $ScAl_2ONC$ are more difficult. The reason is the coincidence of the nitrogen K-peak and the scandium L-peak near 0.35 keV. For $ScAl_2ONC$ the intensity is nearly equal to the peaks for oxygen and carbon (Figure 6). A comparison to ScAlOC and $Sc_3Al_3O_5C_2$ shows that the intensity cannot result from the Sc−L peak alone but must contain a fraction of the N−K line, too. To ensure the comparability, all measurements were done subsequently with the same calibration under identical conditions (15 kV). With the assumption of both elements the fitting results in a N-content of 11%.

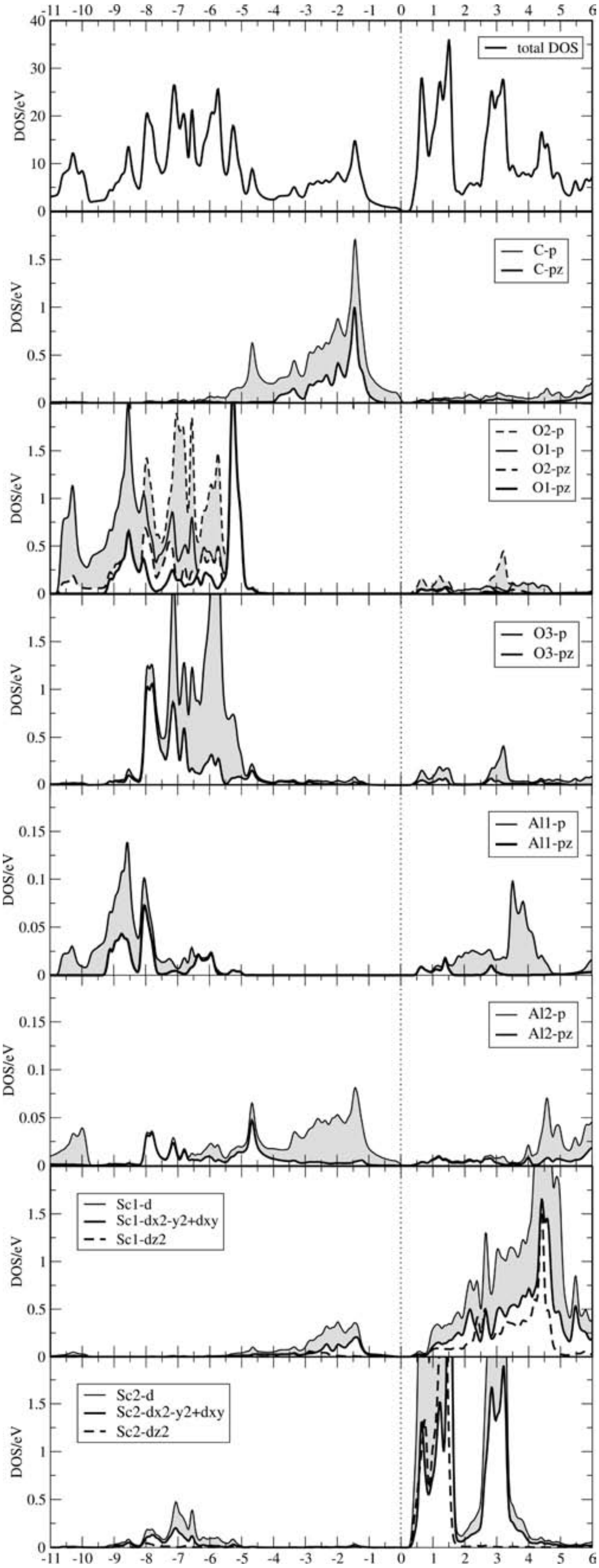

Figure 7. Density of states in $Sc_3Al_3O_5C_2$; from the top down: TDOS of $Sc_3Al_3O_5C_2$; C p-PDOS; O p-PDOS of O1 and O2 (AlO_5-unit); PDOS of O3; p-PDOS of Al1 (AlO_5-unit); p-DOS of Al2 ($AlOC_3$ tetrahedra); Sc1-d-DOS (ScC_6 octahedra); Sc2-d-DOS (ScO_6 octahedra).

