### $RE_4[P_{1-x}(C_2)_x]_3$ (*RE* = La–Nd): the Mixed Anionic Substructure Formed by Phosphorus and Carbon

Pavel S. Chizhov,<sup>[a,b]</sup> Walter Schnelle,<sup>[a]</sup> Ulrich Burkhardt,<sup>[a]</sup> Marcus Schmidt,<sup>[a]</sup> Yurii Prots,<sup>[a]</sup> Evgeny V. Antipov,<sup>\*[b]</sup> and Yuri Grin<sup>[a]</sup>

Dedicated to Professor Rüdiger Kniep on the Occasion of His 65th Birthday

Keywords: Phosphorus; Carbon; Anionic substructure; Electron localizability indicator; Rare-earth metals

**Abstract.** The rare-earth phosphide carbides  $RE_4[P_{1-x}(C_2)_x]_3$  (RE = La, Ce, Pr, Nd) represent the first example of a mixed anionic substructure formed by phosphorus and carbon, being the first step toward the formation of the mixed inorganic P–C species. The peculiarities of the crystal structure, magnetic properties, XAS data, and quantum chemical calculation results confirm the ionic nature of the interaction be-

Introduction

Ternary compounds  $M_x A_y B_z$ , where A and B are non-metallic elements of the 2nd and 3rd row, and M – metal, are widely known and well characterized for many combinations of A and B. One of the few "white spots" are systems M/P/C. Whereas the organic compounds of phosphorus with direct P-C interactions are well known, no crystalline inorganic binaries of phosphorus with carbon comprising heteroatomic P-C bonds were obtained up to now [1a, 1b]. Ternary phases were studied very poorly: only a few metal-rich phosphide carbides of transition metals are known (V<sub>2</sub>PC [2a], Nb<sub>2</sub>PC [2b], V<sub>4</sub>P<sub>2</sub>C [2c], and Cr<sub>8.105</sub>P<sub>6</sub>C<sub>0.76</sub> [2d]). Details of their crystal structures prevent one from suggesting pure ionic character of metal-non-metal interactions. Phosphorus and carbon atoms have different coordinations and are separated from each other in these compounds, as the formation of the P-C frameworks is suppressed by the weakness of the heteroatomic P-C bond, relative to the homoatomic interactions P-P or C-C [3a, 3b] or to the heteroatomic interactions M-P and M-C.

The existence of phosphide carbide of a more electropositive metal (e.g., rare-earth metal *RE*) would give a first example of

\* Prof. Dr. E. V. Antipov

Fax: +7-495-939-47-88

- E-Mail: antipov@inorg348-1.chem.msu.ru
- [a] Max-Planck-Institut für Chemische Physik fester Stoffe Nöthnitzer Str. 40

01187 Dresden, Germany

[b] Chemistry Department

Moscow State University

- Leninskie Gory 1–3 Moscow 119992, Russian Federation
- Supporting Information for this Article is available under http://dx.doi.org/10.1002/zaac.201000023 or from the author.

1318

# tween the rare-earth cations *RE* and phosphorus anions, while complex interaction of $\pi$ states of the C<sub>2</sub> anions and *d* (and/or *f*) states of the *RE* components is indicated. Thus, despite the extensive chemical analogy between the phosphide carbides and phosphide silicides, the atomic interactions stabilizing the structural motif are slightly different.

a mixed anionic substructure formed by phosphorus and carbon. Due to the relative instability of the P–C bond, such compounds may be thermodynamically stable only if direct P–C bonding is absent, i.e. phosphorus and carbon form separated anionic species. For example, both the ethenide anions  $C_2^{4-}$  (in  $RE_2C_3$ :  $[RE^{3+}]_4[(C_2)^4]_3$ ,  $Pu_2C_3$  type) [4a–4c] and phosphide anions P<sup>3–</sup> (in  $RE_4P_{3-x}$ , RE = Eu, Yb) [5a–5e] form cubic *anti*-Th<sub>3</sub>P<sub>4</sub>-like atomic arrangements together with rare-earth cations. The anionic substructure in such compounds can be easily modified by isovalent (e.g.,  $C_2^{4-}/Ge^{4-}$  in germanide carbide  $La_4[Ge_{1-x}(C_2)_x]_3$ ) [6] or heterovalent substitutions (e.g.,  $P^{3-/}$ Si<sup>4–</sup> in phosphide silicides  $RE_4(P_{1-x}Si_x)_{3-z}$ , RE = La-Nd) [7]. Thus, the expected formation of phosphide carbides  $RE_4[P_{1-x}(C_2)_x]_{3-z}$  is investigated in the present work.

