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Synthesis, Structure, Bonding, and Properties of the Oxide Carbide ScAlOC, a New Type of Compound

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Abstract: Single crystals of ScAlOC were obtained by reacting Sc_2O_3 and C in an Al melt at 1600 °C. The crystal structure (space group $R\bar{3}m$, $Z = 6$, $a = 3.2599(7)$ Å, $c = 30.116(9)$ Å, 190 refl., 15 param., $R_1(F) = 0.0212$, $wR_2(F^2) = 0.0397$) can directly be derived from the binary nitrides AlN and ScN. ScAlOC represents a new type of compound. It is the first oxide carbide of a transition metal with an ordered distribution of the anions. They form a cubic closest packing with alternating double layers of C and O while Al and Sc occupy tetrahedral and octahedral voids, respectively. The resulting polyhedra are AlC_3O tetrahedra as well as ScO_6 and ScC_6 octahedra. According to band structure calculations ScAlOC is electron precise with an indirect band gap of 0.6 eV. Calculations of charges and charge densities reveal that the mainly ionic bonding contains significant covalent contributions, too. The black crystals of ScAlOC are very brittle and show a microhardness of 9.0 GPa. Thermal decomposition on air starts at 650 °C; in inert atmosphere ScAlOC is stable up to 1300 °C at least.

Introduction

Metal oxides with a very high lattice energy like Al_2O_3, ZrO_2, and MgO are of outstanding importance as ceramic materials because of their high chemical, mechanical, and thermal stability.[1] Owing to the mostly ionic interaction their crystal structures are practically described in terms of the closest sphere packing of oxide anions, while the cations occupy voids of matching size.[2,3] With respect to hardness and melting points, these oxides are excelled by the carbides of the "early" (i.e., group 4 to 6) transition metals (TiC, WC), which belong to the hardest and highest-melting materials of all.[4] Following a proposal of Hägg[5] these carbides are classified as interstitial carbides. Here the C atoms are located in voids in the closest packing of metal atoms frequently accompanied by partial occupations. It is concluded from the properties (hardness, brittleness, metallic conductivity) and theoretical calculations that the interaction contains covalent, ionic, and metallic contributions as well.[6]

This remarkable difference in bonding characteristics is also noticeable in ternary compounds. Ordered oxide carbides of transition metals are unknown.[7] Only elements of group 3, 4, and 5 are able to form a solid solution of the formula TMO_xC_{1-y} (TM = Sc,[8] Ti,[9] Zr,[10] Hf,[11] V,[12] Nb[13]) with NaCl type structure. These phases are only poorly characterized. They are formed as powders at very high temperatures. Furthermore O and C are difficult to discriminate, and the octahedral voids are partly occupied (i.e., $x \neq y$). For main group elements (group 13, 14, and 15) ternary phases E/O/C are only known for aluminum. Al_2OC was characterized as a mixed crystal with a wurtzite structure.[14] Al_4O_4C[15,16] plays a special role. It is the only oxide carbide with ordered sites for oxygen and carbon and shows a unique structure with AlO_3C-tetrahedra linked by corners and vertices.

In earlier contributions we have already shown that the use of molten metals enables synthetic access to high-melting

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(1) Cawley, J. D.; Lee, W. E. *Oxidic Ceramics in Materials Science and Technology*; Cahn, R. W., Haasen, P., Kramer, E. J., Eds.; Verlag Chemie: Weinheim, Germany, 1994; Vol. 11.

(2) Müller, U., *Anorganische Strukturchemie*; Verlag Teubner: Wiesbaden, Germany, 5. Auflage, 2006.

(3) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford Press: 1984.

(4) Freer, R., (ed.) *The Physics and Chemistry of Carbides, Nitrides and Borides*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990.

(5) Hägg, G. *Z. Phys. Chem., Abt B* **1931**, *12*, 33.

(6) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic Press: New York, 1971.

(7) Villars, P.; Calvert, L. D. *Pearson's Handbook, Crystallographic Data for Intermetallic Phases*; ASM International: Materials Park, OH, 1997 (CD-ROM version 2.0, 2008).

(8) Karen, P.; Hajek, H.; Valvoda, V. *J. Less-Common Met.* **1986**, *120*, 337–344.

(9) Afir, A.; Achour, M.; Saoula, N. *J. Alloys Compd.* **1999**, *288*, 124–140.

(10) (a) Zainulin, Y. G.; Alyamovskii, S. J.; Shveikin, G. P.; Geld, P. V. *Russ. J. Inorg. Chem.* **1973**, *18*, 1052–1053. (b) Constant, K.; Kieffer, R.; Ettmayer, P. *Monatsh. Chem.* **1975**, *106*, 823–832.

(11) (a) Zainulin, Y. G.; Alyamovskii, S. J.; Tskhai, V. A.; Shveikin, G. P.; Geld, P. V. *Inorg. Mater.* **1972**, *8*, 1558–1560. (b) Constant, K.; Kieffer, R.; Ettmayer, P. *Monatsh. Chem.* **1975**, *106*, 973–981.

(12) Zainulin, Y. G.; Alyamovskii, J.; Shveikin, G. P.; D'Yachkova, T. V.; Shilyaeva, O. J. *Inorg. Mater.* **1979**, *15*, 360–362.

(13) D'Yachkova, T. V.; Alyamovskii, J.; Zainulin, Y. G. *Inorg. Mater.* **1987**, *23*, 56–60.

(14) (a) Amma, E. L.; Jeffrey, G. A. *J. Chem. Phys.* **1961**, *34*, 252–259. (b) Grass, V. E.; Raybkov, Y. I.; Goldin, P. A.; Sitnikov, P. A. *J. Struct. Chem.* **2004**, *45*, 100–106.

(15) Jeffrey, G. A.; Slaughter, M. *Acta Crystallogr.* **1963**, *16*, 177.

(16) Meyer, F. D. Diploma thesis, Universität Freibur, 1995.

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compounds which are not obtained by conventional high temperature syntheses.[17] Now we report on ScAlOC as the first oxide carbide of a transition metal, which represents to our knowledge a new type of compounds. At first ScAlOC was obtained as a byproduct from the investigation of scandium borides.[18] After definite identification, a direct method of synthesis was found (see Experimental Section). ScAlOC forms black hexagonal platelets. Powdered samples are of dark-brown color.