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Table 5. Calculated Band Gaps for Oxide Carbides and Related Compounds

compound	ScAlOC	$Sc_3Al_3O_5C_2$	$ScAl_3C_3$	$ScAlO_3$	Al_4C_3	Al_2O_3	Al_4O_4C
LB	Sc1-d_{xz}+d_{yz}	Sc1-d_{xz}+d_{yz}	Sc-d_{xz}+d_{yz}	Sc-d	C2-p	O-p	C-p
VB	C-p	C-p	C-p	O1-p, O2-p	Al1-p	Al1-p	Al3-p
E_g, calc. [eV]	0.6	0.3	0.5	5.0	1.8	7.0	6.0
color of bulk materials	brownish-black	black	black-metallic[16]	colorless[26]	yellow-greenish, sometimes orange-red[13,14]	colorless[17]	colorless[15]

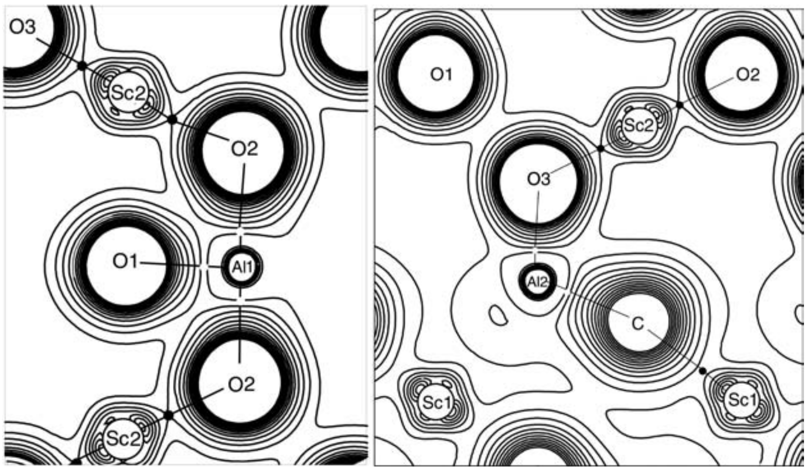

Figure 8. Valence electron density (Bader analysis) of $Sc_3Al_3O_5C_2$ in the *a-c* plane; left, AlO_5 unit; right, $AlOC_3$ tetrahedron and ScO_6 octahedron.

Table 6. Charges for Oxide Carbides and Related Compounds, Calculated with the Bader Formalism

atom (coordination)	ScAlOC	$Sc_3Al_3O_5C_2$	$ScAl_3C_3$	$ScAlO_3$	Al_4C_3	Al_2O_3	Al_4O_4C
Sc1 (C)	+1.88	+1.85	+1.86				
Sc2 (O)	+2.21	+2.22		+2.21			
Al (O/C)	+2.49	+2.52					+2.60
Al (C)			+2.45		+2.35; +2.40		
Al (O)		+2.66		+2.66		+2.63	+2.66
O (Sc/Al)	−1.62	−1.56 −1.60 −1.77(CN 5)		−1.61 −1.63			
O (Al)						−1.76	−1.79; −1.88
C (Sc/Al)	−2.93	−2.94	−2.9; −3.0				
C (Al)			−3.35		−3.20; −3.24		−3.20
C (Sc)							

This is slightly lower than the value expected for $ScAl_2ONC$, but the reliability is reduced. Furthermore, a partial substitution by O/C cannot be excluded. This might explain the slightly enlarged content of O and C (Table 4).

Bonding. Although the scandium aluminum oxide carbides represent a new type of compounds, their structural description and classification is quite simple. In contrast, the understanding of their chemical bonding is a fundamental task because of their uniqueness. First investigations were done for ScAlOC revealing a mainly ionic interaction with higher covalent parts for carbon and scandium. The characterization of further oxide carbides enables to verify the characteristic findings side by side and to compare differences and commonalities of Sc^{3+}/Al^{3+} and O^{2-}/C^{4-}. Therefore, electronic structure calculations were done for $Sc_3Al_3O_5C_2$, too.

