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CHEMICAL STABILITY OF $YBa_2Cu_3O_{7-x}$ TO VARIOUS ATMOSPHERES

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ABSTRACT

The chemical stability of $YBa_2Cu_3O_{7-x}$ in various gas atmospheres (O_2, CO_2, $N_2 + H_2O$, $O_2 + H_2O$ and $CO_2 + H_2O$ at room temperature for 2–50 h and H_2O + air at 40 ° C for 1–312 h) was examined by detecting the evolution and/or absorption of gases and by determining constituent phase changes using X-ray diffraction (XRD). $Y_{1.00}Ba_{2.00}Cu_{3.01}O_{6.93}$ powder, synthesized by the usual method, was used as a starting material. There were almost no changes in desiccated O_2 and CO_2 gases. $YBa_2Cu_3O_{7-x}$ was fairly stable in the $CO_2 + H_2O$ atmosphere compared with $O_2 + H_2O$ and $N_2 + H_2O$. In $CO_2 + H_2O$ a slight evolution of H_2O and CO_2 was detected, but the amount of evolved gas only increased slightly over a long period of exposure (40 h). $YBa_2Cu_3O_{7-x}$ reacted strongly with H_2O to form $Ba(OH)_2 \cdot 8H_2O$ and $BaCO_3$ in $H_2O + N_2$ and $O_2 + H_2O$, and decomposed to $BaCO_3$, $Ba(OH)_2 \cdot 8H_2O$, $Y(OH)_3$ and CuO at 40 ° C in air saturated with H_2O.

INTRODUCTION

The chemical stability of $YBa_2Cu_3O_{7-x}$ to various gases is one of the most important factors determining its practical use. However, reports on the chemical stability are few [1,2].

$YBa_2Cu_3O_{7-x}$ is very unstable in water and decomposes into $BaCO_3$ and/or $Ba(OH)_2$ in a short time. In hot water, the $YBa_2Cu_3O_{7-x}$ perovskite phase disappears within only 10 min, and the sintered solid finally disintegrates into powder. The superconductivity characteristics are also influenced by even a little water vapor [3]. It is reported that CO_2 reacts with $YBa_2Cu_3O_{7-x}$ to generate $BaCO_3$. However, the data regarding the chemical stability to various atmospheres are insufficient and details are not clear.

In this paper the chemical stability of $YBa_2Cu_3O_{7-x}$ was confirmed experimentally by measuring the gas evolution and/or absorption characteristics of $YBa_2Cu_3O_{7-x}$ which had been exposed to various gas atmospheres at room temperature and 40 ° C.

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EXPERIMENT

Synthesis of $YBa_2Cu_3O_{7-x}$

$YBa_2Cu_3O_{7-x}$ was synthesized by the usual method. $BaCO_3$ (Wako Pure Chemicals Ltd., Japan, 99%), Y_2O_3 (Mitsubishi Chemical Industries Ltd., Japan, 99.99%) and CuO, obtained by oxidizing Cu_2O (Wako Pure Chemicals Ltd., Japan) in air at 950 °C for 5 h, were used as starting materials. These were weighed and the composition Y : Ba : Cu = 1 : 2 : 3 was mixed with methanol. The mixture was heated for 15 h at 950 °C in a flow of oxygen gas. After grinding the heated powder, it was pressed into pellets of 10 mm in diameter and 2–3 mm thick, sintered at 950 °C for 15 h, and then cooled to room temperature at a rate of 1–2 °C min^{-1} in oxygen. From the result of X-ray diffraction (XRD), the sintered specimen was found to be single phase, orthorhombic $YBa_2Cu_3O_{7-x}$. The composition of the prepared specimen was $Y_{1.00}Ba_{2.00}Cu_{3.01}O_{0.93}$. The cation composition was determined by chemical analysis and the oxygen content was calculated from the weight change on reduction to Cu, BaO and $Y_4Ba_3O_9$ [4] by heating in hydrogen [5]. The density of the sintered specimen was about 5.0–5.2 g cm^{-3} (relative density about 80%).

Sintered specimens were stored in a desiccator and preserved in dried nitrogen after evacuating the desiccator. The specimen was taken out just before use in the experiments and was ground immediately using a pestle and mortar.

