



Thermodesorption study of barium and strontium cerates

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Abstract

The method of thermodesorption spectroscopy has been used for study of kinetic of hydrogen, oxygen and water molecule release from doped and undoped barium and strontium cerates. It was found that oxygen and water molecules are released from doped barium cerate samples whereas only water molecule desorption took place from doped strontium cerate samples. Shapes of thermodesorption spectra for pure barium cerate indicate that phase transformations take place in low and high temperature regions. It was shown that oxygen molecule desorption from doped barium cerates can be described by a second-order kinetic equation and an activation energies of reaction were determined.

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1. Introduction

Complex oxides with perovskite structures are very interesting, both from scientific and applied point of views, because of their unique properties such as high temperature protonic conductivity [1]. These materials are topical for practical use as membranes of fuel cells and hydrogen sensors. In spite of significant progress in understanding of the nature of proton conductivity, some aspects of this phenomenon are subjects of further investigation.

It is known that the properties of proton conductors depend dramatically on states of hydroxide, hydrogen and especially oxygen ions in the oxide lattice. In

accordance with widely accepted proton transfer in high temperature proton perovskites, oxygen positions serve both as a trap for proton and a pathway for proton movement. That is why it is very important to study the state of oxygen in the lattice and its mobility. The method of thermodesorption spectroscopy (TDS) was used in this study, involving measurement of gas desorption during sample heating with known rate in vacuum. This method allows identification of desorbing gases and gives information about chemical states and mobility of gases “dissolved” in solids.

2. Experimental

In this work BaCeO_3 and SrCeO_3 samples doped with neodymium and yttrium, respectively, were in-

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vestigated. The main focus was studying oxygen and water molecule release from cerates. The samples were synthesized by the inductive melting method. After synthesis samples were annealed at different conditions: in air (650–750 °C, $P_{O_2} \sim 0.2$ atm), “wet” nitrogen (625 °C, $P_{O_2} \sim 1.3 \times 10^{-3}$ atm) and hydrogen (650 °C, $P_{O_2} \sim 2 \times 10^{-7}$ atm).

A special device [2] was used for gas thermodesorption studies (Fig. 1). This device consists of the following main parts: high vacuum chamber; heating device; radio frequency mass-spectrometer.

One by one, samples (up to 7) are thrown into the heating device and thermodesorption spectra of evolved gases are measured. The vacuum system, including vacuum chamber is heated to obtain an acceptable vacuum ($\sim 10^{-5}$ Pa) before the beginning of experiments. During system heating, samples are rested in a water-cooled cool part of chamber. Sample temperatures are monitored by W-Re thermocouple.

Experiments are completely automated. A personal computer with an Advantech PCI-1710HG module is used for sample heating, choice of necessary gas masses, temperature and thermodesorption spectra measurements. The automation allows recording up to six spectra of different gases simultaneously. The sample heating rate was 42 K min^{-1} .

3. Results

The main results of the thermodesorption study of doped and undoped barium and strontium cerates samples are presented in Table 1.

It can be seen from the table that no gas release was found from initial (as received) doped samples. This fact indicates high homogeneity for the samples and strong bonding of “host” oxygen in the lattice. After annealing of doped barium cerate samples in air or “wet” nitrogen, oxygen and water molecules release from the samples take place, and shifts of the temperature corresponding to the maximum of desorption rate are observed for different kind of sample treatments (Fig. 2). No hydrogen, water or oxygen molecules released from undoped and annealed at similar conditions samples in this temperature range. This fact indicates that for water or oxygen molecules to dissolve in the samples, it is necessary to create oxygen vacancies in the oxide lattice. A small amount of oxygen is released from the samples in the high temperature region (Fig. 3). The shape of high temperature peak indicates that different physical processes are responsible for oxygen release from doped and undoped barium cerates. In the former case, oxygen is released from oxygen vacancies, whereas a tetragonal

