JOURNAL OF SOLID STATE CHEMISTRY 97, 224–227 (1992)

BRIEF COMMUNICATIONS

Hydrogen in Perovskites

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Received October 15, 1990; in revised form August 21, 1991

The isotopic method has been used to measure the concentration of hydrogen in as-prepared (Ba, Sr)CeO_3 and (Ca, Sr, Ba)TiO_3 samples. Hydrogen concentrations in the range 0.007 to 0.04 of H per formula unit have been detected for undoped samples, and even more for doped specimens. The influence of cation composition, dopant number density, and preparation method is analyzed. Thermal desorption studies and comparison of hydrogen and oxygen mobilities have been utilized to analyze the state of the dissolved hydrogen. © 1992 Academic Press, Inc.

Introduction

Hydrogen is known to dissolve in perovskites under heating in hydrogen-containing atmosphere. After heating $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ samples in D_2O and O_2 atmospheres at pressures of P = 670–4700 Pa and 270 Pa, respectively, and in the temperature range 700–800°C, deuterium was proved to be present by use of secondary ion mass spectrometry (*1*). Thermal desorption analysis led to be the same conclusion after the treatment in the argon–water vapor flow (*2*). In the first case the deuterium concentration was equal to 0.01–0.05 mole per mole of the solvent; these values increased with partial D_2O pressure and with a decrease in temperature. In the second case the deuterium concentration was found to be of the order of 0.02 mole

Thermal desorption analysis also was used to document the dissolution of hydrogen in both undoped and acceptor-doped $BaTiO_3$ samples, when heated in D_2O and O_2 atmospheres ($P = 5 \cdot 10^2$–2×10^4 Pa for D_2O, and $P = 10^5$ Pa for O_2) at t = 900°C (*3*).

Experimental Technique

We studied cerate and titanate samples prepared by induction melting in cold crucible, by cation coprecipitation by solid state reaction, and by the Verneuil method.

The hydrogen concentration was measured by isotopic equilibration of the sample with a preestablished amount of gaseous deuterium. The experimental setup consisted of a quartz reactor with a volume of 100 cm^3, attached to a mass-spectrometer, and equipment for evacuation, gas injection, for temperature control, and monitoring the pressure. Isotopic exchange of hydrogen with titanates and cerates occurred at t = 750°C.

The sensitivity of the isotopic method was of the order of 10^{18} hydrogen atoms. The experimental error of measuring the atomic fraction of deuterium depends on the isotopic composition (C) and may be approxi-

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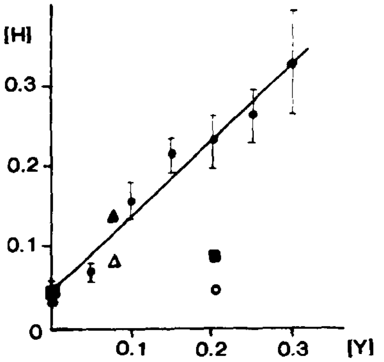

FIG. 1. Hydrogen concentration [H], moles of atoms per mole of oxide, as a function of the dopant concentration [Y], moles of atoms per mole of oxide in $BaCe_{1-y}Y_yO_{3-\delta}$: ● ceramics, prepared by cation precipitation from solution; ○ ceramics after thermal treatment in vaccum. ■ induction melting; and in $SrCe_{0.92}Dy_{0.08}O_{3-\delta}$: ▲ ceramics, △ ceramics after treatment in vacuum.

mated by the function $0.04C(1 - C)$. Hydrogen dissolved in quartz, vacuum joints, and adsorbed water gives rise to a systematic error; therefore, an isotopic exchange with an empty reactor preceded each measurement.

Results and Discussion

The main results are presented in Fig. 1 and are also tabulated in Table I. Hydrogen was detected in all as-prepared samples. Its concentration was calculated according to the relation

$$Q_s = Q_g C_0 (C'_\infty - C_\infty)/C_\infty C'_\infty$$

where Q_s and Q_g are the numbers of moles of hydrogen in the sample and in the gas, respectively; C_0 is the atomic fraction of deuterium at the beginning; C_∞, C'_∞ are the same values at equilibrium with and without the sample. We believe C_∞ in the gas and in the sample to be equal; for, at $t = 750°C$ the separation coefficient is nearly unity (*4*).

We have found that the content of hydrogen is affected by the cation composition, dopant number density, method of preparation, and the subsequent treatment.

1. High valent ions (Ti, Ce) affect hydrogen concentration to a greater degree than alkali-earth ions do. As follows from Table I, (see no. 3, 7, 8, 9) the hydrogen concentration in barium cerate exeeds that of strontium, barium, and calcium titanate.

