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PHASE EQUILIBRIA AND OXIDATION MECHANISMS IN THE LA–S–O SYSTEM

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The phase diagram of the La–S–O system at 1073 K was established with the vacuum seal technique. Six phases exist at this temperature: La_2O_3 (B-type), LaS_2, La_2S_3, $La_2O_2SO_4$, La_2O_2S and $La_2O_2S_2$. The thermodynamic functions for the reaction $La_2O_2SO_4 = La_2O_3 + SO_2 + 1/2\ O_2$ were determined by using the emf method at temperatures from 1123 to 1373 K. The mechanisms of the oxidation reactions in the La–S–O system under different partial pressures of oxygen ($-4.4 < \log P_{O_2} < -0.7$) were also investigated by means of DTA, TG and powder X-ray diffractometry.

Many phases have been reported to exist in the La–S–O system at high temperatures, e.g. La_2O_3, LaS_2, La_2S_3, $La_2O_2SO_4$, La_2O_2S, $La_2O_2S_2$, $La_2(SO_4)_3$ etc. La_2O_3 has five polymorphs [1–4]: A-type (hexagonal), B-type (monoclinic), C-type (cubic), H-type (hexagonal at high temperature) and X-type (structure unknown). The temperature range of stability for each La_2O_3 other than the B-type has been already established [5]. Three polymorphs of La_2S_3 [6–8] are known: α-phase, β-phase and γ-phase. Stable β-La_2S_3 exists at temperatures between 923 and 1623 K. Recently, Besançon *et al.* [9–12] discovered $La_{10}S_{14}O$ with a tetragonal structure and reported that this compound forms a solid solution with β-La_2S_3. LaS_2 with a cubic structure has been synthesized by Flahaut *et al.* [13] and orthorhombic LaS_2 has been reported by Dugue *et al.* [14] and Benazeth *et al.* [15].

The thermodynamic data on the formation of La_2O_3 in the range of temperature from 298 to 1200 K and those for La_2S_3 from 298 to 2400 K have been compiled by Barin *et al.* [16, 17], and those for La_2O_2S have been reported by Laptev *et al.* [18]. Moreover, thermodynamic studies on the $La_2O_2SO_4$–$La_2(SO_4)_3$ and La_2O_3–$La_2O_2SO_4$ systems have been carried out by Kellogg [19] and Grizik *et al.* [4], respectively. Wendlandt *et al.* [20, 21] investigated the thermal decomposition of $La_2(SO_4)_3 \cdot 9\ H_2O$.

In the present paper, the phase relations in the La–S–O system at 1073 K were investigated by using the vacuum seal technique, and the thermodynamic functions for the reaction $La_2O_2SO_4 = La_2O_3 + SO_2 + 1/2\ O_2$ were estimated by the emf method using calcia-stabilized zirconia. Further, the mechanisms of the reactions of oxidation for each compound existing in the La–S–O system were studied under different partial pressures of oxygen by means of DTA, TG and powder X-ray diffraction.

Experimental

Preparation of starting material

a) *Lanthanum oxide*, La_2O_3

Reagent grade La_2O_3 from Wako Pure Chem. Indust. Ltd. was used as starting material. It was heated at 1073 K in air for two days to convert the negligible amount of $La(OH)_3$ present as impurity into oxide, and we thereby obtained hydroxide-free La_2O_3. The material was characterized by powder X-ray diffraction as A-type La_2O_3.

b) *Lanthanum oxide sulfide*, $La_{10}S_{14+x}O_{1-x}$ (β-La_2S_3 phase)

The stoichiometric β-La_2S_3 could not be synthesized, but $La_{10}S_{14+x}O_{1-x}$, a solid solution of tetragonal β-La_2S_3, was prepared by heating La_2O_3 in H_2S (1 ml/s) at 1073 K for one day. The composition x was determined to be 0.06 by thermogravimetry.

c) *Lanthanum oxide sulfiate*, $La_2O_2SO_4$

$La_2O_2SO_4$ was prepared by heating La_2O_3 in SO_2 (1 ml/s) at 1073 K for one day. It has an orthorhombic structure [22].

d) *Lanthanum disulfide*, LaS_2

LaS_2 with a cubic structure was prepared by heating La_2O_3 in H_2S (1 ml/s) at 873 K for three days. The exact composition was $LaS_{1.92}$.

