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Ln_3FeGaQ_7: A new series of transition-metal rare-earth chalcogenides

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ABSTRACT

A new series of transition-metal rare-earth chalcogenides, Ln_3FeGaQ_7 (Ln=Nd, Sm, Gd, Dy, Q=S; Ln=Nd, Gd, Dy, Q=Se), have been synthesized by solid state reactions. They are isostructural and crystallize in the space group $P6_3$. They adopt a three-dimensional framework composed of LnQ_7 monocapped trigonal prisms with the interesting $^1_\infty[FeS_3]^{4-}$ chains and isolated GaQ_4 tetrahedra lying in two sets of channels in the framework. Magnetic susceptibility measurements on Ln_3FeGaQ_7 (Ln=Gd, Dy; Q=S, Se) indicate that they are paramagnetic and obey the Curie–Weiss law. Based on the diffuse reflectance spectra, Ln_3FeGaQ_7 (Ln=Gd, Dy; Q=S, Se) should have band gaps smaller than 0.5 eV. Electronic conductivity measurement on $Dy_3FeGaSe_7$ demonstrates semiconducting behavior with σ_{300}=0.124 S/cm. The first-principles calculations were also performed to study the electronic structures of these compounds.

1. Introduction

The research on the chalcogenides containing a combination of *d*-block transition metal (*M*) and *f*-block lanthanide (*Ln*) or actinide (*An*) elements has been very active for decades. The interaction of itinerant *d* electrons of transition-metal elements and the more localized *f* electrons of lanthanide (*Ln*) or actinide (*An*) and the interplay of the covalent *M*–*Q* (*Q*=chalcogen) bonding with the more ionic *Ln*(*An*)–*Q* bonding have brought many new compounds exhibiting a variety of stoichiometries, structures and interesting physical properties [1–25]. For example, $Ba_8Hg_3U_3S_{18}$ contains infinite chains of US_6 octahedra and nearly linear $[S–Hg–S]^{2-}$ dithiomercurate anions, and shows an antiferromagnetic transition at 59 K [1]; $BaLn_2MS_5$ (*Ln*=La–Nd; *M*=Mn–Co, Zn) crystallize in a tetragonal structure (space group *I*4/*mcm*) based on the stacking of $BaMS_4$ and Ln_2S layers and showed antiferromagnetic ordering at low temperatures [2–6]; $Rb_2Pd_4U_6S_{17}$ contains a network of square-planar PdS_4 and shows a phase transition at 13 K during magnetic susceptibility and specific heat measurements, which may result from either antiferromagnetic ordering or a structural phase transition [7].

Most of the newly synthesized *d*/*f* chalcogenides are quaternary compounds which contain an alkali-metal or alkaline-earth metal as the fourth element, owing in large part to the extensive use of the reactive flux method [26]. Moreover, the *d*-element in these quaternary chalcogenides has often been a magnetically silent group IB metal (Cu, Ag, or Au) or group IIB (Zn Cd, Hg) metal. For example, in the more than seventy chalcogenides belonging to $AMLnQ_3$ (*A*=alkali metal; *M*=Zn, Cd, Hg, Mn, Fe, Co; Ln=Y or rare earth; *Q*=chalcogen) and $AMAnQ_3$ (*A*=alkali metal; *M*=Cu, Ag, Au; An=actinide; *Q*=chalcogen) family, more than 90% compounds contain the non-magnetic group IB or IIB metals [27–36]. In contrast, the study on the structure and property of quaternary chalcogenides containing a magnetic active *d*-block metal, such as Mn, Fe, Co, Ni, has been much more limited. However such compounds may exhibit interesting properties due to the different types of spin–spin interactions, namely the *d*–*d*, *d*–*f*, and *f*–*f* interactions. Moreover, the recent discovery of superconductivity in several kinds of iron-based chalcogenides further demonstrates the importance of chalcogenides incorporating a magnetic active *d*-block metal, such as Fe, Co, and Ni [37–40].