The most significant structural difference between ScAlOC and $Sc_3Al_3O_5C_2$ is the trigonal bipyramidal surrounding of one Al1-site which can also be observed in a significant difference of distribution of partial densitiy of states (PDOS). Figure 7 gives an overview to the distribution of states in $Sc_3Al_3O_5C_2$. All in all the bonding in $Sc_3Al_3O_5C_2$ is quite similar to that in ScAlOC: The PDOS shows that the highest occupied states are dominated by C p states (especially p_x and p_y) while O p states are significantly lower in energy. Furthermore the states of C show more dispersion because of the higher covalence and the greater reduction of the effective charge. The dispersion of the oxygen states, especially O1 and O2, which are part of the AlO_5 layer, is much smaller indicating the more pronounced ionic interaction. A difference between O1 and O2 on the one side and O3 on the other is observable for the energy of the p states. While for both O1 and O2 p_z is higher than p_x and p_y, the p_z states of O3 are lower, similar to the O states in ScAlOC. Therefore the oxygen layer which is added in $Sc_3Al_3O_5C_2$ does not cause a different energy distribution of oxygen states but a

Table 7. Calculated Valence Electron Densities ρ_{val}^{bcp} [a]

[e/A^3]	ScAlOC	$Sc_3Al_3O_5C_2$	$ScAl_3C_3$	$ScAlO_3$	Al_4C_3	Al_2O_3	Al_4O_4C
ρ_{val}^{bcp} (Al−C)	0.46	n.d.	0.43		0.53; 0.55		0.52
ρ_{val}^{bcp} (Al−O)	0.52	0.49; 0.50		0.44; 0.47		0.51	0.50 − 0.71
ρ_{val}^{bcp} (ScC_6)	n.d.	n.d.	0.32				
ρ_{val}^{bcp} (ScO_6)	0.45	0.45; 0.49		0.52; 0.48; 0.46			

[a] n.d.: not to determine.

Table 8. Crystal Radii, Distance to Bond Critical Points (BCPs), and Effective Charges (Bader Analysis) in $Sc_3Al_3O_5C_2$

atom (CN)	effective charge	*r* (crystal)/ *r* (ion)[34] estimated from plot	*d* (*M*/*X*−BCP)	*d* (*M*/*X*−BCP) calculated Wien2k
Sc1 (6)	$Sc^{1.85+}$	0.745/0.885	0.91 (Sc1−C)	
Sc2 (6)	$Sc^{2.22+}$	0.745/0.885	0.85 (Sc2−O2) 0.82 (Sc2−O3)	1.06 (Sc2−O2) 1.07 (Sc2−O3)
Al1 (5)	$Al^{2.66+}$	0.48/0.62	0.61 (Al1−O1) 0.56 (Al1−O2)	0.78 (Al1−O1) 0.78 (Al1−O2)
Al2 (4)	$Al^{2.52+}$	0.39/0.53	0.54 (Al2−O3) 0.59 (Al2−C)	0.77 (Al2−O3) 0.81 (Al2−C)
O1 (3)	$O^{1.77-}$	1.38/1.24	1.26 (Al1−O1)	1.09 (Al1−O1)
O2 (4)	$O^{1.56-}$	1.38/1.24	1.31 (Al1−O2) 1.27 (Sc2−O2)	1.09 (Al1−O2) 1.07 (Sc2−O2)
O3 (4)	$O^{1.60-}$	1.38/1.24	1.28 (Al2−O3) 1.29 (Sc2−O3)	1.07 (Al2−O3) 1.08 (Sc2−O3)
C (6)	$C^{2.93-}$	1.61/1.47[a]	1.43 (Al2−C) 1.46 (Sc1−C)	1.22 (Al2−C)

[a] Not listed, values calculated from Be_2C and *r* (Be^{2+}): 0.41/0.27 Å.

different shape of the oxygen PDOS in comparison to those in ScAlOC.

The different bonding of the two Al atoms is clearly seen, too. The p states of Al1 are well localized at very low energy. The p_x and p_y states of Al2, which are mainly involved in the interaction with carbon, are very broad and significantly higher in energy while the p_z states are more localized and at lower energy.

Also, the Sc atoms are very different. Again there are broader dispersions of the Sc1 d states according to more covalent Sc−C bonds and smaller ones for Sc2 consistent with more ionic Sc−O bonds. The differences can be explained by different d-orbital interactions similar to those in ScAlOC. The trigonal symmetry leads to a splitting of orbital energies according to: $d_{z^2} < d_{xy}, d_{xz} < d_{xy}, d_{x^2-y^2}$. The contribution of the d_{z^2} orbitals to the bonding states is very small while the other orbitals give a significant contribution. The interaction of the d_{xy} and d_{xz} orbitals (π bonding) of Sc atoms with the p orbitals of carbon leads to stronger overlap than with those of oxygen. As a consequence the states of Sc2 are narrower than for Sc1 owing to its higher ionicity (−2.21 vs −1.88, see below).