#### **Results and Discussion**

Our studies revealed the formation of phosphide carbides  $RE_4[P_{1-x}(C_2)_x]_{3-z}$  for light rare-earth metals (RE = La-Nd), giving the first hint for an analogy with the phosphide silicides of the *anti*-Th<sub>3</sub>P<sub>4</sub> structure type [7]. However, while in case of the phosphide silicides  $RE_4(P_{1-x}Si_x)_{3-z}$  monoatomic anions form the anionic substructure,  $RE_4[P_{1-x}(C_2)_x]_3$  compounds reveal an *anti*-Th<sub>3</sub>P<sub>4</sub>-type crystal structure with a random distribution of P and C<sub>2</sub> species (Figure 1, top). Rare-earth phosphide carbides exhibit wide homogeneity ranges (up to  $\approx 0.2 \le x \le 1$ , Figure 2) without any hint for the formation of anionic vacancies (z = 0 in  $RE_4[P_{1-x}(C_2)_x]_{3-z}$ ), that again differentiates them from phosphide silicides. The lattice parameter variation a(x) (x was established from WDXS data) obeys Vegard's law for La, Pr, and Nd in the entire x range, pointing out the conservation of the valence states in the accessible composition

range. In case of the cerium compound, the deviation of a(x) from linearity in the phosphorus-poor region indicates possible changes in the atomic interactions and/or in the valence state of cerium. The differences in size and shape between the P<sup>3–</sup> and C<sub>2</sub><sup>4–</sup> species cause a slight local distortion of the initial structural pattern of the *anti*-Th<sub>3</sub>P<sub>4</sub> type (Figure 1, bottom) with a consequent symmetry reduction.



**Figure 1.** Crystal structure of compounds  $RE_4[P_{1-x}(C_2)_x]_3$ : (top) Orientation of the C<sub>2</sub> dumbbells in the unit cell together with phosphorus atoms (both species occupy commonly the non-metal sites of the *anti*-Th<sub>3</sub>P<sub>4</sub> structure); (bottom) Polyhedra  $REP_{6-x}C_{2x}$  (green),  $PRE_8$  (blue), and (C<sub>2</sub>) $RE_8$  (grey).

According to the results of the single-crystal X-ray diffraction (XRD) experiment (Table 1 and Table 2), the metal substructure remains nearly undistorted with respect to the aristotype, and the phosphorus atoms are still located in the centers of cages. The C<sub>2</sub> dumbbells are slightly shifted along [100] (0.07 Å – 0.40 Å; Figure 1, top) from the center of the oversized *RE*<sub>8</sub> cage causing a reduction of the symmetry from  $I\bar{4}3d$ , (for *anti*-Th<sub>3</sub>P<sub>4</sub>) to *I*2<sub>1</sub>3 (for *RE*<sub>4</sub>[P<sub>1-x</sub>(C<sub>2</sub>)<sub>x</sub>]<sub>3</sub>) for all studied crystals. One should note, that the space group *I*2<sub>1</sub>3, in contrast



**Figure 2.** Composition dependences of the lattice parameter for compounds  $RE_4[P_{1-x}(C_2)_x]_3$ .  $\circ$  – Calculated value for  $La_4[P_{0.64}(C_2)_{0.36}]_3$  single crystal.

to  $I\overline{4}3d$ , is chiral, thus providing the existence of two possible configurations of the structure. The glide mirror planes d of  $I\overline{4}3d$  may become the twinning planes for  $I2_13$  structures. Some evidence of such twinning was observed in case of Nd<sub>4</sub>[P<sub>0.68</sub>(C<sub>2</sub>)<sub>0.32</sub>]<sub>3</sub>, but it was impossible to account for the twinning directly due to the small number of informative (i.e. forbidden in the space group  $I\overline{4}3d$ ) reflections. All of these facts lead also to the relatively low precision of the determined atomic parameters for light (especially carbon) atoms. No indication for the formation of anionic vacancies was observed by independent refinement of the P and C1/C2 occupancies. This finding justifies the use of the linear constraint for these values.