Here, we choose magnetic active *d*-block metal, in particular Fe, in the search of new *d*/*f* chalcogenides. With efforts, we have discovered a new series of quaternary chalcogenides, namely the Ln_3FeGaQ_7 (Ln=Nd, Sm, Gd, Dy, Q=S; Ln=Nd, Gd, Dy, Q=Se) compounds, which represent the first series of compounds in the quaternary *M*/*M*′/*Ln*/*Q* (*M*=transition metal; *M*′=group IIIA metal Ga, In; *Ln*=rare-earth; *Q*=S, Se, Te) system. Ln_3FeGaQ_7 (Ln=Nd, Sm, Gd, Dy, Q=S; Ln=Nd, Gd, Dy, Q=Se) are isostructural and crystallize in the noncentrosymmetric space group $P6_3$. The structure features a three-dimensional framework composed of LnQ_7 monocapped trigonal prisms. One-dimensional $[FeQ_3]^{4-}$ chains of face-sharing FeQ_6 octahedra and

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isolated GaQ_4 tetrahedra lie in two sets of channels in the framework, respectively. According to the magnetism measurements, Ln_3FeGaQ_7 (Ln=Gd, Dy; Q=S, Se) are paramagnetic and obey the Curie–Weiss law. In this paper, we report the synthesis, structural characterization, magnetic and optical properties, electronic conductivity, and electronic structures of Ln_3FeGaQ_7 (Ln=Nd, Sm, Gd, Dy, Q=S; Ln=Nd, Gd, Dy, Q=Se) in detail.

2. Experimental section

2.1. Syntheses

The following reagents were used as obtained: Fe (Sinopharm Chemical Reagent Co., Ltd., 99%), Ga (Sinopharm Chemical Reagent Co., Ltd., 99.99%), S (Sinopharm Chemical Reagent Co., Ltd., 99.99%), Se (Sinopharm Chemical Reagent Co., Ltd., 99.95%), and Ln (Ln=Nd, Sm, Gd, Dy) (Alfa Aesar China (Tianjin) Co., Ltd., 99.9%). The binary starting materials, Ga_2S_3 and Ga_2Se_3, were prepared by the stoichiometric reactions of the elements at high temperatures (1273 K for Ga_2S_3 and 1173 K for Ga_2Se_3) in sealed silica tubes evacuated to 10^{-3} Pa.

Ln_3FeGaS_7 (Ln=Nd, Sm, Gd, Dy). Reaction mixtures of 0.5 mmol of Fe, 0.25 mmol of Ga_2S_3, 1.5 mmol of Ln, and 2.75 mmol of S were loaded into fused-silica tubes under an Ar atmosphere in a glovebox. These tubes were sealed under a 10^{-3} Pa atmosphere and then placed in computer-controlled furnaces and heated to 1373 K in 24 h, left for 48 h, cooled to 593 K at a rate of 3 K/h, and finally cooled to room temperature by switching off the furnace. Needle-shaped crystals with the color of black were found in the ampules. The crystals are stable in air.

$Ln_3FeGaSe_7$ (Ln=Nd, Gd, Dy). Reaction mixtures of 0.5 mmol of Fe, 0.25 mmol of Ga_2Se_3, 1.5 mmol of Ln, and 2.75 mmol of Se were ground and loaded into fused-silica tubes under an Ar atmosphere in a glovebox, then flame sealed under a high vacuum of 10^{-3} Pa. The tubes were then placed in computer-controlled furnaces and heated to 1323 K in 20 h, left for 48 h, cooled to 593 K at a rate of 4 K/h, and finally cooled to room temperature by switching off the furnace. Black needle-shaped crystals were found in the ampules. The crystals are stable in air.

The crystals were manually selected for structure characterization and were later determined as Ln_3FeGaQ_7 (Ln=Nd, Sm, Gd, Dy, Q=S; Ln=Nd, Gd, Dy, Q=Se). Analyses of the crystals with an EDX-equipped Hitachi S-4800 SEM proved the presence of Ln, Fe, Ga, and Q in the approximate ratio of 3:1:1:7.

2.2. Structure determination

Single-crystal X-ray diffraction data for the seven compounds were collected at 293 K on an Oxford Diffraction Xcalibur, Sapphire3, Gemini Ultra diffractometer using graphite monochromated Mo$K\alpha$ radiation (γ=0.71073 Å). The data were collected and reduced using Oxford Diffraction CrysAlisPro software [41], and face-indexed absorption corrections were performed numerically with the use of the program XPREP [42].