The band gap is about 0.3 eV and is in agreement with brownish-black single crystals. A detailed view on the band structure shows that it is an indirect band gap. The lowest states of the conduction band are mainly formed by d states of scandium while the Al p states are higher and preferably in the range of the C p states. This kind of electronic structure is significant for this type of compounds and is always characterized by significant covalence in crystal bonding. This can be pursued for the electronic structure of $ScAl_3C_3$.

The band gaps calculated for ScAlOC, $Sc_3Al_3O_5C_2$, and comparable compounds (Table 5) agree with the color of single crystals and powders. On the one hand band gaps are narrow if there are Sc atoms with d orbitals involved in the valence domains, on the other hand C atoms are responsible for more covalence which results in narrower band gaps, too. O atoms provide large band gaps because of the more ionic influence to bonding in oxides in general. This becomes clear when ordering the compounds according to the value of their band gaps: $Sc_3Al_3O_5C_2 < ScAl_3C_3 < ScAlOC < Al_4C_3 < ScAlO_3 < Al_4O_4C < Al_2O_3$.

According to the Bader formalism[42] effective charges can be calculated from the valence charge densities. As expected the resulting charges are smaller than the idealized values because of the covalent part (Table 6). The charge of Al is higher than for Sc in general because for Sc the d orbitals' participation enlarges the covalent part of the interaction. Bader analysis provides partial charge transfers from the cations to the anions. This charge transfer gives the dimension of ionicity of bonding in $Sc_3Al_3O_5C_2$ in comparison to ScAlOC, $ScAl_3C_3$, Al_4C_3, $ScAlO_3$, Al_4O_4C, and Al_2O_3 (Table 6). According to the O1 p-PDOS, Al1 and O1, which are bound in the AlO_5 unit, show higher charges than the other atoms. The Al1−O bond should be more ionic than the other Al2−O bonds in $Sc_3Al_3O_5C_2$. In fact it is more than just a formalism to explain the structure of $Sc_3Al_3O_5C_2$ by insertion of one formula unit $ScAlO_3$ ($Sc_3Al_3O_5C_2 = 2\ ScAlOC + ScAlO_3$). The additional AlO_5 unit causes an additional "ionic oxide bonding" in $Sc_3Al_3O_5C_2$. The charges calculated are quite similar to those of Al_2O_3 (Al: +2.63; O: −1.75), where Al atoms are coordinated octahedrally by oxygen. Higher effective charges indicate oxide-bonding in general: The charges of Al (+2.66) and Sc (+2.21) in $ScAl_3O_3$ follow the same direction.

The simple structure and its high symmetry enable a clear representation of the valence electron density in real space. Figure 8 shows valence charge densities along the *a*-*c* plane including the AlO_5 unit. Furthermore its topological analysis results in bond critical points, that is, saddle points of the valence electron density, which give insights to the bonding situation.

At first the clear implementation of the bond critical points attracts attention. The absolute values of the electron densities (Table 7) show significant amounts of charge density at bond critical points which indicate regions of covalent bonding. Nevertheless it clearly shows that scandium aluminum oxide carbides continue the row of binary and ternary oxides and carbides according to the bonding properties and should be regarded as mainly ionic compounds.

Furthermore "ionic" radii might be derived from the distances between bond critical points and the center of

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(42) Bader, R. W. F. *Atoms in Molecules. A Quantum Theory.; Int. Series of Monographs on Chemistry*; Clarendon Press: Oxford, 1994.

each atom (Table 8). These values show that the observed values are quite close to the crystal radii as they are given by Shannon.[43] In comparison the different radii of Al1 and Al2 correspond to the unequal effective charge and/or coordination numbers. The differences between Sc1 and Sc2 can be seen as well. In general the values are quite similar to those of ScAlOC. As already pointed out in the discussion on ScAlOC[1] the radius of a C^{4-} anion is difficult to determine because of the lack of ionic carbides with isolated carbon atoms. The results for $Sc_3Al_3O_5C_2$ confirm a value of about 1.45 Å for the crystal radius. This is perfectly in a line with the crystal radii of F^- (1.19 Å), O^{2-} (1.24 Å), and N^{3-} (1.32 Å).

BCPs can also be obtained from a topological analysis, although no BCP is found for the Sc−C bond. This is a well-known problem and was observed for ScAlOC, too. This method yields radii being much closer to the atomic radii which are expected for a mainly covalent bond. Up to now there is little experience on the reliability of this approach, so further investigations seem to be necessary. Among others, calculations for $ScAl_2ONC$ are in progress.