Experimental Section

Synthesis and Characterization. For the synthesis of ScAlOC, Sc_2O_3 and C were reacted with an excess of aluminum (ratio Sc_2O_3/C/Al as 1:0.33:40). The starting materials (total mass: ca. 2 g) were mixed and heated in a corundum crucible at 300 °C/h to 1600 °C under a flow of argon. After a dwelling time of 5 h, it was cooled at 20 °C/h to 600 °C and then the furnace was turned off. The solidified melt was treated with 5 N hydrocloric acid. The only crystalline products were black hexagonal platelets ($Ø_{max.} = 0.6$ mm). Alternatively Al_4C_3 can be used as a dwell of carbon.

Structure Analysis. A hexagonal platelet (diameter 0.3 mm, thickness 0.08 mm) was selected under a microscope. Reflection intensities were measured using a single crystal diffractometer with an image plate detector (Stoe IPDS II, Mo Kα). The indexing routine led to a rhombohedral unit cell. Lattice constants were refined from the data set[19] to $a = 3.2599(7)$ Å and $c = 30.116(9)$ Å. Measurement of 1486 reflections up to $2\theta = 70°$ and merging in Laue class $\bar{3}m$ resulted in a data set of 190 unique reflections (155 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[20] 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. Finally R-values of $R_1(F) = 0.0212$ and $wR_2(F^2) = 0.0397$ were obtained. The refinement of the site occupation factors revealed no significant deviations from a stoichiometric composition. Further details are listed in Tables 1−3. 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-419683.

Characterization. High reaction temperatures and the high reactivity of the melt can lead to unexpected contaminations (crucible, metallic melt, starting material). Therefore single crystals of ScAlOC were analyzed by energy dispersive X-ray spectroscopy (EDX). Solely the elements C, O, Al, and Sc were detected. Observed percentages were 26:26:24:24, in agreement with the X-ray results. According to comparative measurements for compounds with known compositions, the error is estimated to be 2% for C/O and 1% for Al/Sc.

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

Table 1. Structure Determination and Refinement of ScAlOC

crystal shape	hexagonal platelet
crystal color	black lustrous
crystal size	$0.1 \times 0.1 \times 0.015$ mm^3
formula weight	599.70 g/mol
crystal system	rhombohedral
space group	$R\bar{3}m$ - Nr. 166
lattice constants	$a = 3.2599(7)$ Å; $c = 30.116(9)$ Å
cell volume	277.16 Å^3
formula units	6
density, calculated	3.59 g/cm^3
radiation	Mo Kα, graphite monochromator
θ-range	$-4 \le h \le 4, -4 \le k \le 4, -48 \le l \le 48$
temperature	23 °C
$2\theta_{max}$	70°
diffractometer	Stoe IPDS II
mode of measurement	rotation method, $\varphi\Delta = 2°$; 300 s per frame
reflections measured	1486
independent reflections	190
reflections $I > 2\sigma(I)$	155
absorption correction	numerical; program XSHAPE[19]
$R_{int.}$, R_{sigma}	0.101, 0.056
absorption coefficient	4.0 mm^{-1}
extinction coefficient 20	0.0095(17)
max./min transmission	0.631; 0.406
structure solution	direct methods 20
refinement	SHELXL 20
residual electron e$^-$/Å^3 min, max, sigma	+0.45, −0.53, 0.11
weighting function 20	0.0177; 0.0
number of parameters	15
R-factors	$R_1(F) = 0.0212$; $wR_2(F^2) = 0.0397$

Table 2. Coordinates, Thermal Displacement Parameters (in Å^2) and Site Occupation Factors in ScAlOC; Esd's in Parentheses, $U_{11} = U_{22} = 2\,U_{12}$, $U_{23} = U_{13} = 0$

atom	site	x	y	z	U_{eq}	sof[a]	U_{11}	U_{33}
Sc1	3a	0	0	0	0.0058(2)	0.998(8)	0.0056(3)	0.0062(4)
Sc2	3b	0	0	1/2	0.0072(2)	1.000(8)	0.0055(3)	0.0105(4)
Al	6c	0	0	0.73919(3)	0.0052(2)	1.001(8)	0.0057(3)	0.0043(4)
O	6c	0	0	0.19972(7)	0.0069(4)	1.02(2)	0.0086(6)	0.0036(9)
C	6c	0	0	0.61816(11)	0.0066(5)	0.98(2)	0.0060(7)	0.0077(11)

[a] To check for mixed occupations and/or vacancies, site occupation factors were treated by turns as free variables at the end of the refinement.

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 98(2)% and 102(2)%. The assignment is confirmed by displacement parameters and R-values. The permutation O vs C results in significantly higher R-factors of $R_1(F) = 0.063$ and $wR_2(F^2) = 0.14$, residual electron densities of ±3.0 e$^-$/Å^3, and very different values for the displacement parameters (U_{eq}: O-site: 0.021(2), C-site: 0.002(1); sof fixed) and the site occupation factors (O-site: 68(1)%, C-site: 147(2)%; U_{iso} fixed).

Microhardness. Microhardness was measured with the microhardness tester MHT 10 (producer: A. Paar, Austria). 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.[21]

Thermal Investigations. DTA/TG measurements were done with an STA 429 (Fa. Netsch, Selb, Germany). Approximately 10 mg of the sample were heated at 10 K/min up to 1300 °C under a stream of air and argon, respectively.

Vibrational Spectroscopy. FT-IR and FT-Raman measurements were performed with a Bruker IFS66v spectrometer. The IR sample was made of crystalline powder pressed with KBr to pellets. Raman

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(17) (a) Hillebrecht, H.; Meyer, F. *Angew. Chem.* **1996**, *108*, 2655; *Angew. Chem., Int. Ed.* **1996**, *35*, 2499. (b) Hillebrecht, H.; Ade, M. *Angew. Chem.* **1998**, *110*, 981; *Angew. Chem., Int. Ed.* **1998**, *37*, 935. (c) Hillebrecht, H.; Gebhardt, K. *Angew. Chem.* **2001**, *113*, 1492; *Angew. Chem., Int. Ed.* **2001**, *40*, 1445. (d) Vojteer, N.; Hillebrecht, H. *Angew. Chem.* **2006**, *118*, 172–175; *Angew. Chem., Int. Ed.* **2006**, *45*, 165. (e) Adasch, V.; Hess, K.-U.; Ludwig, T.; Vojteer, N.; Hillebrecht, H. *Chem.—Eur. J.* **2007**, *13*, 3450–3458. (f) Vojteer, N.; Schroeder, M.; Röhr, C.; Hillebrecht, H. *Chem.—Eur. J.* **2008**, *14*, 7331–7342.