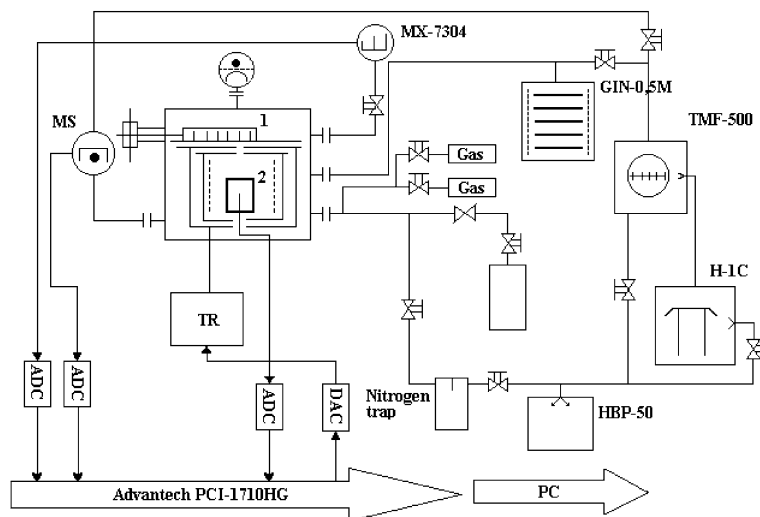


Fig. 1. Schematic of the device for gas thermodesorption studies: 1—cell for samples, 2—heater, MX-7304—radio frequency mass-spectrometer, MS—static mass-spectrometer, GIN-0,5—heteroionic pump, H1-C—steam jet pump, HBP-50—preliminary vacuum pump, TR—high current temperature regulator, PC—personal computer.

Table 1
Temperatures of thermodesorption peaks for different kinds of samples and their preliminary treatments

Samples	Samples treatment	T_{\max} (°C)			
		H ₂	H ₂ O	O ₂	CO ₂
BaCeO ₃	As received	no	270;	no	no data
	Annealed in air	no	no	980	470;
	Annealed in “wet” N ₂	no	no	980	470;
	Annealed in H ₂	no	470	no	330; 420;
BaCe _{0.9} Nd _{0.1} O ₃	As received	no	no	no	430;
	Annealed in air	no	660	800	650; 865
	Annealed in “wet” N ₂	no	720	860	650; 865
	Annealed in H ₂	no	600	no	340; 500;
SrCe _{0.95} Y _{0.05} O ₃	As received	no	no	no	430;
	Annealed in air	no	675	no	660; 850
	Annealed in “wet” N ₂	no	720	no	660; 850
	Annealed in H ₂	no	650	no	625; 750

to cubic phase transformation is responsible for release of “host” oxygen in the second case. Until now, this phase transformation has been reported to be found only in barium cerates. A low temperature water release ($T < 500$ °C) was observed for pure

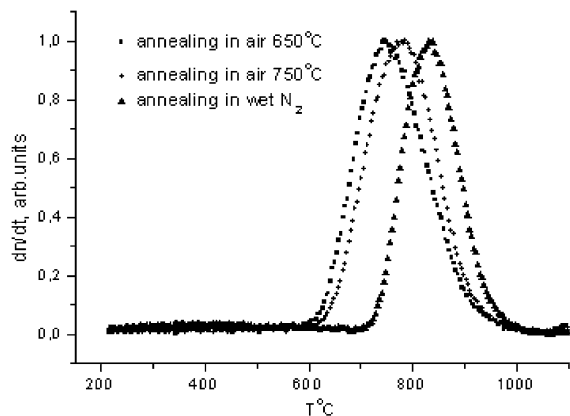


Fig. 2. Normalized spectra of oxygen desorption from BaCe_{0.9}Nd_{0.1}O₃ samples after different oxide pre-treatments.

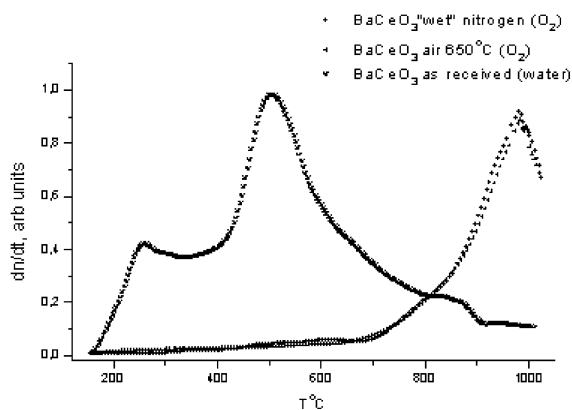


Fig. 3. Oxygen and water molecules release from pure (undoped) BaCeO₃.

barium cerate samples (Fig. 3), probably due to a phase transformation in the oxide.