e) *Lanthanum oxide sulfide*, La_2O_2S

La_2O_2S with a hexagonal structure was prepared by heating reagent grade $La_2(SO_4) \cdot 9\ H_2O$ in H_2 (1 ml/s) at 1173 K for one day.

f) *Lanthanum oxide sulfide*, $La_2O_2S_2$

$La_2O_2S_2$ was prepared by heating LaS_2 in air at 873 K for two days. The single phase $La_2O_2S_2$ could not be obtained, but instead a mixed phase with $La_2O_2SO_4$. Accordingly, the mixed phase sample was used for DTA and TG measurements.

Determination of phase diagram

The above materials and crystalline sulfur were mixed in the desired proportion. 50 vacuum-sealed ampoules containing about 200 mg of sample mixture of various composition were prepared. They were heated at 1073 K for two weeks, followed by quenching to ice temperature. The phase of the quenched sample was identified by powder X-ray diffraction. No evidence of the reaction of any of the samples with the silica tube was found after the experimental runs.

Thermodynamic study

In order to determine the standard Gibbs energy change of the thermal decomposition of $La_2O_2SO_4$

$$La_2O_2SO_4 = La_2O_3 + SO_2 + 1/2\,O_2 \tag{1}$$

the equilibrium partial pressure of oxygen (P_{O_2}) was measured by the usual emf method, using one end closed calcia-stabilized zirconia (c. s. z. with 15% CaO) as a solid electrolyte in the temperature range from 1123 to 1373 K. As a reference material a mixture of nickel and nickel oxide was put inside the c.s.z. tube. The c.s.z. tube was inserted into the mixture of La_2O_3 and $La_2O_2SO_4$ contained in a silica crucible. In order to prevent the oxidation of the sample, oxygen-free nitrogen gas (purified with an oxygen pump made of c.s.z.) was passed onto the surface of the mixture. The emf at each temperature was measured with a high-impedance microvoltmeter. When the emf remained constant for three hours, it was considered that the equilibrium state in the system had been attained. The equilibrium partial pressure of oxygen for the mixture of nickel and nickel oxide as a function of temperature is obtained from the JANAF Thermodynamic Tables [23] as follows:

$$\log P_{O_2}(\mathrm{Ni} + \mathrm{NiO}) = -24507/T(\mathrm{K}) + 8.829\,. \tag{2}$$

The P_{O_2} for reaction (1) is calculated via the following equation:

$$\log P_{O_2}(\mathrm{sample}) = \log P_{O_2}(\mathrm{Ni} + \mathrm{NiO}) - 20.157/T(\mathrm{K}) \times E(\mathrm{mv}) \tag{3}$$

where E and T are the emf and absolute temperature, respectively. At the end of the experiment, both the initial phases of the sample were reidentified. The sample reacted neither with the c.s.z. tube nor with the silica tube.

Mechanisms of oxidation reactions in the La – S – O system

The mechanisms of the reactions of oxidation in the La – S – O system on heating under a P_{O_2} (P_{O_2} range from $10^{-0.7}$ to $10^{-4.4}$ atm) were investigated by means of DTA, TG and powder X-ray diffraction. The materials studied were $La_{10}S_{14+x}O_{1-x}$, LaS_2, La_2O_2S, $La_2O_2S_2$, $La_2(SO_4)_3 \cdot 9\,H_2O$ and $La_2O_2SO_4$. DTA and TG were simultaneously measured with a Thermoflex R · TG – DTA, Rigaku Co. Ltd. The oxygen pressures were controlled by passing N_2, air and a mixture of O_2 an N_2. Oxygen present as impurity in a commercial N_2 cylinder was determined by means of the emf method to have $\log P_{O_2} = -4.4$, while that in air had $\log P_{O_2} = -0.7$. The experimental conditions for DTA were as follows; reference material: α-Al_2O_3, flow rate: 1.6 ml/s, heating rate: 10°/min, sample weight: 15 – 30 mg. Samples were quenched to slightly above or below the temperature at which the DTA peak appeared, and the coexisting phases were identified by powder X-ray diffraction.