(18) Schroeder, M. PhD thesis, Universität Freiburg, 2009; Schroeder, M.; Hillebrecht, H. Unpublished results.

(19) Program XAREA, XSHAPE, XRED, Stoe Cie. Darmstadt, Germany.

(20) Sheldrick, G. M. SHELXTL program package; University of Göttingen: Germany, 1997.

(21) DIN EN 6507.

Table 3. Selected Distances (Å) and Angles (deg) in ScAlOC; Esd's in Parentheses

Sc1−C	2.382(2) 6x	C−Sc1−C	86.34(9)°
−Al	2.8833(8) 6x	C−Sc1−C′	93.66(9)°
−Sc1	3.2599(7) 6x		
Sc2−O	2.129(1) 6x	O−Sc2−O	99.91(7)°
−Al	3.4032(8) 6x	O−Sc2−O′	80.09(7)°
−Sc2	3.2599(7) 6x		
C−Sc1	2.382(2) 3x	Sc1−C−Sc1	86.34(9)°
−Al	2.016(1) 3x	Sc1−C−Al	81.45(3)°/163.2(1)°
		Al−C−Al	107.87(9)
O−Sc2	2.129(1) 3x	Al−O−Sc2	117.87(9)°
−Al	1.840(2)	Sc2−O−Sc2	99.91(7)°
Al−O	1.840(2)	O−Al−C	111.02(9)°
−C	2.016(1) 3x	C−Al−C	107.87(9)°
−Sc1	2.8833(8) 3x		
−Sc2	3.4032(8) 3x		
−Al	3.2599(7) 6x		

measurements were carried out with a Nd:YAG-laser with an output of 100 mW and 1000 scans on single crystals with a Raman microscope. Powder samples were prepared in a 0.3 mm capillary and measured with an output of 400 mW and 5000 scans.

Theoretical 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.[22] In the calculation the following muffin-tin radii R_{mt} were used: Sc = 2.13 au (112.9 pm), Al = 1.72 au (91.2 pm), O = 1.72 au (91.2 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 of $\sim10^{-5}$. The cutoff energy was $R_{mt}\cdot k_{max} = 5$ unitary. 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; 110/IBZ), and the irreducible wedge for band structure plots along the k-path ΓAHKΓMK were calculated with a grid of 80 k-points. Valence charge distribution (ρ_{val}) was described with the program xcrysden.[22]

Structure Descriptions and Discussion

The crystal structure of ScAlOC represents a new and remarkably simple structure type (Figure 1 and 2). If it is described on the basis of the closest sphere packing of the anions, which is justified by the distribution of the charges (see band structure calculations), there is a stacking sequence of **A*BA*BC*ACA*BC*BC*** (according to Jagodzinski (hhcc)$_3$^{2}). C-atoms in hexagonal sequences (*italic*) and O-atoms in cubic sequences (**bold**) are stacked in a way that two layers of the same kind of atoms always alternate. Within this packing the cations are located by turns between the layers. 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.

From this pattern two different Sc atoms result. One is octahedrally coordinated by carbon (Sc−C: 2.382(2) Å), and the other by oxygen (Sc−O: 2.129(1) Å). Aluminum is tetrahedrally surrounded by one O (Al−O: 1.840(2) Å) and three C atoms (Al−C: 2.016(1) Å). These distances reflect the different ionic radii[23] (Sc^{3+}: 0.745 Å, Al^{3+}: 0.39 Å, O^{2-}: 1.38 Å, no value for C^{4-}, see below). While the ScO_6-octahedra are considerably compressed in the direction of the *c*-axis (symmetry D_{3d}, O−Sc−O: 80.1°), the ScC_6-octahedra are less distorted but elongated (C−Sc−C: 93.7°). The AlO_3C-tetrahedra show only small deviations from the ideal symmetry (O−Al−C: 111.0°, C−Al−C: 107.9°).

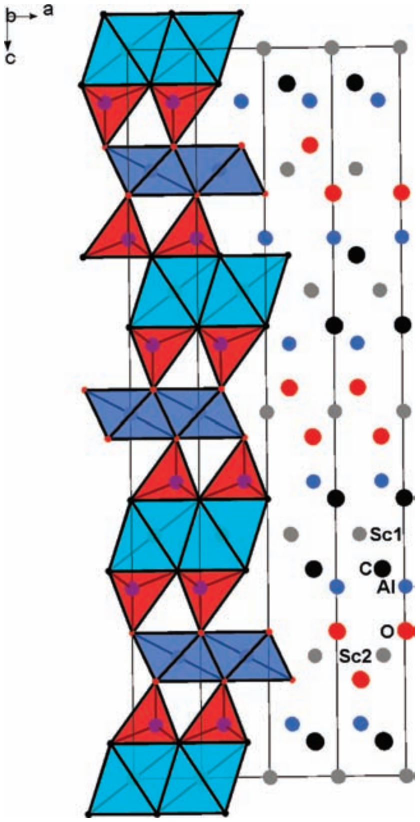

Figure 1. Crystal structure of ScAlOC.

Regarding ScAlOC as an interstitial compound as done usually 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 cubic closest packing structure (sequence ABC) with alternating layers of Al and Sc. C-atoms occupy the octahedral voids, and O-atoms one-half of the tetrahedral between pairs of subsequent layers of metal atoms.

Despite its simplicity and "plausibility," the structure of ScAlOC shows some features which are not found for the binary compounds. Sc_2O_3 with a bixbyite structure mainly has strongly distorted ScO_6-octahedra.[24] In α-Al_2O_3, (corundum) Al is octahedrally coordinated,[2] and in Al_4C_3 there is a distorted tetrahedral surrounding.[25] For $ScC_{0.44}$[26] with a NaCl structure, a direct comparison is prevented by the high underoccupation of the carbon sites. The other binary carbides of scandium (Sc_2C_3,[27] Sc_4C_3,[28] Sc_3C_4[29]) cannot be compared as well. The

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(22) Blaha, P.; Schwarz, K.; Madsen, G. K. H.; Kvasnicka, D.; Luitz, J. *WIEN2K-An Augmented Plane Wave and Local Orbital Program for Calculating Crystal Properties*; TU Wien, 2001.