The interatomic distances (Table 3) agree well with the known values for phosphides and carbides of rare-earth metals. The reduction of the Ce–(P,C) distances with the increase of *x* in Ce<sub>4</sub>[P<sub>1–x</sub>(C<sub>2</sub>)<sub>x</sub>]<sub>3</sub> should be considered as a sign of a partial Ce<sup>3+</sup>  $\rightarrow$  Ce<sup>4+</sup> transition for high *x* values.

Measurements of the magnetic susceptibility gave basic information on the electronic configuration of the RE ions. The compounds  $RE_4[P_{1-x}(C_2)_x]_3$ , except the lanthanum-based one, are antiferromagnets with low T<sub>N</sub> (6-15 K) and reveal Curie-Weiss paramagnetism at elevated temperatures (Figure 3). Effective magnetic moments [8] correspond to the  $4f^{n}d^{0}$  configuration for rare-earth metal atoms (n = 2 or 3 for Pr and Nd,respectively), i.e. to the presence of  $RE^{3+}$  ions. The magnetic behavior of the cerium compounds is more complex and shows an additional discontinuity at approximately 200 K (both for x = 0.27 and x = 0.86), which is not present for the praseodymium and neodymium representatives. Moreover, for large x values (x = 0.86) the compound Ce<sub>4</sub>[P<sub>1-x</sub>(C<sub>2</sub>)<sub>x</sub>]<sub>3</sub> does not exhibit a Curie–Weiss paramagnetism (Figure 3), similarly to the binary Ce<sub>2</sub>C<sub>3</sub> carbide, in which cerium adopts an intermediate valence state (3.4–4.0, dependent on the temperature) [9a, 9b].

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Table 1	. Crystallographic	data for compounds	$RE_4[P_{1-x}(C_2)_x]_3$	(RE = La,	Ce, Pr, Nd).
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Composition		$RE_4[P_{1-x}(C_2)_x]_3$						
RE	La	Ce	Ce	Ce	Pr	Nd		
<i>x</i> (structure refinement)	0.36(2)	0.34(2)	0.42(2)	0.81(2)	0.35(2)	0.32(4)		
x (WDXS data)	-	0.26(2)	0.41(1)	0.86(1)	-	0.25(1)		
Space group		<i>I</i> 2 <sub>1</sub> 3 (no. 199)						
$\alpha / A^{a}$	$8.9300(1)^{b}$	8.7952(1)	8.7636(4)	8.5458(2)	8.8091(2)	8.6763(3)		
$V/Å^3$	712.1	680.4	673.1	624.1	683.6	653.1		
Z 4								
$\rho_{\rm calc}$	5.98	6.31	6.36	6.77	6.31	6.66		
Radiation			Mo-K <sub>a</sub> , 0.7107 Å					
$2\theta$ range	6.5–67.4°	6.5-66.3°	6.6–67.4°	6.7–66.4°	6.5-66.3°	6.6-67.2°		
Total number of reflec-	3128	3885	2994	3624	3023	2757		
tions								
Number of independent	450	428	435	399	438	412		
reflections								
Number of observed re-	352	345	356	338	352	317		
flections $[I_{obs} > 3\sigma(I_{obs})]$								
Weighting scheme			w = 1					
Number of refined para-	17	17	17	14	17	17		
meters								
Extinction coefficient	0.0019(5)	0.0035(2)	0.0040(6)	0.0027(2)	0.017(2)	0.0074(19)		
R( F )	0.028	0.033	0.034	0.021	0.026	0.038		
wR( F )	0.018	0.029	0.023	0.020	0.022	0.043		
Flack parameter	-0.3(9)	-0.3(9)	0.1(1.3)	-0.1(1.8)	0.0(8)	0.3(6)		

a) Lattice parameter is refined from the X-ray powder diffraction data. b) Calculated from the a(x) dependence (see Figure 2).

**Table 2.** Atomic coordinates<sup>a)</sup> and displacement parameters<sup>b)</sup>  $/Å^2$  for compounds  $RE_4(P_{1-x}[C_2]_x)_3$ .

