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Thermoelectrical Investigation of Rare Earth Sulfide Materials

V. V. Sokolov[1], V. V. Bakovetz[1], S. M. Luguev[2], N. V. Lugueva[2]
[1]Nikolaev Institute of Inorganic Chemistry SB RAS, NIIC SB RAS, Novosibirsk, Russia
[2]Amirkhanov Institute of Physic DSC RAS, IPh DSC RAS, Makhachkala, Dagestan. Russia
Email: sokolov@niic.nsc.ru, luguev.if@mail.ru

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ABSTRACT

Results are presented on synthesis and crystal growth of Gd_2S_3 - Dy_2S_3 solid solution sulfides and study of their thermoelectric properties in the range of temperatures 80-400 K. $Gd_{0.2}Dy_{0.8}S_{1.48}$ composition has the best values of thermoelectric efficiency 0.39 x 10^{-3}/K at 400 K.

Keywords: Gd2S3 - Dy2S3 Solid Solution Sulfides; Synthesis; Growth of Crystals; Thermoelectric Properties

1. Introduction

Interest in investigation of rare-earth Ln2S3 sulfides with the structure of Thorium phosphide is bound with possible application of compositions on their base as working elements of thermoelectric energy converters for high temperatures. The researches of GdSy (1.45 ⩽ y ⩽ 1.50) [1,2] showed that some compositions at 1000 K have more high thermoelectric efficiency of Z then Ge-Si solid solution compositions. The structure of Ln2S3 sulfides allows to fill vacancy with rare-earth and other metals and to change their thermoelectric properties. To increase thermoelectric efficiency of material it is usual to decrease its thermal conductivity creating there additional centers of phonon scattering. Such centers for the GdSy system may be presented by the doping paramagnetic ions of rare-earth elements scattering phonons and decreasing thermal conductivity but not modifying electrical characteristics of the compound. The research of Gd1-xDyxS1.48 compositions containing paramagnetic Dy ions showed that in this system near Gd0.2Dy0.8S1.48 have the minimum thermal conductivity [3]. Therefore is of interest to study dynamics of thermoelectric properties of these compositions in dependence from temperature. In this work the synthesis, preparation of crystals in Gd2S3 - Dy2S3 system and their thermoelectric properties in the range of temperatures 80-400 K are presented.

2. Experimental

2.1. Preparation of Gd2S3 and Dy2S3 Sulfides

Sulfides Gd2S3 and Dy2S3 were prepared from high-purity rare earth oxides (99.95%) by H2S sulfidizing at 950– 10000 C [4].

The mixtures of sulfides for crystallization were prepared with 0.1 mol. step.

2.2. Growth of Gd2S3 - Dy2S3 Solid Solution Crystals

Directed crystallization from sulfide melts at 1700 -2000^{0}C in carbon and glass-carbon containers with HF heating was used.

Crystallization of prepared compositions was carried out under inert gas atmosphere for preparation of nonstoichiometric with electron conductivity crystals [5]. Crystallization velocity was 5 - 30 mm/h. The diameter of the obtained cylindrical samples of crystals was 10 mm and height - 10–30 mm.

2.3. Methods of Characterization of Crystals

- XRD - parameters of cubic Th_3P_4 type
- Gravimetric measurements of density
- Measurements of Seebeck coefficient at 20^0 C
- Chemical and gas-chromatografic analysis of composition [6]

2.4. Study of Thermoelectrical Properties

To study thermoelectrical properties the samples were cut from the central part of ingots that was the most uniform. At temperature measurements the composition change on sulfur therefore uncertainty in an index at sulfur +-0.01 is possible.

Measurements of thermal conductivity coefficient were performed with absolute stationary method.

The equipment simultaneously with measurement of κ in the same samples allowed to measure electrical conductivity and Seebeck coefficient at 80-400 K.

3. Results and Discussion

3.1. Characterization of Prepared Crystals

Results of characterization of prepared crystals of Gd_2S_3 - Dy_2S_3 solid solution is presented in **Table 1**.

All crystals have cubic structure of Th_3P_4 type with linear dependence of cell parameters from composition.