Results and discussion

Phase diagram

Table 1 shows the compositions and phases of the quenched samples. From these values the phase diagram for the La – S – O system at 1073 K was determined; this is shown in Fig. 1. The following seven phases existed stably under the present experimental conditions: β-La_2S_3, LaS_2 (cubic), LaS_2 (orthorhombic), $La_2O_2S_2$, La_2O_3 (B-type) and $La_2O_2SO_4 \cdot La_2OS_2$, reported by Verkhovets *et el.* [24], was not found in the present experiment. Only the β-La_2S_3 and LaS_2 phases formed solid solutions with oxygen. Besonçon *et al.* [9 – 12] have reported that oxygen atoms could substitute sulfur atoms in β-La_2S_3 up to 4 mol%. The exact composition of LaS_2 in the

Table 1

Results of firing samples in vacuum-sealed tubes at 1073 K for 2 weeks

Component	Phases	Component	Phases
$La_{0.10}S_{0.65}O_{0.25}$	B + C	$La_{0.17}S_{0.40}O_{0.43}$	B + C
$La_{0.10}S_{0.70}O_{0.20}$	B + C	$La_{0.17}S_{0.45}O_{0.38}$	B + C
$La_{0.10}S_{0.80}O_{0.10}$	A + A′ + B	$La_{0.17}S_{0.50}O_{0.33}$	B + C
$La_{0.10}S_{0.85}O_{0.05}$	A′ + B + C	$La_{0.17}S_{0.55}O_{0.28}$	B + C
		$La_{0.17}S_{0.60}O_{0.23}$	B + C
$La_{0.22}S_{0.30}O_{0.48}$	B + C	$La_{0.17}S_{0.65}O_{0.18}$	B + C
$La_{0.22}S_{0.35}O_{0.43}$	B + C	$La_{0.17}S_{0.80}O_{0.03}$	A + B
$La_{0.22}S_{0.40}O_{0.38}$	B + C		
$La_{0.22}S_{0.45}O_{0.33}$	B + C	$La_{0.29}S_{0.20}O_{0.51}$	B + C + D
$La_{0.22}S_{0.50}O_{0.28}$	B + C	$La_{0.29}S_{0.45}O_{0.26}$	A + B
$La_{0.22}S_{0.60}O_{0.18}$	A + B	$La_{0.29}S_{0.50}O_{0.21}$	A + B
$La_{0.22}S_{0.65}O_{0.13}$	A + B	$La_{0.29}S_{0.55}O_{0.16}$	A + B
$La_{0.22}S_{0.70}O_{0.08}$	A + B	$La_{0.29}S_{0.60}O_{0.11}$	A + B
$La_{0.22}S_{0.75}O_{0.03}$	A + B	$La_{0.29}S_{0.65}O_{0.06}$	A + B
$La_{0.23}S_{0.75}O_{0.02}$	A	$La_{0.30}S_{0.21}O_{0.49}$	B + C + D
$La_{0.23}S_{0.65}O_{0.12}$	A′ + B	$La_{0.30}S_{0.17}O_{0.53}$	C + D
$La_{0.23}S_{0.47}O_{0.29}$	B + C	$La_{0.30}S_{0.10}O_{0.60}$	C + D + F
$La_{0.23}S_{0.37}O_{0.40}$	B + C		
$La_{0.23}S_{0.26}O_{0.51}$	B + C	$La_{0.37}S_{0.61}O_{0.02}$	A + E
$La_{0.23}S_{0.13}O_{0.64}$	C	$La_{0.37}S_{0.56}O_{0.07}$	A + D + E
$La_{0.23}S_{0.11}O_{0.66}$	C + F	$La_{0.37}S_{0.50}O_{0.13}$	A + D + E
		$La_{0.37}S_{0.36}O_{0.27}$	A + D
$La_{0.30}S_{0.68}O_{0.02}$	A	$La_{0.37}S_{0.22}O_{0.41}$	C + D
$La_{0.30}S_{0.55}O_{0.15}$	A + B	$La_{0.37}S_{0.19}O_{0.44}$	C + D
$La_{0.30}S_{0.41}O_{0.29}$	A′ + B	$La_{0.37}S_{0.14}O_{0.49}$	C + D + F
$La_{0.30}S_{0.36}O_{0.34}$	B	$La_{0.37}S_{0.05}O_{0.58}$	C + D + F
$La_{0.30}S_{0.27}O_{0.43}$	B + C + D		

