Reports of the Academy of Sciences of the USSR

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1963

SovietRxiv

Abstract

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Reports of the Academy of Sciences of the USSR

1963. Volume 152, No. 3

PHYSICAL CHEMISTRY

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ELECTROPHYSICAL PROPERTIES OF THE SESQUISULFIDES OF LANTHANUM AND CERIUM

(Presented by Academician A. P. Aleksandrov on 15 V 1963)

The sesquisulfides of lanthanum and cerium are compounds of the type $A_2^{III}B_3^{VI}$, the atoms of whose components are in normal valence states Me^{3+} and S^{2-}. The chemical bond in the sesquisulfides is heterodesmic in character (covalent between sulfur atoms and ionic between sulfur and metal atoms ([1,2])), which, together with their defective structure of the Th_3P_4 type, causes an asymmetry in the distribution of electron density in the crystal lattice; this should be accompanied by the appearance of energy gaps characteristic of semiconductors. However, the electrophysical properties of the lanthanide sesquisulfides, in particular those of lanthanum and cerium, have practically not been studied, apart from a very approximate value of the specific electrical resistivity of Ce_2S_3 at room temperature ([3]), obtained in a purely technological study.

In the present work the specific electrical resistivity of La_2S_3 and Ce_2S_3 was investigated at temperatures of 20° and in the range 100—1000° on polycrystalline samples obtained by sintering in an H_2S atmosphere compacts pressed from powders. The latter were prepared by the methods described in ([2,4]) and had a practically exact stoichiometric composition (for example, in La_2S_3, 25.6% S as against 25.72% S by calculation). The residual porosity of the samples was 13–18% (the number of samples within these porosity limits was 4–6). The specific electrical resistivity was measured by a compensation method according to the usual two-probe direct-current technique, with indirect heating of the samples in a vacuum of 10^{-2}—10^{-3} mm Hg; the thermoe.m.f. was measured relative to alumel reference electrodes by the method of ([5]). The obtained values of the specific electrical resistivity were recalculated to zero porosity by the known formula of V. I. Odelevskii ([8]); the error of determination over the entire temperature range did not exceed 3%, and the error in determining the mean value of the thermoe.m.f. coefficient was 10%. The results obtained are given

in Table 1 and in Fig. 1.

As follows from the temperature dependence of the electrical resistivity (see Fig. 1), both sulfides are impurity p-type semiconductors with the following characteristics:

Sulfide	Temperature of transition to intrinsic conductivity, °C	Activation energy of impurities ΔE_p, eV	Width of the forbidden band, ΔE_0, eV
La_2S_3	600–700	0.32 ± 0.01	1.32 ± 0.02
Ce_2S_3	670 ± 50	0.25 ± 0.03	1.12 ± 0.10

The specific electrical resistivity of Ce_2S_3, as well as the corresponding values of the impurity activation energy and the width of the forbidden band, are somewhat lower than for La_2S_3. This is in good agreement with the maximum stability of the $4f$-electron shell of lanthanum ([6]) and the further increase in

number of possible electronic transitions to the period. In this connection, for lanthanum the possibilities of $f \to d$ transitions are still more restricted because it has one $5d$ electron, whereas for cerium its inherent possibilities of $f \to d$ transitions can be realized completely. The absolute values of the band gaps show that the displacement of the relative maximum of the electron density toward the skeletal framework of the sulfur atom corresponds only to partial organization of the covalent S–S bonds, since when these bonds are saturated the energy barrier would prove to be considerably larger.

Table 1

Temperature dependence of the specific electrical resistivity and thermoelectric e.m.f. coefficient of the sulfides La_2S_3 and Ce_2S_3

Temp., °C	La_2S_3 $\lg \rho_p^*$	La_2S_3 thermoelectric e.m.f., μV/deg	Ce_2S_3 $\lg \rho_p^*$	Ce_2S_3 thermoelectric e.m.f., μV/deg	Temp., °C	La_2S_3 $\lg \rho_p^*$	La_2S_3 thermoelectric e.m.f., μV/deg	Ce_2S_3 $\lg \rho_p^*$	Ce_2S_3 thermoelectric e.m.f., μV/deg
20	7.07	+354	6.14	+574	600	3.45	−71	3.20	+354
100	6.42	+286.0	5.25	+545	700	3.24	−141	3.00	+245
200	4.52	+204	4.58	+517	800	2.84	−223	2.60	+67
300	4.07	+136	4.10	+489	900	1.78	−471	2.30	−291
400	3.70	+76	3.78	+455	1000	0.73	−794	1.70	−670
500	3.55	+44	3.50	+412					

* ρ_{p} –averaged values of the specific electrical resistivity of specimens with porosity of 13-16%.