RE	La ( $x = 0.36$ )	Ce ( $x = 0.34$ )	Ce ( $x = 0.42$ )	Ce ( $x = 0.81$ )	$\Pr(x = 0.35)$	Nd ( $x = 0.32$ )
x(RE1)	0.05985(5)	0.06122(6)	0.44103(6)	0.44742(4)	0.06015(5)	0.0609(1)
$U_{\rm eq}(RE1)$	0.0225(1)	0.0233(1)	0.0224(1)	0.0125(1)	0.0216(1)	0.0241(2)
x(RE2)	0.30983(5)	0.31114(6)	0.19104(6)	0.19736(4)	0.31002(5)	0.3110(1)
$U_{\rm eq}(RE2)$	0.0231(1)	0.0235(1)	0.0228(1)	0.0125(1)	0.0221(1)	0.0245(2)
$g(\mathbf{P})^{c)}$	0.64(2)	0.66(2)	0.58(2)	0.19(2)	0.65(2)	0.68(4)
$x(\mathbf{P})$	0.3728(6)	0.3765(6)	0.8791(8)	0.861(2)	0.3787(6)	0.378(1)
$U_{eq}(P1)$	0.014(2)	0.013(1)	0.016(2)	0.024(6)	0.015(2)	0.014(2)
<i>x</i> (C1)	0.284(5)	0.319(6)	0.820(4)	0.789(2)	0.337(5)	0.319(8)
$U_{eq}(C1)$	0.022(5)	0.017(4)	0.012(4)	0.020(2)	0.011(5)	0.007(6)
<i>x</i> (C2)	0.432(6)	0.465(5)	0.973(4)	0.943(2)	0.479(4)	0.480(6)

a) The atoms occupy the following sites of the space group  $I_{2,3}$  8*R*E1 in 8*a* x,x,x; 8*R*E2 in 8*a* x,x,x; ( $12 \times g_P$ ) P in 12*b* x, 0, <sup>1</sup>/<sub>4</sub>; [ $12 \times (1-g_P)$ ] C1 in 12*b* x, 0, <sup>1</sup>/<sub>4</sub> and [ $12 \times (1-g_P)$ ] C2 in 12*b* x, 0, <sup>1</sup>/<sub>4</sub>. b) ADPs were refined in anisotropic approximation for *R*E1, *R*E2, P, and in isotropic – for C1 and C2,  $U_{iso}(C1)$  and  $U_{iso}(C2)$  were constrained to be equal. For Ce<sub>4</sub>(P<sub>0.19</sub>[C<sub>2</sub>]<sub>0.81</sub>)<sub>3</sub> ADP of the phosphorus position was refined in isotropic approximation. c) Occupancy factor: g(C1) = g(C2) = 1-g(P).

Table 3. Selected interatomic distances /Å in the crystal structures of compounds  $RE_4(P_{1-x}[C_2]_x)_3$ .

RE	La	Ce	Ce	Ce	Pr	Nd
x	0.36(1)	0.34(2)	0.42(2)	0.81(2)	0.35(2)	0.32(4)
d(RE-RE)	3.5603(6)-3.8671(6)	3.4909(7)-3.8097(7)	3.5041(7)-3.7949(7)	3.4911(5)-3.7014(5)	3.5087(6)-3.8165(6)	3.447(1)-3.758(1)
d(RE-P)	2.873(1)-3.347(5)	2.843(1)-3.277(5)	2.810(2)-3.247(6)	2.672(4)-3.365(18)	2.835(1)-3.310(5)	2.800(1) - 3.244(7)
d(RE-C)	2.68(3) - 2.92(4)	2.63(3) - 2.86(4)	2.59(2) - 2.88(3)	2.6248(4)-2.789(1)	2.55(2)-2.93(1)	2.50(4) - 2.82(6)
$d(C-C)^{a}$	1.32(7)	1.29(7)	1.34(5)	1.31(2)	1.26(5)	1.40(9)

a) Distances in the C<sub>2</sub> dumbbell.

The Ce- $L_{\text{III}}$  X-ray absorption spectra of Ce<sub>4</sub>[P<sub>1-x</sub>(C<sub>2</sub>)<sub>x</sub>]<sub>3</sub> at different compositions measured at room temperature simultaneously with CeVO<sub>4</sub> and CeO<sub>2</sub> as references (Figure 4) reveal a  $4f^4$  (Ce<sup>3+</sup>) electronic configuration of cerium for samples with x = 0.17 and 0.46. For a lower content of phosphorus (x =

0.86), an additional peak appeared in the spectrum, indicating the presence of species with  $4f^{\theta}$  (Ce<sup>4+</sup>) electronic configuration, that is in good agreement with the changes of lattice parameters, interatomic distances and magnetic susceptibility measurements.