The structures were solved with Direct Methods implemented in the program SHELXS and refined with the least-squares program SHELXL of the SHELXTL.PC suite of programs [42]. The selected crystals of the three selenides were all found to be twinned with twin ratios of 0.3/0.7; 0.3/0.7; and 0.43/0.57 for Ln=Dy, Gd, and Nd, respectively. The final refinements included anisotropic displacement parameters and a secondary extinction correction. The program STRUCTURE TIDY [43] was then employed to standardize the atomic coordinates. Additional experimental details are given in Table 1, and selected metrical data are given in Table 2. Further information may be found in the Electronic supplementary information.

2.3. Magnetic susceptibility measurements

Due to the low yields in our synthesis and the tiny size of the obtained crystals, only enough Ln_3FeGaQ_7 (Ln=Gd, Dy; Q=S, Se) crystals can be picked for measuring magnetic susceptibility. Single crystals of Ln_3FeGaQ_7 (Ln=Gd, Dy; Q=S, Se) (about 20–30 mg) were ground and loaded into gelatin capsules for measurement of the magnetism. The magnetic susceptibilities were measured by using a Quantum Design SQUID magnetometer (MPMS7T Quantum Design) between 2 K and 300 K in applied field of 10 kOe. The samples were gathered in a sample holder and cooled to the low-temperature limit. The magnetic field was then applied to the samples, then they were slowly warmed to 300 K (zero-field cooling, ZFC), followed by cooling in the field (field cooling, FC). The susceptibility was calculated by dividing by the applied field.

2.4. Diffuse reflectance spectroscopy

A Cary 1E UV–visible spectrophotometer with a diffuse reflectance accessory was used to measure the spectra of Ln_3FeGaQ_7 (Ln=Gd, Dy; Q=S, Se) over the range 500 nm (2.48 eV) to 2500 nm (0.50 eV).

2.5. Electronic conductivity measurement

The electrical resistivity of a single crystal of $Dy_3FeGaSe_7$ was measured along [0 0 1] between 2.0 K and 400 K by standard four-probe DC methods with the use of a Quantum Design PPMS instrument. A crystal, approximately 2 mm in length, was mounted with four leads constructed of 15 μm diameter copper wire, and attached with Dow 4929 N silver paint.

Table 1
Crystal data and structure refinements for Ln_3FeGaQ_7 (Ln=Nd, Sm, Gd, Dy, Q=S; Ln=Nd, Gd, Dy, Q=Se)[a].

	Nd_3FeGaS_7	Sm_3FeGaS_7	Gd_3FeGaS_7	Dy_3FeGaS_7	$Nd_3FeGaSe_7$	$Gd_3FeGaSe_7$	$Dy_3FeGaSe_7$
fw	782.71	801.04	821.74	837.49	1111.01	1150.04	1165.79
a (Å)	9.9041(2)	9.7876(2)	9.6933(3)	9.5946(2)	10.2453(3)	10.0762(2)	9.9956(2)
b (Å)	9.9041(2)	9.7876(2)	9.6933(3)	9.5946(2)	10.2453(3)	10.0762(2)	9.9956(2)
c (Å)	6.0722(2)	6.0989(2)	6.1281(3)	6.1114(2)	6.4076(2)	6.4265(2)	6.3980(2)
V (Å^3)	515.83(2)	505.98(2)	498.65(3)	487.22(2)	582.47(3)	565.07(2)	553.60(2)
ρ_c (g/cm^3)	5.039	5.258	5.473	5.709	6.335	6.759	6.994
μ (cm^{-1})	20.128	22.536	25.153	28.330	38.443	43.450	46.626
$R(F)$[b]	0.0322	0.0203	0.0210	0.0238	0.0412	0.0386	0.0378
$R_w(F_o^2)$[c]	0.0842	0.0463	0.0491	0.0481	0.1082	0.0905	0.0933

[a] For all structures, Z=2, space group=$P6_3$, T=293(2) K, and λ=0.71073 Å.
[b] $R(F)=\sum||F_o|-|F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
[c] $R_w(F_o^2)=\{\sum[w(F_o^2-F_c^2)^2]/\sum wF_o^4)\}^{1/2}$ for all data. $w^{-1}=\sigma^2(F_o^2)+(z\times P)^2$, where $P=(_{Max}(F_o^2, 0)+2F_c^2)/3$.