

Letter to the Editor

# PHYSICO-CHEMICAL PROPERTIES OF CALCIUM DOPED GADOLINIUM AND LANTHANUM CHROMITE

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ХРОМИТОВ ГАДОЛИНИЯ И ЛАНТАНА  
ДОПИРОВАННЫХ КАЛЬЦИЕМ

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Oxides with the perovskite structure having a good electronic conductivity at high temperatures in a wide range of oxygen partial pressure are perspective materials for electrochemical devices [1, 2]. Early investigations of the  $\text{Ln}_{1-x}\text{Ca}_x\text{CrO}_3$  ( $\text{Ln} = \text{Nd, Sm}$ ) and the  $\text{Ln}_0.8\text{Ca}_{0.2}\text{CrO}_3$  ( $\text{Ln} = \text{Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb}$  and  $\text{Lu}$ ) electrical properties of solid solutions showed that their electrical conductivity increased with the calcium content increasing from  $x = 0$  to  $x = 0.4 - 0.5$  and that the calcium doped gadolinium chromite  $\text{Gd}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$  had the highest electrical conductivity in air among these chromites [3, 4].

However, in the range of  $0 \leq X \leq 0.1$  one could see that the dependence of the electrical conductivity on the dope element contents broke. Such a behaviour was observed for the system  $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$  [5].

In this paper the results of investigations of the  $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$  ( $0 \leq X \leq 0.1$ ) and the  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$  ( $0 \leq X \leq 0.8$ ) electrical conductivity at temperatures 873—1273 K and oxygen partial pressures in the gas phase from  $10^4$  to  $10^{-12}$  Pa are presented.

Polycrystalline samples were obtained by a reaction in the solid phase. The initial materials for the preparation of specimens were gadolinium, lanthanum and chromium oxides ( $\geq 99.9\%$ ) and calcium carbonate ( $\geq 99.9\%$ ). The powders taken in the required ratios were carefully ground, pressed and fired at 1700 K during 4h in air. After firing the specimens had sizes of  $45 \times 5 \times 5$  mm. A fourprobe DC technique was used in the measurement of conductivity. The oxygen pressure in the gas phase was regulated by a solid state ( $0.9\text{ZrO}_2 + 0.1\text{Y}_2\text{O}_3$ ) electrochemical pump and controlled by an oxygen sensor.

The X-ray analysis of  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$  showed that the  $\text{GdCrO}_3$  had the disordered structure of orthorhombic perovskite and the calcium dope to gadolinium chromite led to the formation of  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$  solid solutions in which the  $\text{GdCrO}_3$  structure was preserved up to  $X = 0.5$ . At higher values of  $X$  the solid solution on the basis of  $\text{CaCrO}_3$  appeared.

The thermo-e.m.f. investigation of  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$  ( $0 \leq X \leq 0.2$ ) in the temperature range of 873—1273 K in air showed that the absolute value of the Seebeck coefficient decreased with the increase of  $X$  and depended slightly on temperature. The sign of the Seebeck coefficient corresponded to the  $p$ -type conductivity.

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The dependence of electrical conductivity of  $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$  ( $0 \leq X \leq 0.1$ ) and  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$  ( $0 \leq X \leq 0.8$ ) on the temperature in air is given in Fig. 1. It is seen that the electrical conductivity of samples has a semiconductor character and can be described by the relation:

$$\sigma = \frac{\sigma_0}{T} \exp \left[ -E_a / kT \right],$$

where  $\sigma_0$  is a constant for the sample of the given composition;  $E_a$  is the conductivity activation energy,  $k$  is Boltzman's constant,  $T$  is absolute temperature.

The electrical conductivity of  $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$  solid solutions in the range of  $0 \leq X \leq 0.1$  increases ( $\sim 1.5$  order) (Fig. 1a) with the increase of added calcium concentration and reaches the maximum value at  $X = 0.06$  in the whole range of the investigated temperature. The further increase of  $X$  leads to the decrease of electrical conductivity. The activation energy of conductivity in the range of 873—1273 K is small and changes from 0.17 eV at  $X = 0$  to 0.14 eV for the highest conductivity sample with  $X = 0.06$ , then increases to 0.16 eV at  $X = 0.1$ .

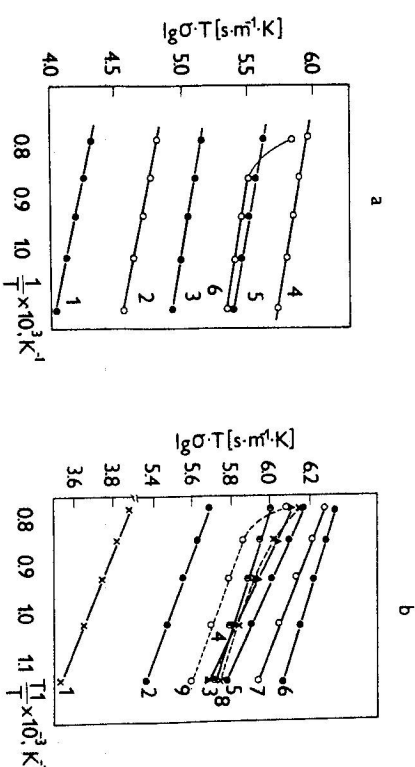


Fig. 1. Dependence of electrical conductivity on temperature in air: a)  $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ ,  $X = 0.0$ ;  $0.02$ ;  $0.04$ ;  $0.06$ ;  $0.08$ ;  $0.1$ ; b)  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$ ,  $X = 0.0$ ;  $0.04$ ;  $0.08$ ;  $0.1$ ;  $0.2$ ;  $0.3$ ;  $0.4$ ;  $0.5$ ;  $0.6$ ;  $0.8$ .