A: LaS_2(cubic), A′: LaS_2 (orthorhombic),
B: $La_2O_2S_2$, C: $La_2O_2SO_4$, D: La_2O_2S, E: $La_{10}S_{14+x}O_{1-x}$, F: La_2O_3

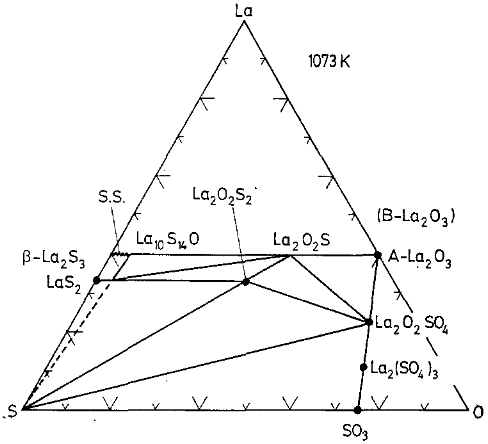


Fig. 1. Phase diagram on the La—S—O system at 1073 K

present study was found to be $LaS_{1.92}$. However, here we could not determine the amount of substituting oxygen atoms in the LaS_2. Consequently, the LaS_2 region is indicated by the broken line in the phase diagram. LaS_2 usually forms a cubic structure, but in a sulfur-rich composition it is transformed to an orthorhombic structure. However, the sulfur pressure could not be determined in the present experiment. According to the literature [5], the A-type La_2O_3 is stable at temperatures from 873 to 2373 K, but under the present experimental conditions the La_2O_3 was of B-type.

Thermodynamic considerations

Figure 2 shows the relation between the logarithm of the equilibrium partial pressure of oxygen and $10^4/T$, measured by the emf method for the following reaction:

$$La_2O_2SO_4 = La_2O_3 + SO_2 + 1/2\, O_2. \qquad (4)$$

The equilibrium partial pressures of sulfur dioxide were calculated by using Eq. (5), derived from the mass balance and the equilibrium constant K_6 of reaction (6):

$$6\, P^2_{SO_2} + K_6^2 P^2_{O_2} P_{SO_2} - 2\, K_6^2 P^3_{O_2} = 0 \qquad (5)$$

$$1/2\, S_2 + O_2 = SO_2 \qquad (6)$$

The mass balance of each element in the gas phase could be expressed as follows:

$$S; \quad P^{i}_{SO_3} = P_{SO_3} + P_{SO_2} + 2\, P_{S_2} \qquad (7)$$

$$O; \quad 3\, P^{i}_{SO_3} = 3\, P_{SO_3} + 2\, P_{SO_2} + 2\, P_{O_2}. \qquad (8)$$

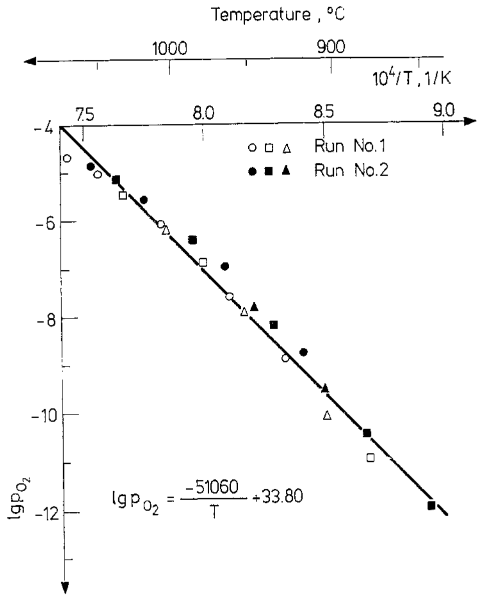


Fig. 2. Equilibrium partial pressure of oxygen *vs.* $1/T$ for the $La_2O_2SO_4$— La_2O_3 system. Open, solid and shaded symbols correspond to a consecutive increase, decrease and again increase of temperature, respectively

where i is the initial value. K_6 is then obtained as

$$K_6 = P_{SO_2}/(P_{S_2}^{1/2}P_{O_2}) \,. \tag{9}$$

Equation (5) was solved by the elimination of P_{SO_3}, P_{SO_3} and P_{S_2} from Eq. (8) by using Eqs (7) and (8). The general expression for K_6 was calculated from literature data [23] by the least squares method as

$$\log K_6 = -4.4739 + 19001/T + 0.1894 \times \log T \,. \tag{10}$$

The expression for the equilibrium constant of reaction (4) was determined via the P_{O_2} measured and P_{SO_2} calculated from Eq. (5) as

$$\log K_1 = 50.93 - 7.6524/T \qquad (1123\text{ K} < T < 1373\text{ K}) \,. \tag{11}$$