**Figure 3.** Temperature dependence of the reciprocal magnetic susceptibility (H = 10 kOe) for compounds  $RE_4[P_{1-x}(C_2)_x]_3$ . Inset: FC/ZFC splitting of the  $\chi(T)$  dependence for  $Pr_4[P_{0.31}(C_2)_{0.68}]_3$  at H = 100 Oe.



**Figure 4.** Ce- $L_{III}$  X-ray absorption spectra of Ce<sub>4</sub>[P<sub>1-x</sub>(C<sub>2</sub>)<sub>x</sub>]<sub>3</sub> for different compositions. Cerium vanadate CeVO<sub>4</sub> was used as a standard for the  $4f^4$  (Ce<sup>3+</sup>) electronic configuration, CeO<sub>2</sub> was used as a standard for the  $4f^{\theta}$  (Ce<sup>4+</sup>) electronic configuration.

The understanding of the chemical bonding in rare-earth phosphide carbides definitely requires the determination of the electronic state of the C2 dumbbell anions. The significant variations of the charge [from -2, as in CaC<sub>2</sub> [9c] up to -6, as in  $La_3(C_2)I_3$  [9d]] may occur due to the possibility of the triple/ double/single bond formation. The bond order is related to the C-C distance, but the precision of the structural data for this value is not sufficient to reveal such a trend (Table 3). Therefore, the ab initio optimization of the C-C distance in  $La_4[P_{1-x}(C_2)_x]_3$  (x = 1/6, 1/3, 1/2, 2/3, 5/6, and 1) was performed. The dependence of renormalized  $E_{tot}$  from d(C-C) was fitted with the Morse potential  $E = E_0 + D[1 - e^{-a(r-r_c)}]^2$ , giving the equilibrium distances  $r_{\rm e}$  in the range of 1.326–1.330 Å (Figure 5), close to d(C-C) determined from single crystal diffraction data (Table 3), and vibrational frequencies  $v_0$  (1412– 1461 cm<sup>-1</sup>), typical for double C-C bond. No dependence of  $r_{\rm e}$  and  $v_{\rm o}$  on x was observed, proving the conservation of C<sub>2</sub><sup>4-</sup> ethenide anions with variation of x.

**Figure 5.** The dependence of the renormalized  $E_{\text{tot}}$  on d(C-C) in La<sub>4</sub>[P<sub>1-x</sub>(C<sub>2</sub>)<sub>x</sub>]<sub>3</sub>. La<sub>2</sub>C<sub>3</sub> was calculated both with the symmetry of the space group  $I\overline{43}d$  (La<sub>2</sub>C<sub>3</sub>) and P1 (x = 1), all mixed species – in the space group P1.

The calculated C–C distance in  $La_2C_3$  [1.330(2) Å] is larger than the one determined from the crystal structure refinement (1.296(9) Å) [9e]; this effect is mainly caused by the LDA approach used for the calculation. The electronic density of states (DOS, Figure 6) for the model compounds  $La_4[P_{1-x}(C_2)_x]_3$  (x = 1/6) and  $La_2C_3$  (x = 1, Figure 6) evidences a well separated valence band, mainly built up by P(s,p), C(s,p)and La(s) states, and a conduction band formed mainly by La(d) states with a small (< 10 %) contribution of La(f) states. This is in a good agreement with a closed-shell (Zintl-Klemmlike) description according to the charge balance  $([RE^{3^+}]_4[(P^{3^-})_{1-x}(C_2^{4^-})_x]_3 \cdot (3-3x)e^-)$  and assumes the presence of free electrons, which seem to be necessary for the stability of the whole structure, similarly to the phosphide silicides [7]. However, the increase of x leads to a increase of the C(p) states contribution to the conduction band (up to 33 % in  $La_2C_3$ , x =1, Figure 6, bottom), indicating a possible interaction of  $\pi$ states of  $C_2$  anions and d (and/or f) states of the cationic substructure.

A deeper insight into the nature of the atomic interactions in the compounds was achieved by means of the electron localizability indicator (ELI) [10] in a ELI-D representation [19a, 19b], a so-called bonding descriptor in real space [11] in combination with the electron density (ELI/electron density approach) [12a, 12b].