(23) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.

(24) Schleid, T.; Meyer, G. *J. Less-Common Met.* **1989**, *149*, 73–80.

(25) Gesing, T. M.; Jeitschko, W. *Z. Naturforsch. B* **1995**, *50*, 196–200.

(26) Shi, Y.; Leithe-Jasper, A.; Tanaka, T. *J. Solid State Chem.* **1999**, *148*, 250–259.

(27) Rassaerts, H.; Nowotny, H.; Vinek, G.; Beneshovski, F. *Monatsh. Chem.* **1967**, *98*, 460–468.

(28) Pöttgen, R.; Jeitschko, W. *Inorg. Chem.* **1991**, *30*, 427–431.

(29) Krikorian, N. H.; Powman, A. L.; Krupka, M. C.; Arnold, G. P. *High Temp. Sci.* **1969**, *1*, 360–365.

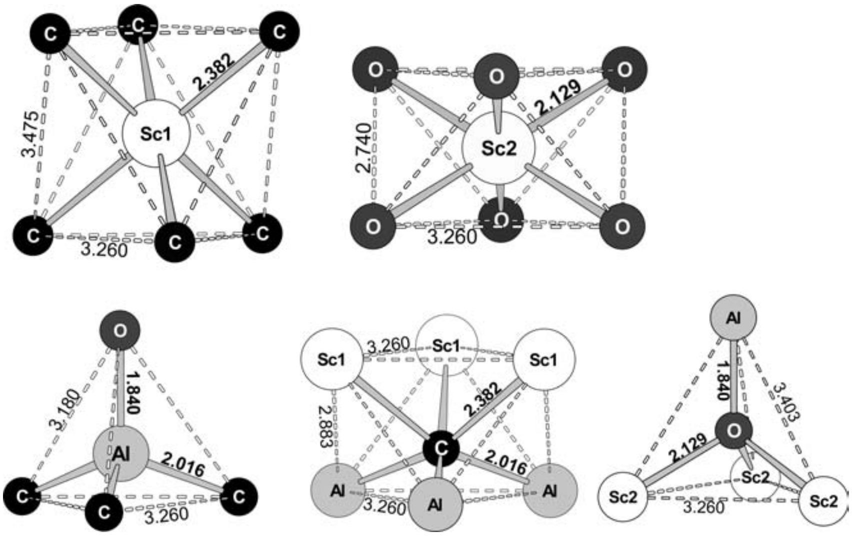

Figure 2. Coordination polyhedra in ScAlOC.

ternary compounds (Al_4O_4C,[15,16] $ScAl_3C_3$,[30] and $ScAlO_3$[31]) show different structural units like AlO_3C-tetrahedra, trigonal bipyramides CAl_5, and quadratic antiprisms ScO_8. Against them the structure of ScAlOC can directly be derived from the structure of (up to now) hypothetical $ScAlN_2$, which might be constructed from the structural features of the binary nitrides ScN (NaCl type)[7] and AlN (wurtzite type).[7]

Although there exist many compounds with octahedral surroundings of O and C (NaCl structures), the differences of radii and electronegativity of O^{2-}/C^{4-} and O/C, respectively, are so great that there are only a few examples for isostructural oxides and carbides or the formation of extended solid solutions. As opposed to these oxidnitrides of aluminum (alone) and, especially, silicon (sione and sialone), there are many more examples according to the greater similarity. Furthermore there is usually no differentiation between the anions, but specific site preferences can be derived from lattice energy calculations. Examples are $Al_{2.83}O_{3.5}N_{0.5}$ with a spinell structure,[32] $Si_{2-x}Al_xN_{2-x}O_{1+x}$,[33] $MLn(Si_{4-x}Al_xO_xN_{7-x})$ (M = Eu, Sr, Ba; Ln = Ho−Yb),[34] and $Nd_4Si_2O_5N_2O_2$.[35] The ordered structures of Si_2N_2O[36] and Ge_2N_2O[37] have an exceptional position. An ordered O/N distribution is also assumed for $CaSi_2O_2N_2$.[38]

Microhardness. Due to the potentially interesting material properties of ScAlOC, the microhardness was measured (see Experimental Section). The first observation was the pronounced brittleness of the crystals. Therefore the measurement following the Vickers method was impossible because the crystals were destroyed. The Knoop method was successful and yielded a hardness of $H_K = 900$ (i.e., $H_K = 9.0$ GPa when reassessed[25]). As expected this value is quite high but clearly below Al_2O_3 (21 GPa[39]), TiC (∼30 GPa[4,6]), and ScN (21 GPa[40]). The chemical stability of ScAlOC against acids is quite high in comparison to Al_4C_3, which is slowly hydrolyzed by water and the very sensitive Sc_4C_3.

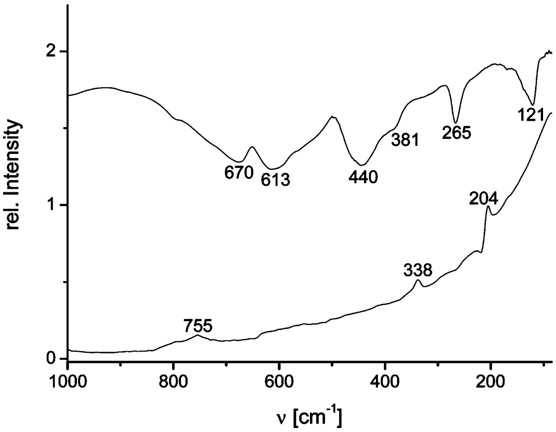

Figure 3. IR (top) and Raman spectra (bottom) of ScAlOC.

Thermal Properties. Under inert atmosphere (argon) ScAlOC is stable up to 1300 °C, while heating on air showed a reaction starting at 600 °C. Above 850 °C the exothermic reaction becomes faster and the mass increases ∼20% up to 1100 °C. This corresponds with the formation of the binary oxides Sc_2O_3 and Al_2O_3 or of $ScAlO_3$, respectively. A more extensive identification was not possible, because the X-ray diffractogram showed an amorphous residue.