From the above equations, the thermodynamic functions of the reaction studied were calculated as follows:

$$\Delta G^\circ = 1.465 \times 10^6 - 7.6524 \times T \quad (\text{J/mol}) \; (1123\text{ K} < T < 1373\text{ K}) \tag{12}$$

$$\Delta H^\circ = 1465 \qquad (\text{kJ/mol}) \tag{13}$$

$$\Delta S^\circ = 975.2 \qquad (\text{J/deg. mol}) \,. \tag{14}$$

A thermodynamic study of the thermal decomposition of $La_2S_2-SO_4$ has also been carried out by Grizik *et al.* [4], but their experimental procedure was different from ours. They studied reaction (15)

$$2\,La_2O_3 + 3\,SO_2 = 2\,La_2O_2SO_4 + 1/2\,S_2 \tag{15}$$

The standard Gibbs energy change and other functions of reaction (4) were calculated by converting their results for reaction (15) in the following way:

$$\Delta G^\circ = 1.643\times 10^5 - 30.09\times T\ \text{(J/mol)}\ (973\ \text{K} < T < 1473\ \text{K}) \tag{16}$$

$$\Delta H^\circ = 164.3 \quad \text{(kJ/mol)} \tag{17}$$

$$\Delta S^\circ = 30.09 \quad \text{(J/deg. mol)} \tag{18}$$

There is a large disagreement between our results and those of Grizik *et al.* [4]. Grizik *et al.* [4] reacted La_2O_3 with SO_2 at various temperatures. They calculated the P_{S_2} by weighing the solid sulfur trapped during the first five minutes. The P_{SO_2} was estimated by subtracting both the weight gain of the starting material and the weight of the trapped sulfur from the quantity of sulfur dioxide passed during the five-minute period. This procedure is based on the assumption that the mixed gas composition stayed in the equilibrium state on passing from higher temperature to lower temperature. This seems to be unreliable. Furthermore, the sulfur deposited during a five-minute period may not be enough to weigh accurately.

In the emf measurement used in the present study, good reproducibility was obtained. According to the literature [20, 21], $La_2O_2SO_4$ decomposes to La_2O_3 in air at temperatures between 1523 and 1573 K. From the present experiment, the decomposition temperature was estimated to be 1481 K and this value is close to that cited in the literature. These facts suggested that our results may be much more reliable.

Mechanisms of oxidation reactions in the La–S–O *system*

The oxidation reactions of all compounds in the La–S–O system were investigated by changing P_{O_2}. However, here we will discuss only the oxidation mechanism of LaS_2 in detail as a typical example, and processes for all other compounds will be summarized in Table 2 on the basis of P_{O_2}.

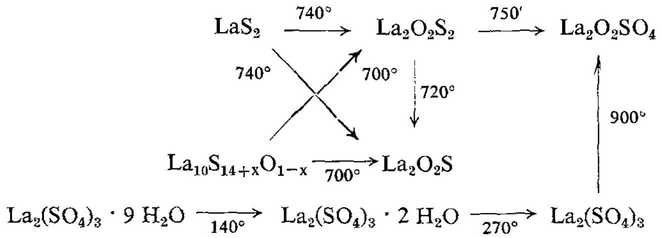
a) *Reactions under the condition* $\log P_{O_2} > -1.3$

Figure 3 shows the DTA and TG curves for five compounds in the $\log P_{O_2}$ range higher than −1.3. LaS_2 corresponds to the curve shown in Fig. 3(b). In the DTA curve two sharp exothermic peaks were detected between 740 and 780°. The TG curve shows an abrupt weight loss and a subsequent weight gain at about 750°, followed by a continuous weight gain from 790 to 900°, while above 900° the weight remained constant. The powder X-ray diffraction pattern of the sample quenched at 740° showed the existence of LaS_2, La_2O_2S and $La_2O_2S_2$, and the sample quenched at 750° was composed of La_2O_2S, $La_2O_2S_2$ and $La_2O_2SO_4$. The final product at