Exposure to various atmospheres

The $YBa_2Cu_3O_{7-x}$ powder was exposed to various gas atmospheres: CO_2, O_2, $N_2 + H_2O$ (using inactive N_2 for carrier gas), $H_2O + CO_2$ and $H_2O + O_2$ for 2–50 h around 20 °C. N_2, O_2 and CO_2 gases (commercial bomb gas, 99.99%) were dried by passing through a silica gel trap and then a P_2O_5 trap; in cases where a moist atmosphere was required they were bubbled through distilled water. They were then introduced into the specimen container. The temperature and humidity of the atmosphere were measured by the sensor in the specimen container. Approximately 700 mg of ground powder specimen were placed loosely in an alumina boat covered with a glass cloth. The gas flow rate was 20–30 ml min^{-1}. The relative humidity was over 90% within 20 min after the experiment had started, and finally reached 100%. The partial pressure of the water vapor was about 17 Torr (2336 Pa) in this condition.

Gas evolution and/or absorption measurement

The phases and the gas evolution and/or absorption behavior of the specimens exposed to various atmospheres were examined by XRD and

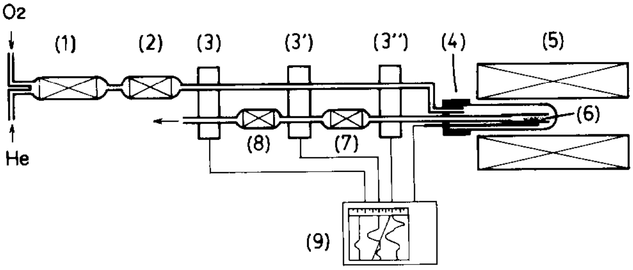

Fig. 1. Construction of apparatus for detecting gas evolution and/or absorption: (1) silica gel trap; (2) P_2O_5 trap; (3) TCD (thermal conductive detector); (4) measurement cell; (5) electric furnace; (6) specimen container; (7) P_2O_5 trap; (8) ascarite trap; (9) recorder.

differential thermal gas analysis (DTGA) [6]. Almost the same weight of specimen, about 80 mg, was used for each DTGA measurement. Measurements were carried out on heating from room temperature to 930–980 ° C, and then on cooling to 800 ° C.

DTGA is one of the thermal analytical methods and is a modified evolution gas analysis (EGA). The construction of the apparatus is shown in Fig. 1. A gas mixture of He and O_2 with a volume ratio of 9 : 1 and a total flow rate of 40 cm^3 min^{-1} was used as the carrier gas. After passing through a silica gel trap (1) and a P_2O_5 trap (2) to remove moisture, the carrier gas was introduced into the reference side of a thermal conductive detector (TCD) (3). Then the carrier gas passed into the measurement cell (4) and over the specimen container (6) in an electric furnace (5). The changes in composition of the carrier gas, caused by the gas evolution and/or absorption in the specimen during heating or cooling, were detected as fluctuations of thermal conductivity by measuring the resistivity difference between the specimen and reference sides of the TCD which was heated by a constant current and was inserted in the path of gas flow. The total changes in the carrier gas composition, the changes other than H_2O and the changes other than H_2O and CO_2 were detected by the TCDs No. 3″, No. 3′ and No. 3, respectively. The peaks obtained by No. 3 were due to O_2.

Although the sensitivity of DTGA is relatively high, a very slow rate of gas evolution and/or absorption seems considerably difficult to detect. In this paper, quantitative analysis was not used.

RESULTS AND DISCUSSION

Table 1 presents a summary of the experiments, the constituent phases except $YBa_2Cu_3O_{7-x}$ before and after DTGA and the weight loss of the specimen during DTGA as a function of gas atmosphere and exposure time. All specimens were single phase $YBa_2Cu_3O_{7-x}$ after DTGA.

TABLE 1

Summary of chemical stability of $YBa_2Cu_2O_{7-x}$ to various gas atmospheres

No.	Exposing condition		Detected phases by XRD [a]		Weight change during DTGA (%)
	Atmosphere	Time (h)	Before DTGA	After DTGA	
1	As synthesized powder		–	–	1.8
2	O_2	50	–	–	2.2
3	CO_2	50	–	–	4.3
4	N_2+H_2O	2	$BaCO_3$(tr)	–	1.5
5	N_2+H_2O	12	$BaCO_3$, unknown	–	7.3
6	N_2+H_2O	40	$BaCO_3$, $Ba(OH)_2 \cdot 8H_2O$(tr)	–	13.8
7	H_2O+O_2	2	$BaCO_3$(tr)	–	3.0
8	H_2O+O_2	12	$BaCO_3$, $Ba(OH)_2 \cdot 8H_2O$(tr)	–	7.5
9	H_2O+O_2	40	$BaCO_3$, $Ba(OH)_2 \cdot 8H_2O$	–	12.8
10	H_2O+CO_2	2	–	–	1.7
11	H_2O+CO_2	12	–	–	1.1
12	H_2O+CO_2	40	$BaCO_3$(tr)	–	3.2

[a] Except $YBa_2Cu_3O_{7-x}$ which was detected in all cases as the main phase.