The electrical conductivity of  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$  (Fig. 1b) also increases with the increase of  $X$  and reaches a maximum at  $X = 0.4$ . A further increase of  $X$  leads to the decrease of electrical conductivity. The activation energy of the electrical conductivity of  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$  also has a low value ( $E_a = 0.15 - 0.3$  eV) in the whole composition range.

Such behaviour of the electro-physical properties of samples is caused by the formation of  $\text{La}_{1-x}\text{Ca}_x\text{Cr}^{3+}_2\text{Cr}^{4+}_x\text{O}_3$  and  $\text{Gd}_{1-x}\text{Ca}_x\text{Cr}^{3+}_2\text{Cr}^{4+}_x\text{O}_3$  solid solutions in which the conductivity is the result of the hopping mechanism or the conduction of these compositions is secured by the hole hopping from ion  $\text{Cr}^{4+}$  to ion  $\text{Cr}^{3+}$  and their conductivity should increase with the increase of  $X$  as the concentration of  $\text{Cr}^{4+}$  increases with it. This is confirmed by the decrease of the Seebeck coefficient of  $\text{Gd}_{1-x}\text{Ca}_x\text{CrO}_3$  with the increase of  $X$ . The decrease of electrical conductivity and the increase of  $E_a$  of  $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$  in the range of  $0.06 < X < 0.1$  are connected with the formation of low conducting intercrystal layers of  $\text{CaO}$  (as  $\text{SrO}$  in the system  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$  [5]).

The decrease of electrical conductivity of  $Gd_{1-x}Ca_xCrO_3$  at  $X > 0.4$  is caused by the appearance of the  $CaCrO_3$  second phase.

The results of investigations of the electrical conductivity dependence on  $P_{O_2}$  at 1273 K are given in Fig. 2. In the oxygen pressure range of  $P_{O_2} = 10^4 - 10^{-6}$  Pa the electrical conductivity of  $Gd_{1-x}Ca_xCrO_3$  depends slightly on  $P_{O_2}$  (Fig. 1a). At the increase of the calcium content in the solid solutions an increasing dependence of electrical conductivity on  $P_{O_2}$  is observed (curves 2, 3 Fig. 2a). At low  $P_{O_2}$  ( $P_{O_2} < 10^{-6}$  Pa) the electrical conductivity decreases especially at a high concentration of the dope element. This is caused obviously by the vacancy formation process in the oxygen sublattice and by the decrease of concentration of the current carriers.

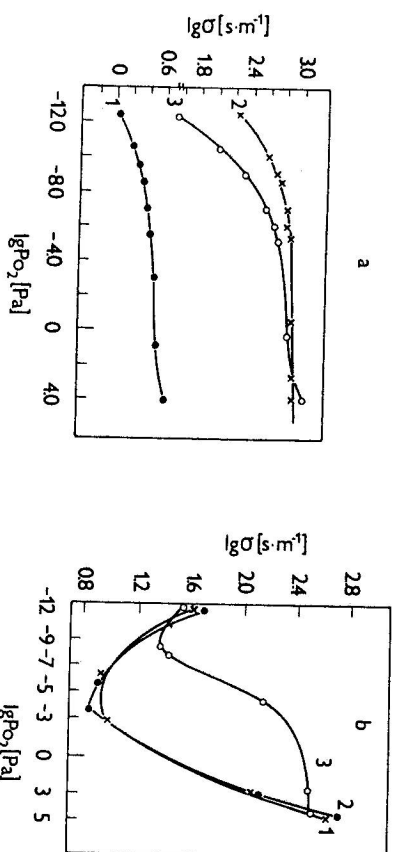


Fig. 2. Dependence of electrical conductivity on  $P_{O_2}$  at 1273 K: a)  $Gd_{1-x}Ca_xCrO_3$ ,  $X = 1 - 0.0$ ; 2 - 0.1; 3 - 0.2; b)  $La_{1-x}Ca_xCrO_3$ ,  $X = 1 - 0.04$ ; 2 - 0.06; 3 - 0.08.

Table 1

The coefficient of  $Gd_{1-x}Ca_xCrO_3$  of thermal expansion in the temperature range of 573–1273 K in air.

$x$	0	0.1	0.2	0.3	0.4	0.5
$\alpha \times 10^6 [K^{-1}]$	7.5	7.6	8.7	8.8	9.1	11.6

All the samples of  $La_{1-x}Ca_xCrO_3$  are  $p$ -type semiconductors in the range of  $P_{O_2} = 10^4 - 10^{-3}$  Pa (Fig. 2b). Their electrical conductivity drops with the decrease of  $P_{O_2}$ . But at a further decrease of  $P_{O_2}$  the type of the  $La_{1-x}Ca_xCrO_3$  conductivity changes. The electrical conductivity of the investigated materials increases with the decrease of  $P_{O_2}$  that is typical for the  $n$ -type semiconductors. It is necessary to note that the range of  $p$ - $n$  transition depends on the dope element concentration and moves to a low  $P_{O_2}$  with the increase of the calcium concentration in  $La_{1-x}Ca_xCrO_3$ .

The  $Gd_{1-x}Ca_xCrO_3$  coefficient of thermal expansion in air as a dependence on  $X$  in the temperature range of 573–1273 K is given in table 1.

The values of the electrical conductivity and of the coefficient of thermal expansion show that some compositions of  $La_{1-x}Ca_xCrO_3$  and  $Gd_{1-x}Ca_xCrO_3$  can be used as interconnection materials in electrochemical devices on the basis of a stabilized  $ZrO_2$  solid electrolyte and as electrodes of oxygen sensors [4].

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