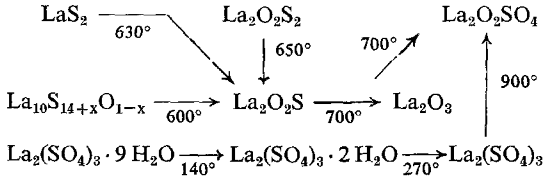
Table 2

Reaction processes in La – S – O system

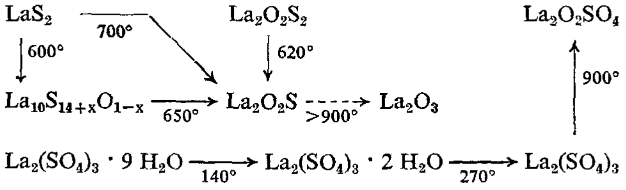
(1) log $P_{O_2} > -1.3$



(2) $-2.4 < \log P_{O_2} < -2.0$



(3) $\log P_{O_2} < -2.7$



900° was identified as $La_2O_2SO_4$. From these facts, the following reactions may be proposed for the first exothermic peak:

$$2\,LaS_2 + 4\,O_2 \rightarrow La_2O_2S + 3\,SO_2 \tag{19}$$

$$2\,LaS_2 + 3\,O_2 \rightarrow La_2O_2S_2 + 2\,SO_2. \tag{20}$$

Considering the abrupt weight loss in the first stage, reaction (19) may be thought to be predominant. The following reactions are considered responsible for the second exothermic peak:

$$La_2O_2S + 2\,O_2 \rightarrow La_2O_2SO_4 \tag{21}$$

$$La_2O_2S_2 + 3\,O_2 \rightarrow La_2O_2SO_4 + SO_2, \tag{22}$$

The change in weight agreed well with the theoretically estimated weight difference between LaS_2 and $La_2O_2SO_4$. The present oxidation process is in agreement with

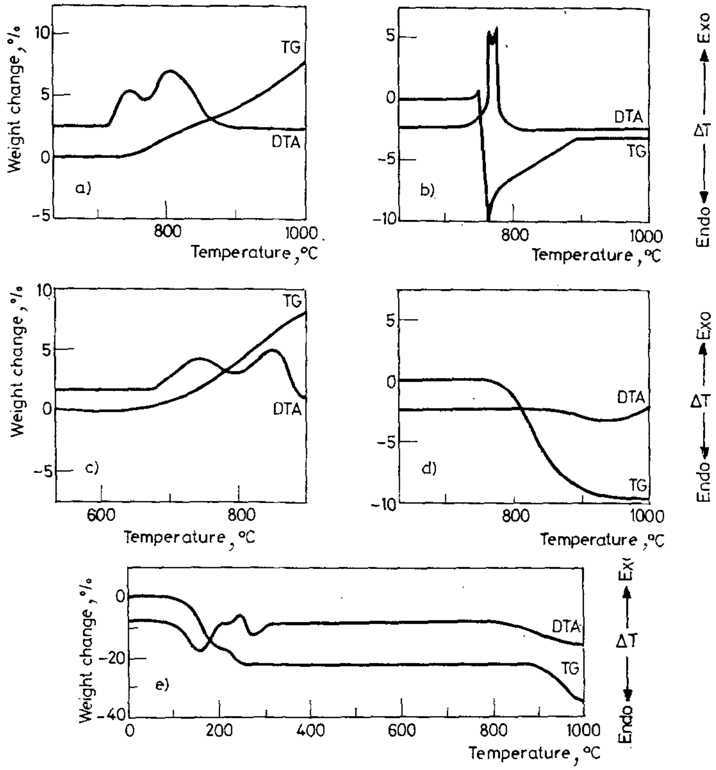


Fig. 3. DTA and TG curves for the La–S–O system at log $P_{O_2} > -1.3$. (a) $La_{10}S_{14+x}O_{1-x}$ (La_2S_3), (b) $LaS_{1.981}$(LaS_2), (c) La_2O_2S, (d) $La_2O_2S_2$, (e) $La_2(SO_4)_3 \cdot 9\,H_2O$

the result reported by Toide *et al.* [25], except for the peak temperature noted by them.