2. The hydrogen concentration–dopant number density relationship was investigated for $BaCe_{1-y}Y_yO_{3-\delta}$ samples doped with Y in the range $y = 0$–0.3. The hydrogen concentration [H] increased linearly with Yttrium density [Y], though $[H] \neq 0$ at $[Y] = 0$, because hydrogen can dissolve in undoped barium cerate as well; see Fig. 1.

3. The hydrogen concentration depends on the conditions of the synthesis. Induction-melted samples were poorer in hydrogen than Verneuil-grown (numbers 6 and 7 in the table) or those prepared by cation coprecipitation (numbers 2 and 4).

It is well known, (see, e.g., (*3*)), that perovskites can incorporate hydrogen defects according to the reaction

$$H_2O_{(g)} + V_0^{\cdot\cdot} + O_0 = 2OH^{\cdot},$$

where $V_0^{\cdot\cdot}$, O_0 and $OH^{\cdot}$ represent the oxygen vacancy, oxygen lattice site, and hydroxide ion, respectively. Formation of oxygen vacancies may be caused either by doping of barium cerate with Y, or by Ti^{3+} and Ce^{3+} ions in undoped samples (*5*); hence, the difference in the solubility of hydrogen in undoped barium titanate and barium cerate is presumably related to the difference in Ti^{3+} and Ce^{3+} densities. The linear [H]–[Y] relationship leads to the conclusion that most of the vacancies are filled with $OH^{\cdot}$ ions.

Measurements of mobility of hydrogen and oxygen in $BaCeO_3$, along with thermal desorption studies of titanates and cerates, provide information on the state of the dissolved hydrogen atoms. A subsequent exchange of the sample with hydrogen and oxygen (see Ref. (*6*) for more details) provides the following values of the diffusion

TABLE I

THE HYDROGEN CONTENT IN PEROVSKITES

Compound	NN	Synthesis	Synthesis temperature (°C)	Mass spectra of evolved gases	H at %
$BaCe_{1-y}Y_yO_{3-\delta}$	1	cation coprecipitation	1450	$H_2 \approx H_2O$; $NO \approx NO_2$	4 ± 1; $y = 0.0$
	2	from solution		$H_2 < H_2O$; $NO < NO_2$	22 ± 2; $y = 0.2$
	3	induction	2147	$H_2 \approx H_2O$; $CO > CO_2$	4 ± 1; $y = 0.0$
	4	melting		$H_2 \approx H_2O$; $CO > CO_2$	8 ± 2; $y = 0.2$
$SrCe_{0.92}Dy_{0.08}O_{3-\delta}$	5	ceram. synth.	1200	$H_2 \approx H_2O$; $CO \approx CO_2$	14 ± 2
$SrTiO_3$	6	Vernel method	2037	H_2; CO	2.6 ± 0.3
	7	induc. melting	2037	$H_2 \gg H_2O$; $CO > CO_2$	1.0 ± 0.2
$Ba_{0.98}Sr_{0.02}TiO_3$	8	induc. melting	1617	$H_2 \gg H_2O$; $CO > CO_2$	0.7 ± 0.3
$CaTiO_3$	9	induc. melting	1967	$H_2 \gg H_2O$; $CO > CO_2$	0.8 ± 0.2

coefficients: $D_H = (3.8 \pm 0.1) \times 10^{-7}$ cm^2 sec^{-1}, $D_0 = (4.2 \pm 0.7) \times 10^{-9}$ cm^2 sec^{-1} at 650°C. The large difference of D_0 and D_H, of two orders of magnitude, suggests that hydrogen transport occurs independently of oxygen ions and is governed by a mechanism that is characterized by a higher mobility. The diffusion coefficient of hydrogen in $SrCe_{0.92}Dy_{0.08}O_{3-\delta}$ was found to be $(2 \pm 0.1) \times 10^{-7}$ cm^2 sec^{-1}, consistent with the proton conductivity measurements in barium and strontium cerates (*7–11*). The conclusion that oxygen is bound to the lattice more tightly than hydrogen is also supported by thermal desorption analysis. Titanates and undoped barium cerate generate mainly hydrogen molecules. The H_2 partial pressure-to-H_2O partial pressure ratio is specified in Table I.

Conclusion

Hydrogen defects can penetrate into both doped and undoped perovskites from the ambient atmosphere at the temperature of synthesis. We have assumed that when one H_2O molecule dissolves, one oxygen vacancy is filled and two hydroxide ions occupy oxygen sites. The dissolved hydrogen concentration is strongly influenced by cation composition, dopant density, and method of preparation. Hydrogen bonding with the lattice is weaker than that of oxygen; therefore, it migrates through the crystal as a separate proton, not as a hydroxide ion. Under desorption this hydrogen is released in molecular form.

Acknowledgments

The authors are grateful to Dr. A. V. Strelkov and Dr. A. R. Kaul for helpful discussion, and to Drs. A. V. Strelkov, B. T. Melech, and V. P. Gorelov for the preparation of the samples used in this work.

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