Effects of O_2, CO_2 and H_2O atmospheres

Figure 2 shows the DTGA curves of specimens exposed to O_2, CO_2 or $N_2 + H_2O$ and without exposure. The specimen which was not exposed and the specimens exposed to O_2 and CO_2 gave almost the same DTGA curves. From the results of DTGA, in these three cases the evolved and/or absorbed gases were not H_2O and CO_2; O_2 was thought to be evolved from the constituent elements of $YBa_2Cu_3O_{7-x}$. O_2 gas evolution from these specimens began at about 340–360 °C, increased gradually and clearly decreased at 590–610 °C. This decrease in O_2 evolution at 590–610 °C was observed reproducibly at an almost constant temperature in these cases. It corresponded to the phase transition temperature of $YBa_2Cu_3O_{7-x}$ from an orthorhombic to a tetragonal form [7]. After this, O_2 gas evolution continued and decreased at about 850 °C; however, a strong gas evolution peak was observed at about 900 °C. When the specimens were cooled from 960 °C, an O_2 gas absorption peak, which corresponded to the O_2 evolution at about 900 °C, was observed.

In contrast, four DTGA peaks of H_2O evolution and two peaks of O_2 absorption were observed for the specimen exposed to a $N_2 + H_2O$ atmosphere in the temperature range room temperature to 400 °C (Fig. 2(d)). The O_2 evolution at 700–800 °C is different from that of the other three specimens. CO_2 evolution at about 850 °C seems to be due to the decom-

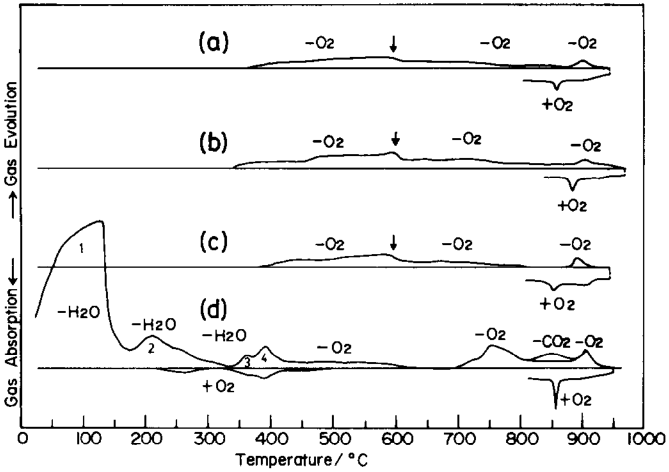

Fig. 2. Gas evolution and/or absorption of $YBa_2Cu_3O_{7-x}$ specimens exposed to various atmospheres: (a) as synthesized powder; (b) in O_2 for 50 h; (c) in CO_2 for 50 h; (d) in $N_2 + H_2O$ for 40 h.

position of a carbonate formed by the reaction between the specimen and the CO_2 gas evaporated from the distilled water in the water vapor generator. The DTGA curves relating to H_2O evolution are similar to DTA data [8] of the thermal decomposition of $Ba(OH)_2 \cdot 8H_2O$. However, the dehydration peak accompanying the decomposition of $Ba(OH)_2$ at 600–900 °C, predicted by DTA [8], could not be detected for this specimen. CO_2 evolution at about 850 °C corresponds to the thermal decomposition of $BaCO_3$ [9]. These results agree with XRD data (Table 1).

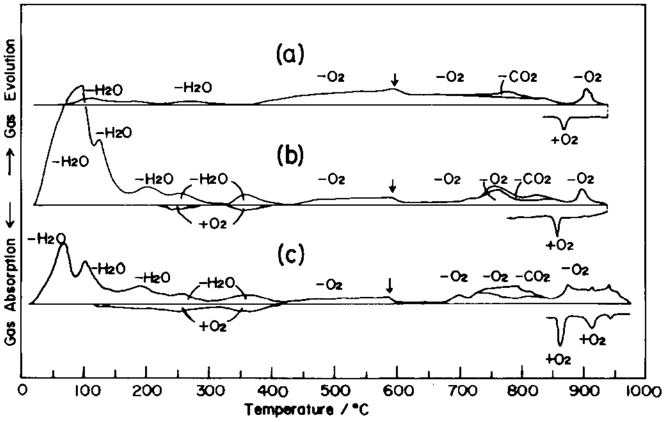

Fig. 3. Gas evolution and/or absorption of $YBa_2Cu_3O_{7-x}$ specimens exposed to various atmospheres: (a) in $CO_2 + H_2O$ for 12 h; (b) in $O_2 + H_2O$ for 12 h; (c) in $N_2 + H_2O$ for 12 h.