b) *Reactions under the condition* $-2.0 > \log P_{O_2} > -2.4$

The DTA and TG curves for four compounds at $-2.0 > \log P_{O_2} > -2.4$ are shown in Fig. 4. In the DTA curve for LaS_2 (Fig. 4(b)), a broad exothermic peak was detected at temperatures between 630 and 750°. In the TG curve a weight loss between 630 and 700 and a subsequent weight gain from 700 to 1000° were observed. The products at 1000° were identified as a mixture of $La_2O_2SO_4$ and La_2O_3 (A-type). The powder X-ray diffraction patterns of samples quenched at temperatures between 680 and 900° reveal that the first weight loss is caused by the reaction

$$2\,LaS_2 + 4\,O_2 \rightarrow La_2O_2S + 3\,SO_2 \qquad (23)$$

while the second is due to reactions (21) and (24)

$$La_2O_2S + 3/2\,O_2 \rightarrow La_2O_3 + SO_2\,. \qquad (24)$$

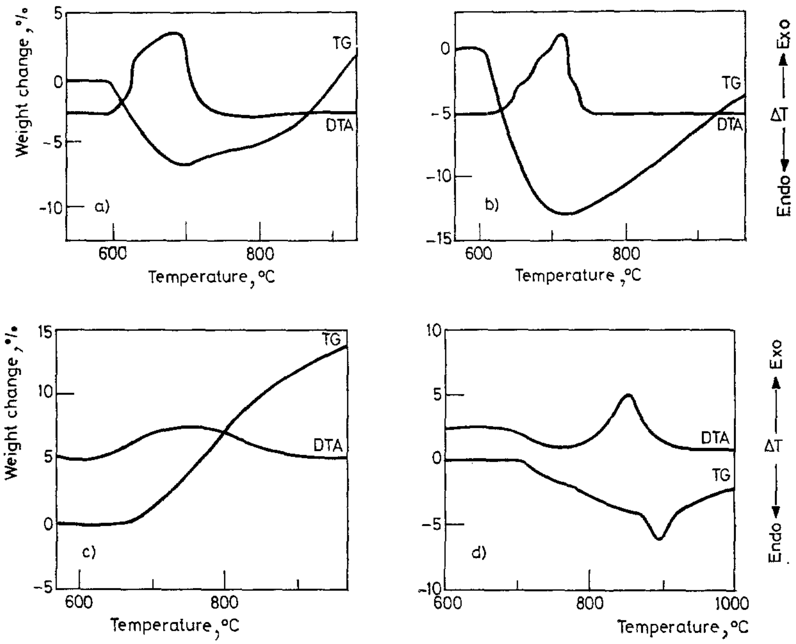


Fig. 4. DTA and TG curves for the La—S—O system at $-2.0 > \log P_{O_2} > -2.4$. (a) $La_{10}S_{14+x}O_{1-x}(La_2S_3)$, (b) $LaS_{1.918}((LaS_2)$, (c) La_2O_2S, (d) $La_2O_2S_2$

In this case the weight gain phenomenon in the TG curve supports the predominance of reaction (21).

c) *Reactions under the condition* $\log P_{O_2} < -2.7$

Figure 5 shows the DTA and TG curves for four compounds at $\log P_{O_2} < -2.7$. In the DTA curve for LaS_2 (Fig. 5(b)), two broad exothermic peaks were observed at 600–720° and 720–800°. The TG curve also showed two steps of weight loss, in agreement with the DTA peaks. The profile of the weight loss was parabolic at temperatures between 600 and 720°, and at temperatures above 720° it was linear. The powder X-ray diffraction patterns of the samples quenched at 720° and 850° showed the existence of β-La_2S_3, LaS_2 and La_2O_2S, and of β-La_2S_3 and La_2O_2S, respectively. On the basis of these results the following two reactions may be considered to take place:

$$2\,LaS_2 + O_2 \rightarrow La_2S_3 + SO_2 \tag{25}$$

$$2\,LaS_2 + 4\,O_2 \rightarrow La_2O_2S + 3\,SO_2\,. \tag{26}$$

In the second step the reaction may be as follows:

