

Electrical Conductivity and Catalytic Properties of Non-stoichiometric Oxides of Lanthanum, Samarium and Neodymium. Part-IV

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Non-stoichiometric oxides of La, Sm and Nd have been prepared from solid state decomposition of their carbonates. Electrical conductivity, magnetic susceptibility and catalytic activity have been studied. Samples obtained from carbonates are found to be more reactive than those obtained from nitrates. These oxides show semiconducting behaviour.

Rare earth compounds have been a subject of considerable interest in recent years^{1,2}. All rare earth elements form sesquioxides in which the metal ions are presumed to exist in trivalent state. Some of these materials are magnetic semiconductors and represent a typical class of narrow energy band solids. Polarons or localised charge carriers are expected to be formed and transport properties of these compounds should be considered from this point of view. In continuation of our studies on the electrical transport, magnetic properties and catalytic activities of non-stoichiometric oxides of rare earth elements, we report here the electrical conductivity, magnetic susceptibility and catalytic activities of non-stoichiometric oxides of La, Sm and Nd.

Results and Discussion

The values of rate constant, energy of activation and frequency factors as calculated from the initial slopes of the rate curves are given in Table 1. The result reveals that the samples prepared at 600° are the most reactive and the reactivity decreases with the rise in temperature of decomposition. The same pattern was also observed in case of the samples prepared from nitrates¹. It is also obvious that the oxygen content of the samples decreases as the temperature of decomposition increases except for the samples of La and Nd prepared at 960°. Thus oxygen contents seem to control the catalytic activity of the samples. Consequently, the catalytic activity decreases with the decrease in oxygen content. This observation has already been reported earlier¹ while studying catalytic activity of the oxide samples obtained from nitrates for the decomposition of H₂O₂. However, the samples of La and Nd prepared at 960° have got the higher values of oxygen content in comparison to that prepared at lower temperatures though their catalytic activity maintains the same decreasing trend. The higher oxygen contents for these samples have been attributed to

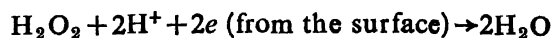
the range of non-stoichiometry of high temperature modification in the direction of higher oxygen contents to achieve the block structures. These have essentially the same structures even though these have different composition. One interesting observation noted was that there is no period of induction, indicating that retention of oxygen by the catalyst wholly or partially is not probable in this system.

When compared with the results for the decomposition of H₂O₂ in presence of oxides obtained from carbonates and in presence of oxides prepared from nitrates, it has been noted that the activity of the oxides from carbonates is greater than that obtained from nitrates. Probably the higher concentration of active sites on the surface of oxides from carbonate makes them more active catalytically. However, this conclusion needs further corroboration.

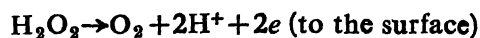
In order to ascertain that the similar mechanism is operative in presence of these samples also for the decomposition of H₂O₂ the effect of change of pH value of the medium on rate constant was studied. It was noted that around pH 7, the rate constants have the minimum value showing that the decomposition is rapid both in acidic and alkaline medium. The same observation was also observed in the previous work¹.

In view of the observations, the mechanism of decomposition in the two media may be depicted as shown below.

In acidic medium :



In alkaline medium :



The values of magnetic susceptibility are given in Table 1. Samples obtained from lanthanum carbonate are found to be diamagnetic, and those from neodymium and samarium carbonates are paramagnetic. These values in case of neodymium

