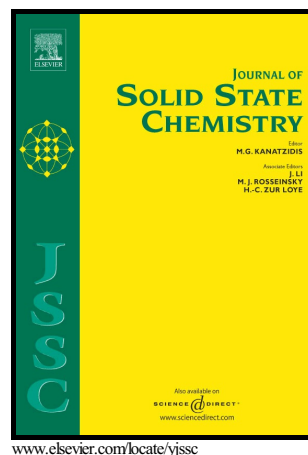


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PII: S0022-4596(17)30080-4  
DOI: <http://dx.doi.org/10.1016/j.jssc.2017.03.009>  
Reference: YJSSC19713

To appear in: *Journal of Solid State Chemistry*

Received date: 14 January 2017

Revised date: 2 March 2017

Accepted date: 4 March 2017

Cite this article as: Abishek K. Iyer, Wenlong Yin, Emma J. Lee, Xinsong Lin and Arthur Mar, Quaternary rare-earth sulfides  $\text{RE}_3\text{M}_{0.5}\text{GeS}_7$  (RE = La–Nd, Sm; M = Co, Ni) and  $\text{Y}_3\text{Pd}_{0.5}\text{SiS}_7$ , *Journal of Solid State Chemistry*, <http://dx.doi.org/10.1016/j.jssc.2017.03.009>

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# Quaternary rare-earth sulfides $RE_3M_{0.5}GeS_7$ ( $RE = La-Nd, Sm$ ; $M = Co, Ni$ ) and $Y_3Pd_{0.5}SiS_7$

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## Abstract

The two metal-deficient series of quaternary Ge-containing sulfides  $RE_3M_{0.5}GeS_7$  ( $RE = La-Nd, Sm$ ;  $M = Co, Ni$ ), as well as the related Si-containing sulfide  $Y_3Pd_{0.5}SiS_7$ , were prepared by reactions of the elements at 1050 °C. Single-crystal X-ray diffraction analysis performed on all compounds confirmed noncentrosymmetric hexagonal structures (space group  $P6_3$ ,  $Z=2$ ) with cell parameters in the ranges of  $a = 10.0-10.3$  Å and  $c = 5.7-5.8$  Å for  $RE_3Co_{0.5}GeS_7$  and  $RE_3Ni_{0.5}GeS_7$ , or  $a = 9.7891(3)$  Å and  $c = 5.6840(4)$  Å for  $Y_3Pd_{0.5}SiS_7$ . They are classified as  $La_3Mn_{0.5}SiS_7$ -type structures, with  $M$  atoms centred within octahedra (in contrast to  $La_3CuSiS_7$ -type structures in which  $M$  atoms occupy trigonal planar sites) and Ge atoms centred within tetrahedra, both types of polyhedra being arranged in one-dimensional stacks aligned along the  $c$ -direction. Charge balance requirements dictate half-occupancy of the  $M$  sites. However, bond valence sum arguments indicated that the  $M$  atoms are somewhat underbonded within these octahedral sites, so that there is evidence that in some compounds, they can also enter the

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