For comparison, similar experiments were carried out with strontium cerates samples doped by yttrium. No gas release occurred from SrCe_{0.95}Y_{0.05}O₃ samples without preliminary annealing, and only water molecule release was observed in thermodesorption spectra of the samples after all types annealing (Table 1). It should be noted that temperature corresponding to the maximum of desorption rate for water release from SrCe_{0.95}Y_{0.05}O₃ is higher than for BaCe_{0.9}Nd_{0.1}O₃ samples (Fig. 4).

Only water molecule desorption took place from barium and strontium cerates samples treated in hy-

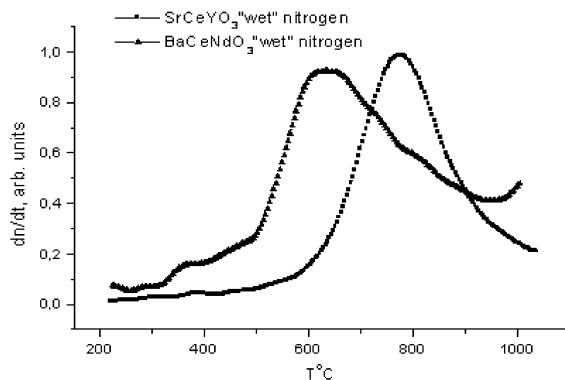


Fig. 4. Water molecules release from BaCe_{0.9}Nd_{0.1}O₃ and SrCe_{0.95}Y_{0.05}O₃ after annealing in “wet” nitrogen ($P_{O_2} \sim 1.3 \times 10^{-3}$ atm).

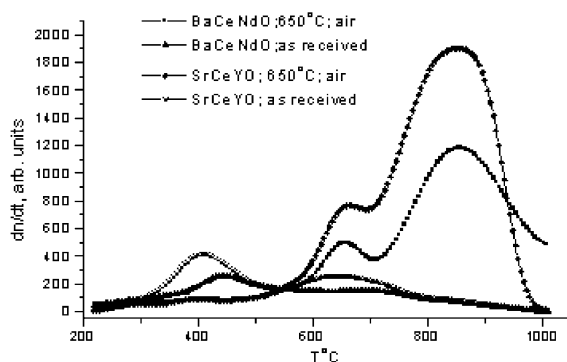


Fig. 5. Influence of barium and strontium cerate annealing on carbon dioxide molecule desorption.

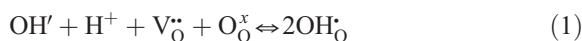
drogen ($P_{O_2} \sim 2 \times 10^{-7}$ atm); no oxygen release was found from $BaCe_{0.9}Nd_{0.1}O_3$ samples in this case (see Table 1).

Carbon dioxide molecules are released from barium and strontium cerates annealed as above (Fig. 5). Two weak low temperature peaks of CO_2 ($T \sim 430$ and 650 °C) were found in TDS spectra of initial (as received) samples. Preliminary sample annealing in air leads to significant changes in CO_2 thermodesorption spectra with disappearance of low temperature peak and appearance of new high intensity peak at $T \sim 850$ °C. Our results confirm the suggestions of Ryu and Haile [3] that barium cerate interacts with CO_2 with formation of $BaCO_3$. The authors also suggested that $BaCO_3$ decomposition took place at temperatures above 600 °C. As it can be seen from the Table 1, there are several stages of CO_2 release from the oxide in thermodesorption spectra. Since the presence of this impurity in sample leads to degradation of ceramic oxide properties, it is necessary to avoid contact of cerates with CO_2 and carbonates.

4. Discussion

It is suggested that during annealing of doped cerates in air or “wet” nitrogen, a dissociation of water molecules on sample surface and dissolution into the oxide takes place. As a result of this, acid–base interaction hydroxide ion and proton are formed. Hydrogen ion (proton) joins to “host”-oxygen ion. So,

two hydroxide ions are formed [4]. This process can be represented as:



Because sample annealing was carried out at a high partial pressure of oxygen, it can penetrate into the oxide and occupy oxygen vacancies also



During sample heating in vacuum, reactions (1) and (2) go in the reverse directions; as a result, peaks for oxygen and water molecule release appeared in thermodesorption spectra. It is known that bonding of oxygen in the lattice is weakened by attached hydrogen ions and we suppose that hydroxide ions both from vacancy and “host”-site types are responsible for water molecule desorption from the oxides. Bonding of oxygen with vacancy near doping ion is weaker in comparison with bond of oxygen ions in pure cerates because of the lower valence of the dopant ion. So, we consider that release of this “weak” bounded oxygen take place.