Analysis of the electron density in accordance with the Quantum Theory of Atoms in Molecules [12a, 12b] (i.e. construction of the zero-flux surfaces in the gradient field of ED) reveals complex shapes of the QTAIM atoms for the lanthanum, phosphorus and carbon atoms in direct space, as it may be expected from the topology of the crystal structure (Figure 7). Integration of the electron density within the basins bounded by the zero-flux surfaces yields for lanthanum less electrons as in a neutral atom, for phosphorus and carbon more



**Figure 6.** Electronic density of states (DOS) for  $La_4(P_{1-x}[C_2]_x)_3$  (x = 1/6) and  $La_2C_3$ .

electrons in comparison with neutral atoms. Thus, the charge transfer takes place in agreement with the element's electronegativities: lanthanum forms the cationic substructure, carbon and phosphorus – the anionic one.



Figure 7. QTAIM atoms of lanthanum, phosphorus, and carbon in  $La_4[P_{2/3}(C_2)_{1/3}]_3$ .

The shape of only one representative for each atom type is presented in vicinity of the coordination sphere of the  $C_2$ group. Further details of atomic interaction were investigated by analysis with the electron localizability indicator. The ELI-D distribution in La<sub>4</sub>(P<sub>2/3</sub>[C<sub>2</sub>]<sub>1/3</sub>) has a pronounced shell-like character for the inner shells of the phosphorus atoms. The valence shell of the phosphorus atoms is relatively compact in accordance with the closed-shell picture, but is already structured deviating from the sphere-like distribution and reflecting the influence of the closely located lanthanum cations and ethenide anions (Figure 8, top). Three different attractors are observed for the C<sub>2</sub> species (Figure 8, bottom, Figure 9 top and middle): one is located between the carbon atoms indicating the direct bonding; two others are found on the outer sides of the dumbbell and are interpreted as lone-pair-like. In the vicinity of the lanthanum atoms (Figure 8, top) only five shells can be recognized in the inner region, which means that the electrons of the sixth shell (6s) are transferred to the anionic part of the structure. The penultimate shell (i.e. the fifth one, Figure 8 top) of the lanthanum atoms is slightly structured towards the neighboring phosphorus atoms, towards the middle point of the C-C dumbbell and, in some cases, towards the center of a tetrahedron formed by the neighboring lanthanum atoms. The first two peculiarities indicate participation of the electrons of the penultimate shell of lanthanum atoms in the interactions with the anions. The quantum chemical analysis of this feature is reported in references [18a, 18b]. In the compound  $Ce_4(P_{1/2}Si_{1/2})_3$  such structuring of the penultimate shell of the cerium atoms was observed precisely towards the cen-



**Figure 8.** Electron localizability indicator (ELI-D, *Y*) for  $La_4[P_{2/3}(C_2)_{1/3}]_3$ : (top) section in C–La–P plane; (bottom) isosurface in the vicinity of the  $C_2$  anion with the electron counts for bonding and lone-pair-like attractors.

ters of the phosphorus and silicon anions [7], which reveals a detectable difference in the atomic interactions between the cationic and anionic substructures of the phosphide silicides, and phosphide carbides with *anti*-Th<sub>3</sub>P<sub>4</sub> crystal structure. The third feature suggests the additional interaction between the lanthanum atoms and is supported also by an additional local attractor of ELI-D in this region (Figure 8, bottom)



**Figure 9.** ELI-D basins fort the lone-pair-like attractors (top) and bonding attractor (middle) in the C<sub>2</sub> group as well as the bonding attractor in the center of a La<sub>4</sub> tetrahedron for La<sub>4</sub>[ $P_{2/3}(C_2)_{1/3}$ ]<sub>3</sub>.

The electron counts of the structural species determined by the combined ELI/electron density approach (Figure 8 and Figure 9) yields the formal charge of -2.7 for the anion  $[(P^{3.0})_{2/3}(C_2^{2.1})_{1/3}]$ , similar to -2.91 for the phosphide silicide  $[(P^{2.52-})_{1/2}(Si^{3.30-})_{1/2}])$  [7]. The charge distribution between the anionic components in the phosphide carbide is different in comparison with the silicide. Especially the formal charge of the  $C_2$  group deviates strongly from the expected  $C_2^{4-}$ . The possible reason for that finding is a known difficulty in the handling of the *f* states in the solid-state quantum chemical calculations. The so obtained anion requires for the charge balancing 2.03 electrons from each lanthanum atom, i.e. mostly electrons of the sixth shell with minor participation of the fifth shell. The remaining electrons of the fifth shell realize the multi-center interactions between the lanthanum atoms.