Effects of CO_2, O_2 and N_2 gases saturated with H_2O vapor

The stability of $YBa_2Cu_3O_{7-x}$ to $CO_2 + H_2O$, $O_2 + H_2O$ and $N_2 + H_2O$ atmospheres containing saturated H_2O vapor at 20 °C were examined. DTGA curves of specimens exposed for 12 h in each gas atmosphere are shown in Fig. 3. The most interesting phenomenon is that H_2O evolution at low temperature was hardly observed for specimen (a) exposed to $CO_2 + H_2O$ in contrast with the other two specimens ((b) and (c)). The volume of CO_2 and O_2 gases evolved from the specimen exposed to $CO_2 + H_2O$ around 800 °C was also smaller than the volumes evolved from the other two specimens. No phase other than $YBa_2Cu_3O_{7-x}$ was detected in the specimen exposed to $CO_2 + H_2O$. The specimens exposed to $O_2 + H_2O$ and $N_2 + H_2O$ for 12 h showed almost the same behavior as described in the previous section.

Influence of the exposure time in various gas atmospheres

The DTGA curves of specimens exposed to $CO_2 + H_2O$, $O_2 + H_2O$ and $N_2 + H_2O$ atmospheres for various periods of time are shown in Figs. 4, 5 and 6, respectively.

The volume of gas evolved from the specimen exposed to $CO_2 + H_2O$ was smaller than that from specimens exposed to $O_2 + H_2O$ and $N_2 + H_2O$ (see Table 1, Fig. 4), even for a longer exposure. Single phase $YBa_2Cu_3O_{7-x}$ after 2 and 12 h exposure, and a small amount of $BaCO_3$ in addition to $YBa_2Cu_3O_{7-x}$ after 40 h exposure, were observed by XRD in the specimen before DTGA. The gas evolution and/or absorption behavior in $O_2 + H_2O$ and $N_2 + H_2O$ seemed to be fundamentally the same (Figs. 5 and 6). After 2 h exposure, weak H_2O and CO_2 gas evolution was observed in both cases.

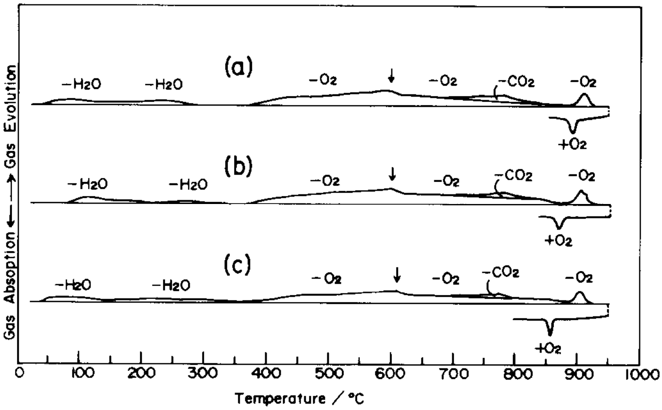

Fig. 4. Gas evolution and/or absorption of $YBa_2Cu_3O_{7-x}$ specimens exposed to $CO_2 + H_2O$ for various periods of time: (a) 2 h; (b) 12 h; (c) 40 h.

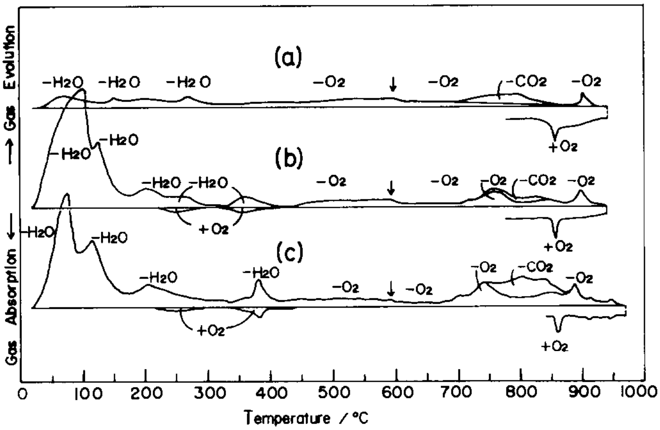

Fig. 5. Gas evolution and/or absorption of $YBa_2Cu_3O_{7-x}$ specimens exposed to $O_2 + H_2O$ for various periods of time: (2) 2 h; (b) 12 h; (c) 40 h.