Two oxygen ions must meet one another at the surface to form an oxygen molecule before leaving the sample; the kinetics of oxygen molecule release from the cerates can be described by a second-order kinetic equation:

$$\frac{dn}{dt} = -vn^2 \exp\left(-\frac{E}{RT(t)}\right)$$

where $n(t)$ —oxygen concentration, E —activation energy, T —temperature, v —rate constant.

This suggestion is also confirmed both by shape of oxygen release peaks and dependence of temperature of oxygen peak on oxygen concentration in the barium cerate lattice (Fig. 2): the higher the oxygen concentration, the lower the temperature of the oxygen peak. Different oxygen concentrations in the oxides were obtained by different sample treatments (annealing at different temperatures and different partial pressure). It should be noticed that, in this case, oxygen molecule release cannot be described by a first-order kinetic reaction or by oxygen diffusion. The activation energy of desorption deter-

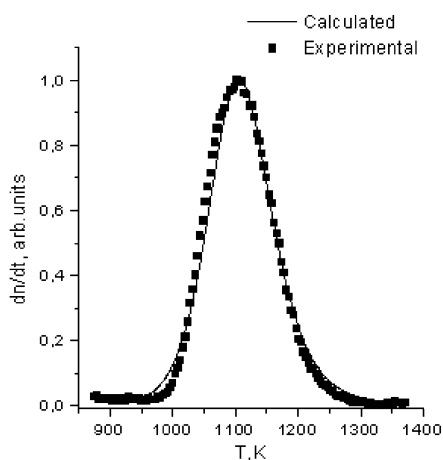


Fig. 6. Calculated and experimental spectra of oxygen molecule desorption by $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_3$ samples annealed in “wet” nitrogen.

mined by fitting calculated and experimental spectra was 2.99 eV for samples treated in “wet” nitrogen, and $\nu = 10^{13} \text{ s}^{-1}$. Experimental and calculated oxygen desorption spectra are shown in Fig. 6 with good agreement between experimental and calculated spectra.

Analyses of thermodesorption data of barium and strontium cerates and their comparison with data given in Ref. [5] permit the following conclusion—oxygen can occupy oxygen vacancies in barium cerates but not in strontium cerates. It is known that doping of barium and strontium cerates by low valency cation leads to formation of oxygen vacancies in the oxides. Dependences of oxygen stoichiometry on oxygen pressure [5] have shown that nonstoichiometric oxygen is present only in barium not in strontium cerate samples, in agreement with our conclusion. At the same time, oxygen release was found only with barium cerate samples. Nonstoichiometric oxygen in the barium cerate lattice is only weakly bonded. “Host” oxygen is bonded strongly in both barium and strontium cerates, and no oxygen release from doped strontium and undoped barium cerates is found.

It is interesting to note that doped barium cerates samples have cubic symmetry at high temperature, mixed conductivity (proton–oxygen) [6] and oxygen release in this study of thermodesorption spectra. Strontium cerates have a rhombic structure, they are

pure proton conductors and no oxygen release is observed in their thermodesorption spectra. Differences in oxide structure are responsible for dissimilar oxygen behavior in the two cerates systems.

The complexity of water desorption spectrum from barium cerate samples indicates that several different concurrent processes are responsible for water release in this case, in good agreement with conclusions above.

5. Conclusion

The main results of this study are

- Oxygen can occupy oxygen vacancies only in barium but not strontium cerates, oxygen desorption from barium cerates is controlled by second-order reaction ($E = 2.99 \text{ eV}$).
- Hydrogen ion weakens “host” oxygen bonding in strontium cerates and as a result leads to water desorption from the oxide.
- Both “host” and “guest” oxygen are responsible for water molecule desorption from barium cerates.
- Cerates have a tendency to react with carbon dioxide. It is necessary to take it into account at synthesis and thermal treatment of the oxides.

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