The interactions of the  $\pi$  states of C<sub>2</sub> anion and d (and/or f) states of the cationic substructure observed in the electronic DOS may be visualized in the ELI-D representation in form of the structuring of the penultimate shell and by lower electron counts in the valence region comparing with the Zintl-like counting scheme. These interactions, in combination with an four-center bonding between the lanthanum atoms, seem to be responsible for the stability of the carbides  $RE_2C_3$  (in contrast to  $RE_4Si_3$ , which do not exist) [7] and for the oxidation  $Ce^{3+} \rightarrow Ce^{4+}$  in  $Ce_4[P_{1-x}(C_2)_x]_3$  for large x. At the same time, the formation of ternary compounds  $RE_4[P_{1-r}(C_2)_r]_3$  (RE = La, Ce, Pr, Nd) in phosphorus-rich region (higher relative stability in comparison to hypothetical binary compounds  $RE_4P_3$ ) seems to be caused by the mostly ionic interactions between the anionic and cationic substructures, as in  $RE_4(P_{1-x}Si_x)_{3-z}$  [7]. The heterovalent substitution  $(P^{3-}/Si^{4-} \text{ or } P^{3-}/C_2^{4-})$  changes the total valence electron concentration, moving it to the range, where the anti-Th<sub>3</sub>P<sub>4</sub> structural motif is stable. It should be noted, that the homogeneity range border in the phosphorusrich region is nearly the same both for phosphide carbides and phosphide silicides. Some indications for oxygen intercalation into RE4 tetrahedra were observed, judging by lattice parameters difference for samples, synthesized in alumina crucibles and glassy carbon crucibles. This fact is in agreement with the observation of ELI-D maximum in the center of RE<sub>4</sub>.

#### Conclusions

The rare-earth phosphide carbides  $RE_4[P_{1-x}(C_2)_x]_3$  (RE = La, Ce, Pr, and Nd) represent the first example of a mixed anionic substructure formed by phosphorus atoms and C2 groups commonly occupying the centers of the  $RE_8$  polyhedrons. Together with the recently published RERu2PC and REOs2PC compounds [17] the phosphide carbides of the rare-earth metals represent the first step toward the formation of mixed inorganic P-C species. The peculiarities of the crystal structure, magnetic properties, X-ray absorption data, and quantum chemical calculation results reveal the predominantly ionic nature of the interactions between the rare-earth cations and phosphorus anions. In addition, interaction of  $\pi$  states of C<sub>2</sub> anions and d states of lanthanum in La<sub>4</sub>[ $P_{2/3}(C_2)_{1/3}$ ]<sub>3</sub>, as well as the multicenter interaction in the lanthanum substructure is indicated revealing a bonding difference between phosphide carbides and phosphide silicides despite their extensive crystallographic analogy. A deeper understanding of the composition and temperature dependence of the valence dynamics of cerium in  $Ce_4(P_{1-x}[C_2]_x)_3$  system requires a more elaborate investigation.

#### **Experimental Section**

All synthetic operations were performed in an argon-filled glove box. Rare-earth metals (Lamprecht, 99.9 %), red phosphorus (99.999 %, Alfa Aesar, annealed in vacuo at  $10^{-4}$  mbar), and graphite powder (99.9 %, Chempur) were used for preparations. First, the precursors *REP* and *REC*<sub>2</sub> were prepared by sintering the elements (preceded by arc-melting in case of *REC*<sub>2</sub>), then they were mixed with the additional amount of *RE*, pressed into a pellet, put into a glassy carbon crucible

1323

in a sealed tantalum ampoule, and exposed to several subsequent steps of annealing (900 °C–1250 °C) with intermediate regrinding. The composition of the main phase was investigated by means of WDXS (Cameca SX100 electron microprobe, *RE*NiP compounds as standards, carbon content was calculated by difference) after the metallographic investigation. The lattice parameters of the compounds were determined from powder XRD data (Huber G670 Image Plate Guinier camera,  $\lambda = 1.5406$  Å, LaB<sub>6</sub> as an internal standard, a = 4.15692 Å) applying the program WinCSD [13a].