TABLE 1—KINETIC DATA FOR DECOMPOSITION OF 0.5% H₂O₂ IN PRESENCE OF OXIDE SAMPLES

Oxide sample from	Decomp. temp. °C	Empirical formula	Magnetic susceptibility × 10 ⁶ erg g ⁻¹	Elec. cond. Ω ⁻¹ cm ⁻¹ at 373 K	Specific rate (× 10 ³ min ⁻¹) at			E _a kcal mol ⁻¹	log 10A
					30°	40°	50°		
La-carbonate	600	LaO _{1.50}	0.040	1.54 × 10 ⁻¹⁰	0.380	0.490	—	—	—
	700	LaO _{0.87}	-0.400	1.36 × 10 ⁻¹⁰	0.375	1.160	5.200	29.698	21.95
	800	LaO _{0.59}	0.230	2.65 × 10 ⁻¹⁰	0.225	1.080	3.200	26.320	19.40
	960	LaO _{1.72}	0.225	2.05 × 10 ⁻¹⁰	0.224	0.540	1.000	15.030	11.19
Nd-carbonate	600	NdO _{4.26}	29.520	2.10 × 10 ⁻¹⁰	0.270	0.760	2.990	25.680	19.03
	700	NdO _{2.20}	10.220	2.30 × 10 ⁻¹⁰	0.437	0.620	1.100	8.897	7.02
	800	NdO _{0.76}	23.430	2.00 × 10 ⁻¹⁰	0.200	0.500	1.560	21.430	15.83
	960	NdO _{1.28}	33.870	9.80 × 10 ⁻¹¹	0.123	0.310	1.270	23.760	17.23
Sm-carbonate	600	SmO _{4.12}	5.340	2.72 × 10 ⁻⁹	0.550	1.420	4.100	19.312	14.52
	700	SmO _{2.19}	4.080	1.02 × 10 ⁻¹¹	0.294	0.760	1.260	16.630	12.31
	800	SmO _{0.77}	3.650	1.30 × 10 ⁻¹⁰	0.226	0.710	2.000	21.250	15.69
	960	SmO _{1.31}	4.180	2.70 × 10 ⁻¹⁰	0.467	1.020	2.420	16.860	12.14

oxides are higher. The results (Table 1) reveal that with the increase in decomposition temperature the oxygen content is decreased, and such is also the trend of magnetic susceptibility values.

The results of variation of electrical conductivity of different oxide samples in the temperature range 373–873 K show almost the same pattern of variation in the electrical conductivity. Two distinct temperature regions showing different electrical behaviour were observed. Above 633 K the conductivity increases with increase of temperature indicating semiconducting behaviour. The conductivity values remain more or less unchanged below 633 K. These observations on conductivity values are explained in terms of band theory. In this case 5*d* band is the conduction band of the solid and O²⁻ band is the valence band. The 5*d* band is a narrow band (1 eV wide at room temperature) and an electron in this band would form small or intermediate polarons with small mobility. Thus the conductivity in this solid may probably be dominated by polarons. As the charge transport excitation of electron from the valence O²⁻ (2*p* band) to cation M³⁺ (5-band) is expected to be of the order of 3 eV at normal temperature, the samples in the present study are good insulators. The conductivity data in the temperature range 633–923 K can be expressed by the expression,

$$\sigma = \sigma_0 \exp(-E_a/2KT)$$

More or less below temperature 633 K, the conductivity remains practically constant. As the present samples were prepared by solid state decomposition, imperfection of different natures is bound to be present. This would lead to the presence of numerous isolated traps and thereby electrons would be trapped. Below 633 K there might be strong interactions of trapped electrons with cations leading to the probable formation of small polarons. Since the energy of activation (E_a) is 0.05 eV, the con-

ductivity does not change with the increase of temperature in these ranges.

The Seebeck coefficient (α) measurements showed LaO_{1.72}, LaO_{1.50}, NdO_{4.26}, NdO_{2.20}, SmO_{4.12}, SmO_{3.91} to be *n*-type and LaO_{0.59}, LaO_{0.87}, NdO_{0.76} to be *p*-type.

The compensation effect, i.e. a relation between *A* and *E* of the form (log *A* = *E*/*a* + *b*), is also observed in the present investigation. The occurrence of compensation effect for the hydrogen peroxide decomposition by lanthanum oxides might be attributed to the distribution of catalytic sites on the surface.

Experimental

Carbonates of La, Nd and Sm (Indian Rare Earths Ltd.) were used as such. H₂O₂ (G.R., Sarabhai) was used without further purification. The method of preparation of the samples was essentially the same as described earlier³.

Decomposition of H₂O₂ was studied according to the procedure reported earlier¹. The reaction was studied in the acidic medium (pH = 4.5) at three different temperatures viz. 30, 40 and 50°. The metals in the oxides were estimated adopting the reported procedure⁴.

The magnetic susceptibility was determined with a Guoy magnetic balance. The experiment was conducted at 5 A and field strength 5.945 × 10³ gauss. The electrical conductivity was measured as described previously¹.

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