Vibrational Spectra. Figure 3 shows the vibrational spectra of ScAlOC. According to the black color of the sample, it was diluted with KBr and the power of the laser was reduced.

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(30) Gesing, T. M.; Jeitschko, W. *J. Solid State Chem.* **1998**, *140*, 396–400.

(31) Sinclair, W.; Eggleton, R. A.; Ringwood, A. E. Z. *Kristallogr.* **1979**, *149*, 307–314.

(32) Lejus, A.-M. *Bull. Soc. Chim. Fr.* **1962**, 2123–2126.

(33) Lindquist, O.; Sjoeberg, J.; Hull, S.; Pompe, R. *Acta Crystallogr., Sect. B* **1991**, *47*, 672–678.

(34) Lieb, A.; Kechele, J. A.; Kraut, R.; Schnick, W. Z. *Anorg. Allg. Chem.* **2007**, *633*, 166–171.

(35) Lieb, A.; Kraut, R.; Schnick, W. Z. *Anorg. Allg. Chem.* **2006**, *632*, 1496–1500.

(36) (a) Indrestedt, I.; Brosset, C. *Acta Chem. Scand.* **1964**, *18*, 1879–1886. (b) Sjoeberg, J.; Helgesson, G.; Idrestedt, I. *Acta Crystallogr. C* **1991**, *47*, 2438–2441. (c) Bischoff, A.; Grund, T.; Jording, T.; Heying, B.; Hoffmann, R.-D.; Pöttgen, R. *Z. Naturforsch. B* **2005**, *60*, 1231–1234.

(37) Jorgensen, J. D.; Srinivasa, S. R.; Labbe, J. C.; Roult, G. *Acta Crystallogr., Sect. B* **1979**, *35*, 141–142.

(38) Höppe, H. A.; Stadler, F.; Oeckler, O.; Schnick, W. *Angew. Chem.* **2004**, *116*, 5656–5659; *Angew. Chem., Int. Ed.* **2004**, *43*, 5540−5542.

(39) Sachdev, H. *Nachr. Chem.* **2003**, *51*, 911–916.

(40) Gall, D.; Petrov, I.; Hellgren, N.; Sundgren, J. E.; Greene, J. E. *Appl. Phys.* **1998**, *84*, 6034–6041.

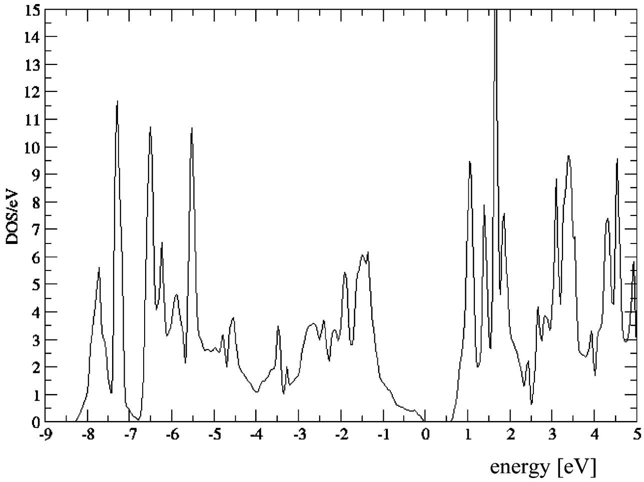

Figure 4. Total density of states (TDOS) in ScAlOC.

Therefore the quality of the spectra is not the best, but Raman modes at 755, 338, 204 cm^{-1} and IR modes at 670, 613, 440, 381, 265, and 121 cm^{-1} were clearly detected.

The spectra of the yellow Al_4C_3 are much better resolved.[18] They showed Raman active modes at 857, 492, 335, 287, and 251 cm^{-1}. IR bands were observed at 749 (broad), 604, 462, 352, and 178 cm^{-1}.

The possibility to record vibrational spectra of ScAlOC is in agreement with the description of the bonding situation as an electron precise compound where the ionic interaction contains significant covalent amounts.

Bonding. While the structural description and classification of ScAlOC is quite simple, the chemical bonding is not. Similar to silicates considerable covalent fractions are expected because of the high charge−radius ratio. Furthermore the unique structure of ScAlOC enables us to investigate side-by-side differences and commonalities of Sc^{3+}/Al^{3+} and O^{2-}/C^{4-}. So density of states and band structure calculations were done for ScAlOC and some related compounds.[18] The first Brillouin zone for a rhombohedral cell (hexagonal setting) and the k-path were chosen according to Lacroix-Orio et al.[41] Charge transfers from the ions were determined according to the Bader method.[42]

The band gap (TDOS) in ScAlOC amounts to 0.6 eV (Figure 4), which agrees with the color of the single crystals and powders. According to Figures 6 and 7, it is an indirect band gap (Γ→M). The partial density of states (PDOS, Figure 5) shows 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 due to the higher covalency and the greater reduction of the effective charge for carbon (see below). The different covalency of O/C is clearly seen in the “fatband representations (Figure 6). The lowest states of the conduction band are mainly formed by the d-states of scandium. The Al p-states are higher and preferably in the range of the C p-states. This explains why ScAlOC is black but Al_2OC and Al_4O_4C are colorless according to the larger band gap. But within the ionic picture, ScAlOC is an electron-precise compound and shows all the persuant structural features. Nevertheless subtle differences can be seen.

