MS15-1-8 Gd_3PS_3 and Gd_3PSe_3: two gadolinium phosphide chalcogenides with Th_3P_4-type crystal structure
#MS15-1-8

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Abstract
Chalcogenides of the rare-earth elements with the Th_3P_4-type structure are well-known throughout the chemical and crystallographic community. Several representatives of the binary sesquisulfides, -selenides and -tellurides RE_2Ch_3 (RE = La – Nd, Sm, Gd – Tb; Ch = S – Te) crystallize with this structure motif [1–2] and represent a cation-deficient variant of the Th_3P_4 prototype, occupying only 10.667 of the 12 possible cationic positions in the cubic unit cell to satisfy charge-neutrality according to $(RE^{3+})_{2.667}\square_{0.333}(Ch^{2-})_4$ for Z = 4. On the other hand, this allows for insertions of further metal cations like Na^+ to yield $NaRE_8Ch_{12}$ (metallic according to $(Na^+)(RE^{3+})_8(Ch^{2-})_{12}(e^-)$) [3] or even additional RE^{3+} cations leading to the composition RE_3Ch_4 (also metallic according to $(RE^{3+})_3(Ch^{2-})_4(e^-)$) [4]. Another example for the versatility of this structure is shown by the series of europium pnictogenide chalcogenides Eu_4Pn_2Ch (Pn = P – Bi, Ch = S – Te) [5], which crystallize in the *anti*-type arrangement of the Th_3P_4 structure. Here, divalent Eu^{2+} cations occupy the former sixfold surrounded anion site and the former cation site is hosting a 2:1 mixture of pnictogenide and chalcogenide anions according to $(Eu^{2+})_4[(Pn^{3-})_2(Ch^{2-})_1]$.The two new gadolinium phosphide chalcogenides Gd_3PS_3 (CSD-2169111) and Gd_3PSe_3 (CSD-2169112) could be obtained by replacing part of the Ch^{2-} anions in gadolinium sulfide and -selenide Gd_3Ch_4 with P^{3-}, resulting in formally ionic compounds with a statistically occupied mixed-anion site and a fully occupied cation site according to $(Gd^{3+})_3[(P^{3-})_1(Ch^{2-})_3]$. So both compounds crystallize in the cubic space group $I\bar{4}3d$ (no. 220) with Z = 4. They exhibit the lattice parameters $a(Gd_3PS_3)$ = 841.45(6) pm and $a(Gd_3PSe_3)$ = 868.79(6) pm, respectively, which are slightly larger for the sulfide, but somewhat smaller for the selenide than those of the corresponding C-type gadolinium sesquichalcogenides (a(C-Gd_2S_3) = 838.47(9) pm [6] and a(C-Gd_2Se_3) = 872.56(5) pm [7] for Z = 5.333). Gd^{3+} is surrounded by eight anions (P^{3-} and Ch^{2-} in a statistic fashion with a molar ratio of 1:3) forming a trigonal dodecahedron (d(Gd–P/S = 282 – 301 pm, d(Gd–P/Se = 290 – 312 pm), whereas the anionic site exhibits a trigonal hemiprismatic coordination sphere with six Gd^{3+} cations in its vicinity (Figure 1, see Table 1 for the atomic coordinates). Energy dispersive X-ray spectroscopy (EDXS) measurements were conducted to verify the composition of Gd_3PS_3 and Gd_3PSe_3 successfully.

Table 1. Atomic positions, equivalent isotropic displacement parameters and coordination numbers (*C.N.*) for Gd_3PS_3 and Gd_3PSe_3.

Atoms		x/a	y/b	z/c	U_{eq} / pm^2	C.N.
Gd_3PS_3						
Gd	(12a)	$^3/_8$	0	$^1/_4$	132(2)	8
P/S	(16c)	0.07268(12)	x/a	x/a	96(5)	6
Gd_3PSe_3						
Gd	(12a)	$^3/_8$	0	$^1/_4$	175(3)	8
P/Se	(16c)	0.17803(8)	x/a	x/a	81(4)	6

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Cubic unit cell of Gd3PS3 and Gd3PSe3.