The same dependence is in density of crystals from composition.

Deviation of composition from stoichiometry from Gd_2S_3 to Dy_2S_3 agree with their phase diagrams.

Increasing of Seebeck coefficient from Gd_2S_3 to Dy_2S_3 to

agree with deviation composition from stoichiometry of crystals.

3.2. Results of Thermoelectric Measurements

Temperature dependences of thermal conductivity coefficient in Gd_2S_3 - Dy_2S_3 system for the series of compositions at 80 - 400 K are presented in **Figure 1**.

Up to $Gd_{0.6}Dy_{0.4}S_{1.48}$ thermal conductivity weakly depends on the concentration of Dy ions and $Gd_{0.2}Dy_{0.8}S_{1.490}$ sample has minimal thermal conductivity in this system (**Figure 2**).

Analysis of thermal conductivity is made in paper [3]. Substantial decrease of thermal conductivity coefficient is observed for the compositions with x > 0.6, and minimal value κ — at x = 0.8. Such dependence of thermal conductivity coefficient of the samples unusual for phonon heat transfer is results from phonon scattering by paramagnetic ions of Dysprosium.

Results of Seebeck coefficient and electrical conductivity measurements are presented on **Figure 3** and **4**.

Temperature dependence of Seebeck coefficient and electrical conductivity has the same character that usual metals or doped semiconductors. At constant concentration of carriers of a current and decrease of their mobility with growth of temperature Seebeck coefficient linearly grows and electrical conductivity decreases.

Table 1. Characteristics of crystals in Gd2S3 - Dy2S3 system.

Composition mol. Gd_2S_3	Parameter of cell, Å	Index *y* in $Gd_{1-x}Dy_xS_y$ exp.	Index *y* in $Gd_{1-x}Dy_xS_y$ calc.	Density d, g/ cm^3 exp.	Density d, g/ cm^3 calc.	Seebeck coeff. α, mkV/ K
1	8.372	1.466	1.464	6.30	6.29	62
0.9	8.365	1.464	1.467	6.33	6.34	68
0.8	8.358	1.471	1.470	6.35	6.35	77
0.7	8.350	1.476	1.477	6.36	6.37	72
0.6	8.340	1.479	1.480	6.39	6.39	80
0.5	8.331	1.478	1.482	6.42	6.43	76
0.4	8.328	1.479	1.473	6.46	6.45	88
0.3	8.323	1.488	1.482	6.47	6.45	107
0.2	8.311	1.490	1.487	6.50	6.49	110
0.1	8.302	1.489	1.486	6.54	6.53	104
0	8.292	1.493	1.495	6.55	6.56	125

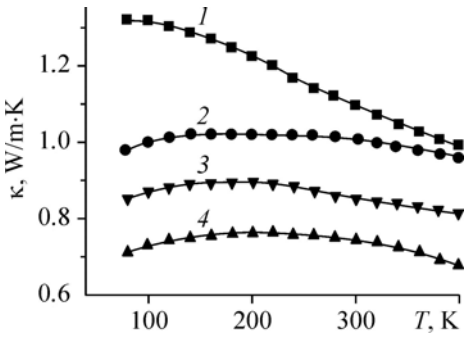

Figure 1. Temperature dependences of thermal conductivity coefficient of $GdS_{1.48}$ (1), $Gd_{0.6}Dy_{0.4}S_{1.48}$ (2), $DyS_{1.48}$ (3), $Gd_{0.2}Dy_{0.8}S_{1.48}$ (4).

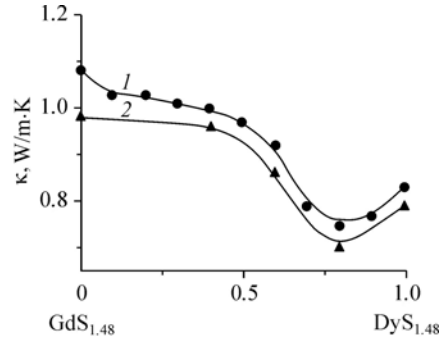

Figure 2. Concentration dependences of thermal conductivity coefficient of solid solutions $Gd_{1-x}Dy_xS_{1.48}$ at 300 (1) and 400 K (2).