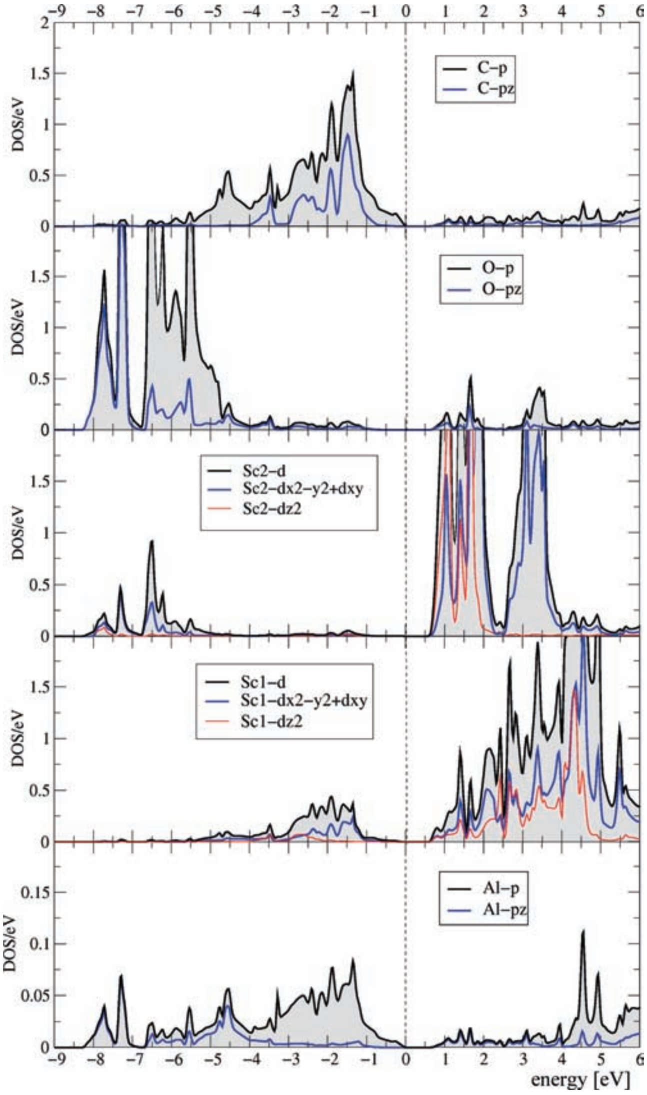

Figure 5. Partial density of states (PDOS) in ScAlOC; from the top down C, O, Sc2 and Sc1, differentiated d-orbitals of Sc, Al.

The d-states of Sc contribute much more to the DOS than the p-states of Al. This agrees with the more ionic interaction of Al and its higher effective charge (see below). Furthermore the different surroundings of Sc are obvious. Oxygen-coordinated Sc2 shows very narrow bands, while the bands of Sc1 are much broader. Mainly the band dispersion indicates a higher covalency of the Sc−C interaction and is consistent with the lower charge transfer from the Sc1-cation (60%) as shown in the “fat-band” plots of band stucture (Figure 7): Here the Sc2−O interaction shows a less distinct dispersion owing to its ionicity, while the Sc1−C interaction should be more covalent to the broad dispersion of the Sc1 d-states. These findings agree with the effective charges of Sc1 (AiM charge: +1.88, see below) and Sc2 (AiM charge: +2.21) and with the broad dispersions of C states as well. But an explanation can be made for the Sc-bonding based on the nature of the d-orbital interactions. The ScC_6 and ScO_6 octahedra are elongated respectively compressed in the *c* direction. The reduced symmetry resulting for these octahedra (approximately e_g and t_{2g} orbitals which cannot exist here) leads to a splitting of orbital energies according to $d_{z^2} < d_{xz}, d_{yz} < d_{xy}, d_{x^2-y^2}$. The partial DOS of the split d-states (Figure 5) show partial occupation of all

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(41) Lacroix,-Orio, L.; Tillard, M.; Belin, C. *Solid State Sci.* **2008**, *10*, 5–11.

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

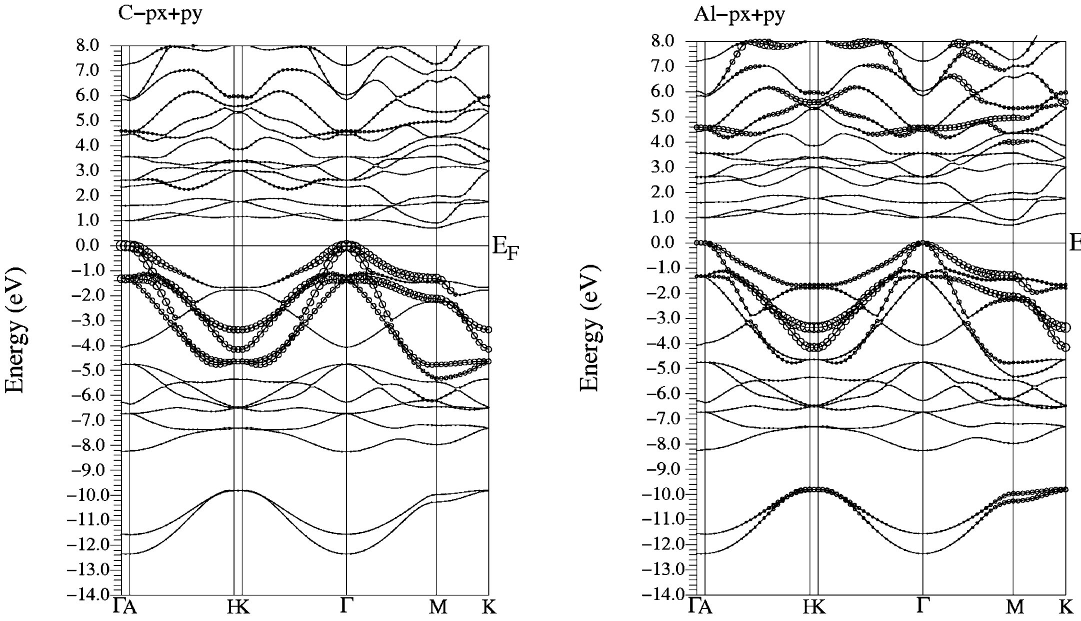

Figure 6. Fatband plots for C (left) and Al (right) p-states.

