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Crystal structure and magnetic properties of $R_3Co_{0.5}GeS_7$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Tm) and $R_3Ni_{0.5}GeS_7$ (R = Y, Ce, Sm, Gd, Tb, Dy, Ho, Er and Tm)

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ABSTRACT

The crystal structure of quaternary compounds $R_3Co_{0.5}GeS_7$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Tm) and $R_3Ni_{0.5}GeS_7$ (R = Y, Ce, Sm, Gd, Tb, Dy, Ho, Er and Tm) ($La_3Mn_{0.5}SiS_7$ structure type, space group $P6_3$, Pearson symbol *hP*23) was determined by means of X-ray single crystal diffraction. The R atoms are located in trigonal prisms with two additional atoms, the Co (Ni) atoms occupy octahedra, the Ge atoms are located in tetrahedra. Magnetic properties of the compounds $R_3Co_{0.5}GeS_7$ (R = Sm and Gd) and $R_3Ni_{0.5}GeS_7$ (R = Gd, Dy, Er and Tm) were studied down to 1.72 K. Their magnetic behaviour is governed by trivalent rare-earth and divalent transition-metal constituents. In each material, the magnetic exchange interactions are dominated by antiferromagnetic correlations, which promote long-range magnetic orderings at low temperatures.

1. Introduction

Designing new functional materials with increasingly complex compositions (ternary and quaternary) has become a primary direction in modern science and technology. Complex rare-earth-based chalcogenides are interesting due to their specific thermal, electrical, magnetic and optical properties. In recent years, various chalcogenide materials find numerous applications in the field of infrared and nonlinear optics. Systematic investigation of complex rare earth chalcogenide systems is an important way for discovering new materials with useful properties [1,2].

Recently, we reported on the crystal structures and the magnetic properties of the compounds $R_3Mn_{0.5}GeS_7$ (R = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er) and $R_3Fe_{0.5}GeS_7$ (R = Y, La, Ce, Pr, Sm, Gd, Tb, Dy, Ho, Er and Tm), crystallizing with the $La_3Mn_{0.5}SiS_7$-type structure (space group $P6_3$) [3,4]. Here, we present our results obtained for the compounds $R_3Co_{0.5}GeS_7$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Tm) and $R_3Ni_{0.5}GeS_7$ (R = Y, Ce, Sm, Gd, Tb, Dy, Ho, Er and Tm).

2. Experimental details

Samples with the nominal compositions $R_3Co_{0.5}GeS_7$ and $R_3Ni_{0.5}GeS_7$ (R = rare earth metal, except for Eu, Yb and Lu) were prepared by solid state syntheses carried out in resistance furnaces. The calculated amounts of the elemental constituents (the purity was better than 99.9 wt. %) with the atomic ratio R:M:Ge:S = 3:0.5:1:7 (M = Co, Ni) were sealed in evacuated quartz tubes. The ampoules were first heated with a rate of 30 °C per hour up to 1150 °C, and then kept at this temperature for 3 h. Afterwards, the samples were cooled slowly (10 °C per hour) down to 500 °C, and annealed at this temperature for 720 h. Subsequently, the ampoules were quenched in cold water.

The obtained materials were checked by X-ray powder diffraction (XRD) using a DRON-4-13 powder diffractometer (CuK_α radiation, $10° \leq 2\Theta \leq 100°$, step scan mode with a step size of 0.05° and counting time of 5 s per data point). Phase analysis was carried out. Small single crystals suitable for crystal structure investigations were selected from all the prepared $R_3Co_{0.5}GeS_7$ samples and most

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Table 1
Crystal data and structure refinement details of the $R_3Co_{0.5}GeS_7$ (R = Y, La, Ce, Pr, Nd and Sm) compounds.