$$La_2S_3 + 3\,O_2 \rightarrow La_2O_2S + 2\,SO_2\,. \tag{27}$$

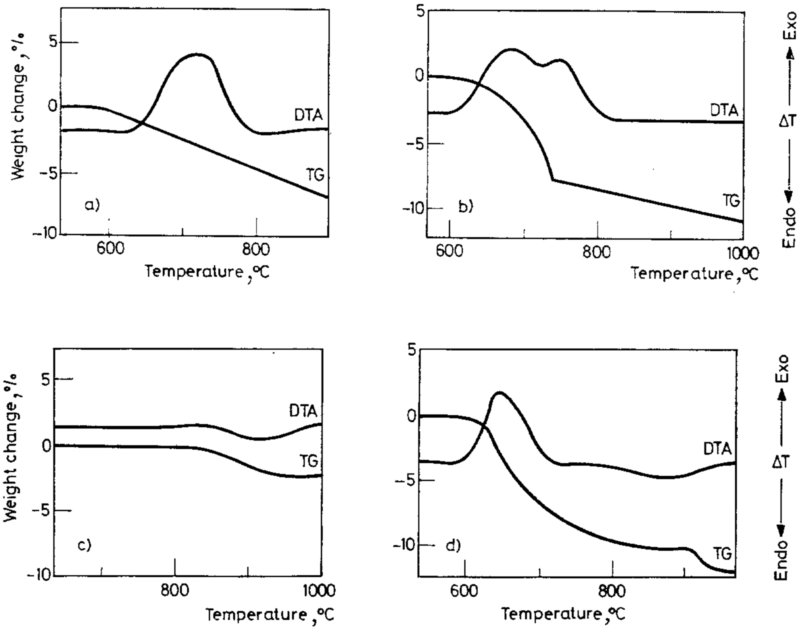


Fig. 5. DTA and TG curves for the La—S—O system at log $P_{O2} < -2.7$. (a) $La_{10}O_{14+x}S_{1-x}$ (La_2S_3), (b) $LaS_{1.919}(LaS_2)$, (c) La_2O_2S, (d) $La_2O_2S_2$

As seen from Table 2, the phases of the final products were dependent on the P_{O_2}. $La_2O_2SO_4$ was the only compound stable in air in the present experiment. From the phase diagram in Fig. 1, we can predict the order of increasing activity of oxygen for the final three compounds as $La_2O_2SO_4 > La_2O_3 > La_2O_2S$. This agrees well with the results observed in the present study, of the oxidation steps depending on the P_{O_2}.

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Zusammenfassung — Das Phasendiagramm des La—S—O-Systems bei 1073 K wurde bestimmt. Bei dieser Temperatur liegen 6 Phasen vor, und zwar La_2O_3 (B-Typ), LaS_2, La_2S_3, $La_2O_2SO_4$, La_2O_2S und $La_2O_2S_2$. Für die Reaktion $La_2O_2SO_4 = La_2O_3 + SO_2 + 1/2\ O_2$ wurden die thermodynamischen Funktionen im Temperaturbereich von 1123—1373 K nach der EMF-Methode bestimmt. DTA, TG und Pulver-Röntgendiffraktometrie wurden zur Untersuchung der Mechanismen der im La—S—O-System verlaufenden Oxydationsreaktionen herangezogen, wobei der Sauerstoffpartialdruck in den Grenzen von $-4.4 < \log p_{O_2} < -0.7$ variiert wurde.

Резюме — С помощью вакуумной изолированной техники была установлена фазовая диаграмма системы La—S—O при 1073 К. При этой температуре существует шесть фаз: La_2O_3 (Б-типа), LaS_2, La_2S_3, $La_2O_2SO_4$, La_2O_2S и $La_2O_2S_2$. Используя метод э. д. с., были определены термодинамические параметры реакции $La_2O_2SO_4 = La_2O_3 + SO_2 + 1/2\ O_2$ в температурном интербале 1123—1373. С помощью ДТА, ТГ и порошковой рентгенодиффрактометрии исследованы механизмы реакций в системе La—S—O б области парциальных давлений кислорода $-4.4 < \log P_{O_2} < -0.7$.