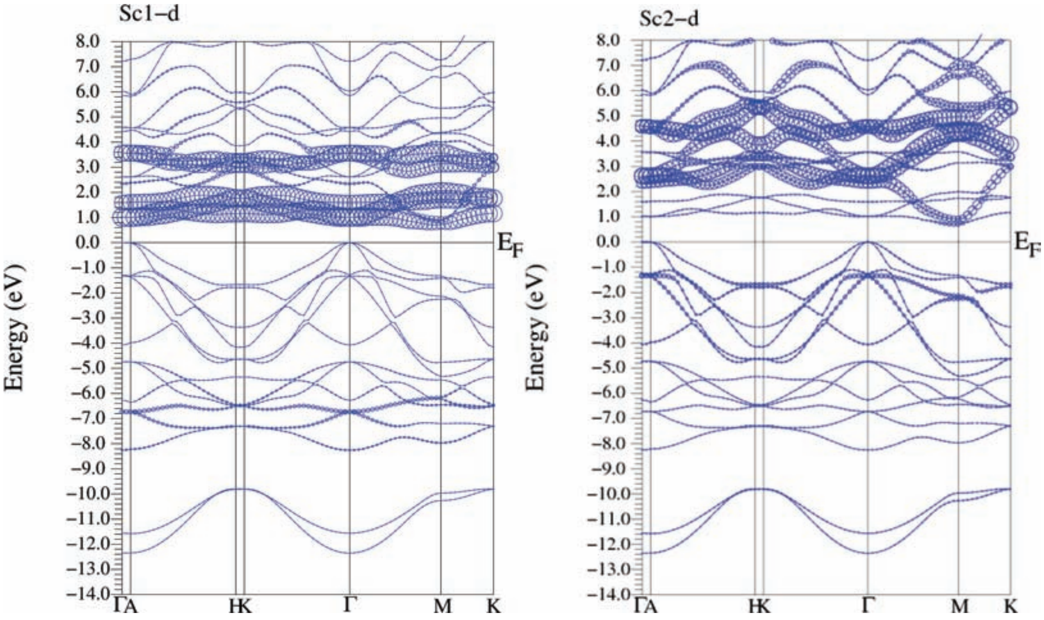

Figure 7. Fatband plots for Sc1 (left) and Sc2 (right).

d-states, but states of major π character (d_{xz}, d_{yz}, and d_{xy}) are more dominant. The contribution of the d_{z^2}-orbitals to the bonding states, which is expected to be σ-bonding, is very small while the other orbitals give a significant contribution. The interaction of the d_{xz} and d_{yz} orbitals with the p-orbitals of oxygen and carbon could lead to a significant covalent interaction in general.

The simple structure and its high symmetry enable a clear representation of the valence electron density in real space (Figure 8). Furthermore its topological analysis results in bond critical points (bcp's), i.e., saddle points of the valence electron density, which give insights to the bonding situation. First, the clear implementation of the bond critical points attracts attention. The absolute values of the electron densities (Al−O: 0.52 e$^-$/Å^3, Al−C: 0.46, Sc−O: 0.45, Sc−C: 0.40) are mainly determined by the size of the atoms in share, i.e. Al−X > Sc−X; M−O > M−C.

Second, the distances of bcp's to the corresponding ions/atoms allow an estimation of the radii. It is well-known that the division of the anion-to-cation distance into ionic radii is clear-cut. The set of ionic radii (IR) by Shannon[43] bases on a value of 1.40 Å for O^{2-} with CN 6 and gives the following values: Sc^{3+} 0.745 Å, Al^{3+} 0.39 Å (CN 4), F^- 1.33 Å, O^{2-} 1.38 Å (CN 4), N^{3-} 1.46 Å (CN 4). C^{4-} is not listed, but a value between 1.54 and 1.56 Å can be estimated. Furthermore crystal radii (CR) can be defined. For this the division is quite close to the

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(43) (a) Shannon, R. D.; Prewett, C. T. *Acta Crystallogr., Sect. B* **1969**, *25*, 925–946. (b) Shannon, R. D. *Acta Crystallogr., Sect. B* **1970**, *65*, 1046–1048.

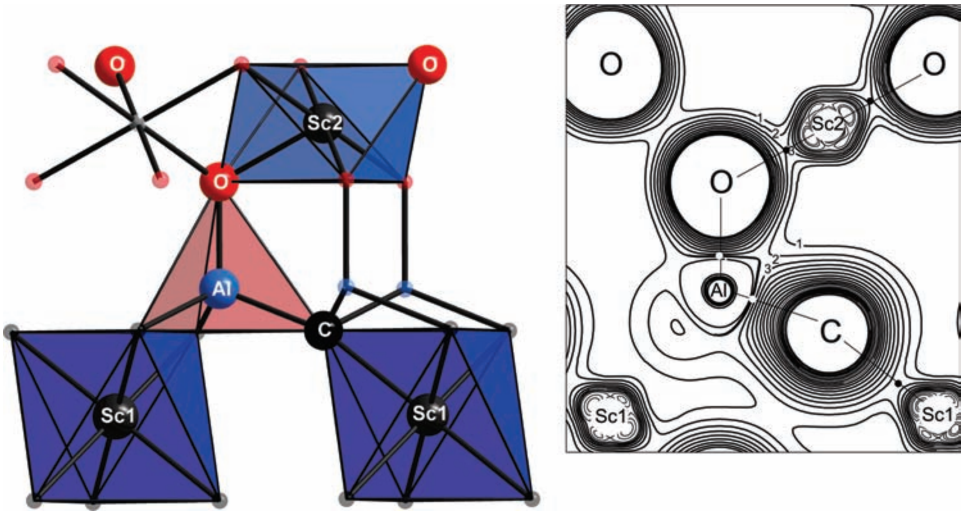

Figure 8. Valence electron density of ScAlOC (Bader analysis) and corresponding cutout of the crystal structure; labeled atoms are in the same plane.

minimum of the electron density.[44] Starting with a value of 1.19 Å for F^- and CN 6, the values obtained are as follows: Sc^{3+} 0.885 Å, Al^{3+} 0.53 Å (CN 4), O^{2-} 1.24 Å (CN 4). Values for N^{3-} and C^{4-} are not listed but can be estimated to be 1.32 and 1.42 Å, respectively. Independently, which data set is used as a comparison to the distances observed in ScAlOC shows that these values are significantly higher (except Sc−O). Nevertheless it is obvious that the distances between bond critical points and involved atoms are quite close to the crystal radii. For Al there are distances of 0.58 to 0.59 Å from Al−O and Al−C, and for Sc 0.84 Å (Sc−O) and 0.92 Å (Sc−C), respectively. The corresponding values for oxygen are 1.29 Å (O−Sc) and 1.25 Å (O−Al), and for carbon 1.43 Å (C−Al) and 1.46 Å (C−Sc).

The ionic radius of C^{4-} is a problem (probably therefore not listed), because extremely ionic carbides with a formal C^{4-} (methanides) are only known to be with highly charged cations (Be_2C and Al_4C_3). From a Be−C distance of 1.88 Å and a crystal radius of 0.41 Å for Be^{2+} (IR: 0.27 Å), a value of 1.47 Å is calculated for C^{4-}. In Al_4C_3 the shortest Al−C distance is 1.93 Å (CN: 5),[35] so the share for C^{4-} is 1.40 Å. In total the electron density in ScAlOC is in agreement with the description as a mainly ionic compound, including the carbide-anion "C^{4-}". Furthermore the difference between the two Sc ions is clearly seen.