It should be mentioned that for ternary carbides of transition metals and rare earth elements with isolated carbon atoms (for example Pr_2MoC_2 and $Pr_2Mo_2C_3$) Kniep et al. have found a remarkably high covalent Mo−C bonding interaction.[44] Therefore, they described these compounds as "carbometallates" with Pr^{3+} cations and 2D- (Pr_2MoC_2) or 3D-arrangements ($Pr_2Mo_2C_3$) of tetrahedral complex anions $MoC_4{}^{n-}$. But compared to scandium aluminum oxide carbides the electronegativities (Pauling) are different, favoring a more covalent bond Mo−C than Sc−C. Alternatively one can expect that the filled d states of Mo interact more efficient with the p orbitals of carbon than the empty d states of Sc.

Nevertheless, the bonding situation in oxide carbides and, in particular, for the C^{4-} species is a very special one. Therefore, it is the topic of further theoretical work and thermodynamic calculations. Furthermore, NMR-measurements are in progress as there are several NMR-active nuclei (^{45}Sc, ^{27}Al, ^{13}C, ^{15}N). Additionally it is planned to amend the measurements by the calculation of NMR shifts and coupling parameters on the basis of band structure calculations.

Conclusions

The structures of $Sc_3Al_3O_5C_2$ and $ScAl_2ONC$ continue and extend the building principle of oxide carbides first discovered for ScAlOC.

The variation of the structures only affects those layers of anions which include aluminum cations, ScC_6 and ScO_6 layers remaining. These quaternary compounds consist of closest packed anions and cations whereas the sequence of the anions is different. All octahedral voids and half of the tetrahedral voids are occupied with the cations. In comparison to closely related compounds like Al_4C_3 and $ScAl_3C_3$, one can observe similar and typical bond distances. Characteristics for this type of compounds can be listed as follows:

(1) The compounds ScAlOC, $Sc_3Al_3O_5C_2$, and $ScAl_2ONC$ are stochiometric and electron precise compounds.
(2) Sc atoms occupy exclusively octahedral voids and are coordinated only with one sort of anion, carbon or oxygen.
(3) Al atoms usually occupy tetrahedral voids and are coordinated with all sorts of anions.
(4) If this occupation of tetrahedral voids with Al atoms leads to neighboring layers of tetrahedral voids with different occupation, like in $ScAl_3C_3$ (full and half occupation) or $Sc_3Al_3O_5C_2$ (half and zero occupation), there will be a formal shift of Al atoms into the empty voids. In consequence a trigonal bipyramidal coordination of aluminum might be observed like in $Sc_3Al_3O_5C_2$.
(5) Bonding is always characterized by both covalent and ionic fractions. Covalent bonding is caused by d-p-π-bonding because of the involved Sc d orbitals and C p orbitals. Higher ionic amounts result from "oxide-bonding" which emerges in oxygen-rich variations of ScAlOC (i.e., $Sc_3Al_3O_5C_2$).

Interestingly similar building principles were also found for other high-melting transition metal compounds. In these multinary compounds the crystal structures show the characteristic features of the underlying binary compounds. One example are ternary carbides of the composition $(MC)_n$-(MA)[45] (so-called "MAX-phases", i.e., Ta_4AlC_3, Ta_3AlC_2, Ta_2AlC[46] with M = Ta, A = Al, and n = 1, 2, 3), where the carbide part $(MC)_n$ is a cutout of the NaCl type and the intermetallic part MA represents a hexagonal closest packing. For the ternary borides $(MB_2)_nAl$ like Cr_4AlB_6, Cr_3AlB_4, Fe_2AlB_2[47] the motif of the cubic body centered packing (AlM_8) is combined with the trigonal prisms BM_6 of the binary borides MB, M_2B_3, and M_3B_4. In the boride carbides $(NbB)(NbB_2)_n(NbC)_m$ (for example: Nb_3B_3C, $Nb_4B_3C_2$, $Nb_6B_4C_3$, $Nb_7B_3C_3$)[48] the motifs of binary carbides and binary borides are combined. In all these cases synthesis and crystal growth were enabled by using molten metals as a flux. The different compounds were obtained by relatively small variation of the conditions of reaction (i.e., temperature, cooling rates, molar ratios). This might explain why the different variants can be yielded as (more or less) single phase samples despite the (probably) small differences of their formation energies.

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