The high specific resistance at room temperature shows that the concentration of free carriers corresponds to the nondegenerate state of the semiconductor. The thermoelectric e.m.f. coefficient at temperatures corresponding to impurity conduction has a positive sign and exhibits an inversely proportional dependence on temperature, which can be expressed by the formula of N. L. Pisarenko ([7]), simplified for the case of dominant diffusion of carriers of one sign, in the form:

$$\alpha_t = \frac{+k}{e}\left(B + \frac{1}{2}\frac{\Delta E_{\text{p}}}{kT}\right), \tag{1}$$

where B is a constant depending on the impurity concentration and the carrier-scattering mechanism, and ΔE_{p} is the impurity activation energy. The corresponding calculations gave $B = 1.98$ for La_2S_3, and $B = 0$ for Ce_2S_3; then formula (1) may be written as:

for La_2S_3

$$\alpha_t = +86\left(\frac{1}{2}\frac{\Delta E_{\text{p}}}{kT} - 1.98\right),$$

for Ce_2S_3

$$\alpha_t = +\frac{1}{2}\frac{\Delta E_{\text{p}}}{eT}\ \mu\text{V/deg}.$$

Fig. 1. Temperature dependence of the electrical resistivity of La_2S_3 (1) and Ce_2S_3 (2)

$$\left(\lg \rho_{\text{p}} = f\left(\frac{10^3}{T}\right)\right)$$

When α_t is calculated from these formulas, the error is comparable with the experimental error.

In the intervals 500-600° for La_2S_3 and 700-800° for Ce_2S_3, the thermoelectric e.m.f. coefficient changes sign. It should be noted that the characteristic Debye –

temperature, calculated from the experimentally determined values of the coefficient of thermal expansion ($9.90 \cdot 10^{-6}$ for La_2S_3 and $10.45 \cdot 10^{-6}$ for Ce_2S_3), proved to be very close to the indicated temperature values (913–928° K, or on the average 650° C).

In the region of intrinsic conductivity the negative thermo-e.m.f. coefficient is directly proportional to temperature and is well described by the empirical formulas:

$$\text{for } La_2S_3 \quad \alpha_t = -[250 + 3(t - 800)] \ \mu V/\text{deg};$$

$$\text{for } Ce_2S_3 \quad \alpha_t = -4(t - 800) \ \mu V/\text{deg}.$$

The temperature dependences of the specific electrical resistivity and of the thermo-e.m.f. coefficient, as well as the sign of the latter, make it possible to assume that the mobility of holes in the temperature region close to room temperature is higher than the mobility of electrons, since the concentration of impurity electrons and holes (ions of impurity atoms) cannot be different. This agrees well with the concepts of carrier scattering by ionized impurities, in which light electrons are scattered much more strongly than holes. With increasing temperature, thermal vibrations of the lattice begin to play a role; in this case the heavier holes are carried along by phonons more strongly than electrons, which gradually leads to an equalization of the carrier mobilities and to a decrease of the thermo-e.m.f. At temperatures close to the transition temperature to intrinsic conductivity, the diffusion fluxes of carriers of both signs fully compensate one another and the thermo-e.m.f. coefficient becomes equal to zero. The growth of the negative thermo-e.m.f. coefficient in the region of intrinsic conductivity is evidently due both to a decrease in hole mobility (caused by their strong entrainment by phonons) and to an increase in the concentration of intrinsic conduction electrons.

The high value of the thermo-e.m.f. coefficient in the high-temperature region and its practically linear dependence on temperature in the region of intrinsic conductivity are of importance for making thermoelectrodes for temperature sensors from the sesquisulfides of lanthanum and cerium and for use in converters (their thermoelectric figure of merit coefficient proved to be approximately $Z_{1200^\circ} = 10^{-3}$ deg^{-1}).

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Received
6 V 1963

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Note: Figure translations are in progress. See original paper for figures.