According to the Bader formalism[42] formal 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: Sc1: +1.88, Sc2: +2.21; Al: +2.49; O: −1.62; C: −2.93. The charge of Al is higher than that for Sc in general because for Sc the d-orbital participation enlarges the covalent part of the interaction. Furthermore the charge of C-coordinated Sc1 is significantly more decreased (~40%) than that for Sc2 coordinated by oxygen (~25%). The same observation can be made for $ScAl_3C_3$,[18] a compound with many structural similarities but without O-coordinated Sc atoms: Sc: +1.86; Al1, Al2, Al3: +2.45; C1 (only surrounded by Al atoms): −3.35; C2, C3: −2.90 (Sc- and Al-coordinated). The anion's charges in ScAlOC are significantly reduced as well. The relative reduction is greater for carbon (~25%) than for oxygen (~20%). For reasons of comparison, calculations were also done for binary and ternary compounds yielding the following results: Al_2O_3: +2.63/−1.76; Al_4C_3: +2.4/−3.2; Al_4O_4C: +2.65/−1.85/−3.2).[18] Also for these compounds, the reduction of the charge is obvious, but the main ionic character is maintained.

The closest relationship is observed for Al_3BC.[45] In a special way Al_3BC is singular like ScAlOC as well, because it is the only stoichiometric boridecarbide with isolated octahedrally coordinated B atoms besides the isolated C atoms. Formally the Al cations occupy tetrahedral and trigonal-bipyramidal voids in a hexagonal closest packing with alternating layers of B- and C-atoms. Band structure calculations[18] show a band gap of 1.0 eV and charges of −3.85 for B, −3.34 for C, and +2.40 for Al. The highest states of the valence band are affected by p_x- and p_y-states of boron, the lowest part of the conduction band by p_x- and p_y-states of that aluminum which is bonded to boron. With it Al_3BC shows very similar features like ScAlOC.

All these calculations are in a line with the description of ScAlOC as a mainly ionic compound with distinctive differences between Sc/Al and O/C. Nevertheless the bonding situation of 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).

Conclusions

Single crystals of ScAlOC, the first oxide carbide of a transition metal which exhibits an ordered distribution of the anions, are obtained from molten aluminum. The crystal structure combines the motifs of the binary nitrides ScN and AlN in a way that the anions form the closest sphere packing where the layers are arranged in pairs. Scandium is located in the octahedral voids of the sequences with the same kind of anions thus forming layers of ScC_6 and ScO_6 octahedra. Aluminum is placed in one-half of tetrahedral voids between these layers forming AlC_3O-tetrahedra. Despite the close similarity to the binary nitrides, there are marked differences to the structures of the binary and ternary carbides and oxides.

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(44) West, A. R. *Solid State Chemistry and its Applications*; J. Wiley: Chichester, 1984.

(45) Meyer, F. D.; Hillebrecht, H. *J. Alloys Compd.* **1997**, *252*, 98–102.

According to band structure calculations ScAlOC is an indirect semiconductor with a band gap of 0.6 eV. Calculated charges, charge densities, and ionic radii follow the expected tendencies (effective charges: $Al^{3+} > Sc^{3+}$, $C^{4-} > O^{2-}$; effective radii: $Al^{3+} < Sc^{3+}$, $O^{2-} < C^{4-}$; covalency: $Al^{3+} < Sc^{3+}$, $O^{2-} < C^{4-}$). According to the high charges there are significant amounts of covalency. Because ScAlOC is one of the few ionic carbides with isolated C atoms (methanides), it offers a unique chance to study the bonding situation of the carbide anion C^{4-}.

Within the ionic picture, ScAlOC is an electron-precise compound and shows all the expected structural features. The black color results from the quite low Sc d-states.

The simple relation of ScAlOC to the isoelectronic nitrides and the adaptability of the cations give good reasons for the existence of further ordered oxide carbides of scandium and other rare earth metals. The versatility of molten metals should provide experimental access to new representatives of this new type of compounds. We expect crystal structures on the basis of building units as it is known for ternary carbide MAX-phases, $(MC)_n(MA)$,[46] for example, Ta_4AlC_3, Ta_3AlC_2, Ta_2AlC;[47] borides $(MB_2)_nAl$ like Cr_4AlB_6, Cr_3AlB_4, Fe_2AlB_2;[48] and boride carbides $(NbB)(NbB_2)_n(NbC)_m$ Nb_3B_3C, $Nb_4B_3C_2$, $Nb_6B_4C_3$, $Nb_7B_3C_3$[17c].

Furthermore there is a wide range of possibilities for the substitution of anions and/or cations as well. This is of special interest with reference to the very recently discovered superconductivity of pnictide oxides (for example LaFePO[49]). This structure type shows remarkable similarities to ScAlOC in regard to the same composition and the parallel existence of two structurally different cations and anions as well.

For ScAlOC the possible exchange of C^{4-}/O^{2-} by N^{3-} is obvious by the close structural similarity. For the cations the substitution of Al^{3+} by 3d transition metals and of Sc^{3+} by cations like Mg^{2+}, Ce^{4+}, and/or other rare earth metals is feasible. The maintenance of an electron precise composition (i.e., semiconducting) is expected but not mandatory.

While we have first hints for the existence of further oxide carbides, there are no ones for the occurrence of substitutions.

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Supporting Information Available: Further data of the structure refinement are deposited. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) Barsoum, M. W. *Prog. Solid State Chem.* **2000**, *28*, 201.

(47) Etzkorn, J.; Ade, M.; Hillebrecht, H. *Inorg. Chem.* **2007**, *46*, 1410.

(48) Gebhardt, K. PhD Thesis, University Bayreuth, 2002.

(49) (a) Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. *J. Am. Chem. Soc.* **2008**, *130*, 3296–3297. (b) Johrendt, D.; Pöttgen, R. *Angew. Chem.* **2008**, *120*, 4860–4863; *Angew. Chem., Int. Ed.* **2008**, *47*, 5540−5542.