Single crystals for diffraction investigation were selected in the glove box and sealed in glass capillaries. The experiment was carried out with the Rigaku AFC-7 four-circle diffraction system, equipped with a Mercury 70 CCD detector. The structure was solved by direct methods [13b, 13d] and refined using the JANA2000 [13c], SHELX-97 [13d] with WinGX interface [13e] and WinCSD [13a] program packages.

Magnetization (*M*) measurements were made with a Quantum Design MPMS XL-7 SQUID magnetometer. The temperature dependence of the magnetic susceptibility  $\chi = M/H$  was measured in different external fields (*H* = 100 Oe–10 kOe) in the temperature range of 1.8 K–400 K.

The Ce- $L_{III}$  X-ray absorption spectra of polycrystalline samples Ce<sub>4</sub>[P<sub>1-x</sub>(C<sub>2</sub>)<sub>x</sub>]<sub>3</sub> were recorded at room temperature in a transmission arrangement at the EXAFS II beam line E4 of HASYLAB at DESY. Wavelength selection was realized by means of a Si(111) double crystal monochromator, which yields an experimental resolution of approximately 2 eV (FWHM) for the experimental setup at the Ce- $L_{III}$  threshold of 5745 eV. Experimental data were measured using CeVO<sub>4</sub> and CeO<sub>2</sub> as external references for energy calibration. Deconvolution of the XAS spectra was made by the program XASWin [14].

The electronic structure calculations and ab initio structure optimization for  $La_4[P_{1-x}(C_2)_x]_3$  were carried out using the FPLO 7 [15a] program package. La(4f5s5p5d6s6p6d7s), P (2s2p3s3p3d4s4p), and C (1s2s2p3s3p3d) basis orbitals were used, the calculation was performed within the LDA approach [15b]. The structural models before ordering, for simplicity, were assumed to have  $I\bar{4}3d$  symmetry; the lattice parameter a was determined from the equation  $\alpha(\text{\AA}) = 9.0037$  – 0.2046x (see Figure 2), the x coordinate for the La1 atom [x(RE1)]was calculated as x(La1) = 0.0641 - 0.012x (this equation is determined from the series of structure refinements from powder diffraction data). After ordering the symmetry was reduced to P1. The calculation was done in 64 k-points in the inverse Brillouin zone, inequivalent 384 tetrahedra were used for the integration over the Brillouin zone.  $E_{tot}$ was calculated for 12 values of the carbon coordinate  $x_{\rm C}$  (position 24d:  $x_{\rm C}, 0, 1/4$  of the space group  $I\bar{4}3d$ ) in the range of 0.279–0.328 for each composition, the obtained values were renormalized for the total number of C<sub>2</sub> dumbbells in the unit cell. After fitting  $E_{tot}(x_C)$  the equilibrium atomic coordinates were obtained. The calculation of ELI-D distribution [19a, 19b] for  $La_4[P_{2/3}(C_2)_{1/3}]_3$  was preceded by the band structure calculation by the TB-LMTO-ASA method [15c-15e], La(6s, 5d, 4f), P(3s, 3p) and C(2s, 2p) orbitals were used in the basis directly, while La(6p), P(3d), and C(3d) functions were downfolded. Muffin-tin spheres radii were 1.777-2.198 Å for La, 1.501-1.521 Å for P, and 0.740 Å for C atoms. The calculation was done in 8 k-points, 24 inequivalent tetrahedra were used. The electron localizability indicator (ELI) was evaluated according to [10] with a ELI-D module implemented within the TB-LMTO-ASA program package [15f]. The topology of the ELI-D was analyzed using the program Basin [16] with a consecutive integration of the electron density in basins, which are bound by zero-flux surfaces in the ELI-D gradient field.

**Supporting Information** (see footnote on the first page of this Article): Calculation parameters (atomic coordinates, radii of Muffin-tin spheres).

#### Acknowledgement

P.S.Ch. acknowledges the fellowship of the *Max-Planck-Gesellschaft*. The authors greatly appreciate the helpful discussions with *Miroslav Kohout* and *Ulrich Schwarz*. This work was partially supported by the *Russian Foundation for Basic Research* (RFBR), grant no 06-03-33066a.

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Received: January 11, 2010 Published Online: May 20, 2010