Empirical formula	$Y_3Co_{0.5}GeS_7$	$La_3Co_{0.5}GeS_7$	$Ce_3Co_{0.5}GeS_7$	$Pr_3Co_{0.5}GeS_7$	$Nd_3Co_{0.5}GeS_7$	$Sm_3Co_{0.5}GeS_7$
Formula weight	593.21	743.21	746.83	749.21	759.20	777.53
Space group	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)
Structure type	$La_3Mn_{0.5}SiS_7$	$La_3Mn_{0.5}SiS_7$	$La_3Mn_{0.5}SiS_7$	$La_3Mn_{0.5}SiS_7$	$La_3Mn_{0.5}SiS_7$	$La_3Mn_{0.5}SiS_7$
Unit cell dimensions	a = 9.729(1) Å c = 5.7744(9) Å	a = 10.3181(7) Å c = 5.8091(6) Å	a = 10.2168(7) Å c = 5.7843(6) Å	a = 10.1474(7) Å c = 5.7735(5) Å	a = 10.0868(7) Å c = 5.7606(5) Å	a = 9.9766(7) Å c = 5.7469(5) Å
Volume	473.3(1) Å^3	535.60(8) Å^3	522.89(7) Å^3	514.85(7) Å^3	507.58(7) Å^3	495.37(7) Å^3
Number of formula units per unit cell	2	2	2	2	2	2
Calculated density	4.162 g/cm^3	4.608 g/cm^3	4.743 g/cm^3	4.833 g/cm^3	4.967 g/cm^3	5.213 g/cm^3
Absorption coefficient	23.665 mm^{-1}	16.546 mm^{-1}	17.751 mm^{-1}	18.961 mm^{-1}	20.178 mm^{-1}	22.734 mm^{-1}
F(000)	549	657	663	669	675	687
Crystal color	Red	Black	Black	Black	Black	Black
Crystal size	0.11 × 0.04 × 0.04 mm	0.07 × 0.05 × 0.04 mm	0.08 × 0.04 × 0.04 mm	0.06 × 0.05 × 0.05 mm	0.07 × 0.05 × 0.04 mm	0.07 × 0.06 × 0.04 mm
Θ range for data collection	2.42–27.47	3.95–27.43	4.21–27.42	4.02–27.46	4.67–27.48	4.09–27.30
Index ranges	$-12 \le h \le 12$ $-12 \le k \le 12$ $-7 \le l \le 7$	$-13 \le h \le 13$ $-13 \le k \le 13$ $-7 \le l \le 7$	$-13 \le h \le 12$ $-13 \le k \le 13$ $-7 \le l \le 7$	$-10 \le h \le 13$ $-13 \le k \le 12$ $-7 \le l \le 7$	$-13 \le h \le 12$ $-12 \le k \le 13$ $-7 \le l \le 7$	$-12 \le h \le 12$ $-12 \le k \le 12$ $-6 \le l \le 7$
Reflections collected	6286	4650	4536	4525	4420	4342
Independent reflections	734 [R(int.) = 0.0880]	815 [R(int.) = 0.0312]	794 [R(int.) = 0.0318]	787 [R(int.) = 0.0333]	760 [R(int.) = 0.0298]	735 [R(int.) = 0.0333]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Absolute structure parameter	−0.03(1)	−0.01(2)	−0.02(1)	−0.02(2)	0.00(2)	−0.02(1)
Data/restraints/parameters	734/1/37	815/1/37	794/1/38	787/1/37	760/1/37	735/1/38
Goodness-of-fit on F^2	1.086	1.218	1.235	1.042	1.118	1.069
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0388, $wR2$ = 0.0642	$R1$ = 0.0182, $wR2$ = 0.0414	$R1$ = 0.0138, $wR2$ = 0.0305	$R1$ = 0.0187, $wR2$ = 0.0317	$R1$ = 0.0165, $wR2$ = 0.0353	$R1$ = 0.0146, $wR2$ = 0.0295
R indices (all data)	$R1$ = 0.0448, $wR2$ = 0.0659	$R1$ = 0.0187, $wR2$ = 0.0416	$R1$ = 0.0144, $wR2$ = 0.0306	$R1$ = 0.0223, $wR2$ = 0.0323	$R1$ = 0.0172, $wR2$ = 0.0354	$R1$ = 0.0163, $wR2$ = 0.0298
Extinction coefficient			0.0453(8)			0.0151(4)
Largest diff. peak and hole	0.841 and −0.980 e/Å^3	0.591 and −1.303 e/Å^3	0.609 and −1.260 e/Å^3	0.508 and −0.714 e/Å^3	0.868 and −1.019 e/Å^3	0.605 and −0.802 e/Å^3