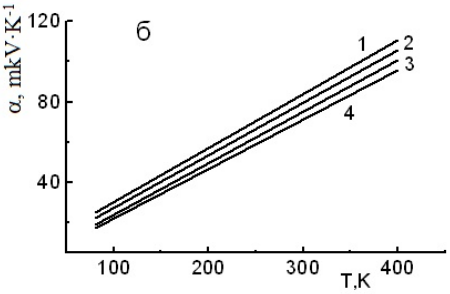

Figure 3. Temperature dependences of Seebeck coefficient of $Gd_{0.3}Dy_{0.7}S_{1.48}$ (1), $Gd_{0.2}Dy_{0.8}S_{1.48}$ (2), $Gd_{0.1}Dy_{0.9}S_{1.48}$ (3), $GdS_{1.48}$ (4).

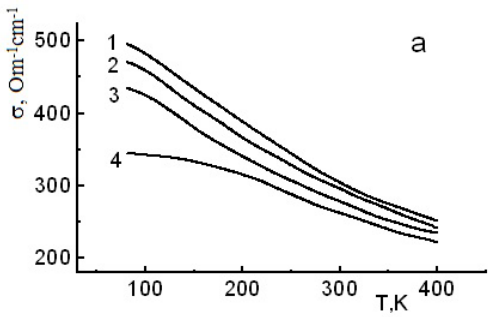

Figure 2. Temperature dependences of electrical conductivity of $GdS_{1.48}$ (1), $Gd_{0.1}Dy_{0.9}S_{1.48}$ (2), $Gd_{0.2}Dy_{0.8}S_{1.48}$ (3), $Gd_{0.3}Dy_{0.7}S_{1.48}$ (4).

Replacement of Gadolinium by Dysprosium as it was established earlier [7], at 300 K changes of Seebeck coefficient growth and electrical conductivity lowering no more than for 18 % within $Gd_{1-x}Dy_xS_{1.48}$ compositions. At 80 K electrical conductivity of $Gd_{0.3}Dy_{0.7}S_{1.48}$ is lower for 30%, than at $GdS_{1.48}$.

On the basis of experimental data of Seebeck coefficient and electrical and thermal conductivity the thermoelectric efficiency ($Z = \alpha^2\sigma/\kappa$) of the studied compositions was calculated. $Gd_{0.2}Dy_{0.8}S_{1.48}$ composition has the best values of this parameter among the samples investigated in this work. Values Z for the studied samples at 300 and 400 K are presented in the **Table 2**.

Thus, study of thermal conductivity, Seebeck coefficient and electrical conductivity of $Gd_{1-x}Dy_xS_{1.48}$ compositions in a range of temperatures 80-400 K showed that the main contribution to heat transfer to them is brought by fluctuations of a crystal

Table 2. Thermoelectric properties of some $Gd_{1-x}Dy_xS_{1.48}$

composition.

Composition	**-α, mkV·K^{-1} 300 K**	**σ, Om^{-1}cm^{-1} 300 K**	**κ, W m^{-1}K^{-1} 300 K**	**Z·10^3, K^{-1} 300 K**	**Z·10^3, K^{-1} 400 K**
$GdS_{1.48}$	72	304	1.04	0.16	0.27
$Gd_{0.3}Dy_{0.7}S_{1.48}$	83	262	0.80	0.23	0.34
$Gd_{0.2}Dy_{0.8}S_{1.48}$	80	278	0.74	0.24	0.39
$Gd_{0.1}Dy_{0.9}S_{1.48}$	75	298	0.84	0.20	0.32

lattice. It is established that replacement of atoms of a Gadolinium by Dysprosium reduces thermal conductivity with growth of deficiency of a crystals and additional scattering of phonon on paramagnetic Dy ions. On the basis of experimental data in all studied temperature interval the $Gd_{0.2}Dy_{0.8}S_{1.48}$ sample has maximal value of thermoelectric efficiency.

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