Strong H_2O evolution peaks corresponding to the thermal decomposition of $Ba(OH)_2 \cdot 8H_2O$ and an unknown phase (Table 1) were observed after 12 and 40 h exposure. O_2 and CO_2 evolution peaks were clearly observed at about 750–850 °C after 12 and 40 h. In some cases, the O_2 evolution peak near 900 °C split into three or four peaks. Within the limits of this experiment the gas evolution behavior in the temperature range 700–950 °C is not sufficiently clear to understand the phenomena systematically. Further experiments using other analytical methods are required.

Stability of sintered $YBa_2Cu_3O_{7-x}$ in H_2O vapor saturated air

The chemical stability of $YBa_2Cu_3O_{7-x}$ exposed to a combination of H_2O vapor and various carrier gases is very different. As the air contains

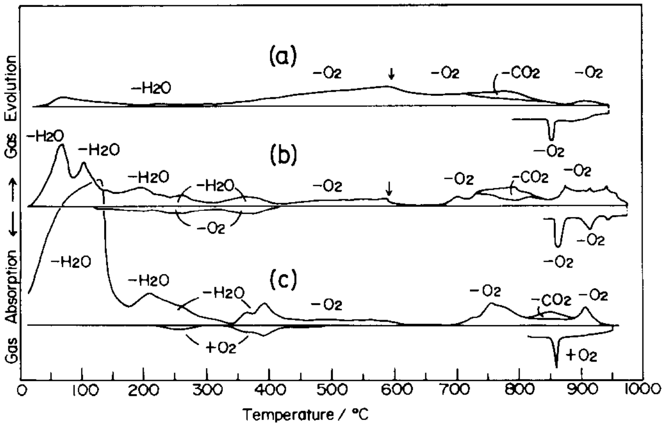

Fig. 6. Gas evolution and/or absorption of $YBa_2Cu_3O_{7-x}$ specimens exposed to $N_2 + H_2O$ for various periods of time: (a) 2 h; (b) 12 h; (c) 40 h.

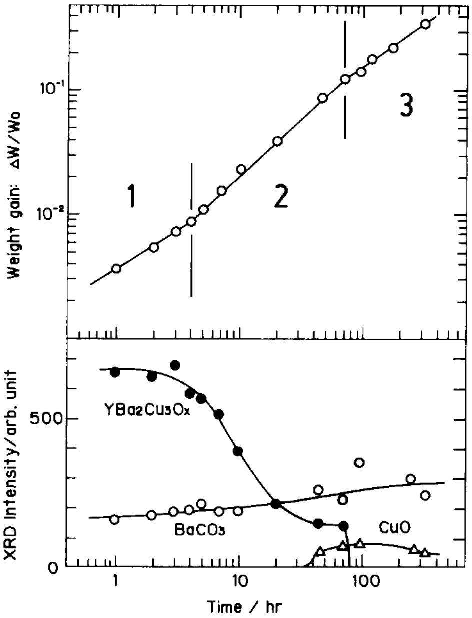

Fig. 7. Weight gain and constituent phases of the specimen surface determined by XRD versus exposure time.

H_2O and CO_2 it is important to reveal the effect of air containing H_2O vapor on the sintered $YBa_2Cu_3O_{7-x}$ specimen. A sintered specimen with a density of 5.3 g cm^{-3} was exposed to air saturated with H_2O vapor at 40 ° C for various exposure periods. The weight gain and the phase changes on the surface of the specimen versus the exposure period are shown in Fig. 7. Specimen weight increased with increasing exposure time. The relationship between weight and time can be divided into three regions on the basis of the slope of the line. Although the XRD intensity of $YBa_2Cu_3O_{7-x}$ was almost constant in region 1, it decreased sharply in region 2 and disappeared in region 3. CuO appeared just before the disappearance of $YBa_2Cu_3O_{7-x}$. The intensity of $BaCO_3$ increased with increasing exposure time over the entire range.

From the XRD of the specimen exposed for 312 h, $BaCO_3$ and CuO were found on the surface and $BaCO_3$, $Y(OH)_3$, CuO, $Ba(OH)_2 \cdot 8H_2O$ and BaO(tr) were found in the bulk of the specimen; $YBa_2Cu_3O_{7-x}$ was not detected either on the surface or in the bulk.

Chemical stability of $YBa_2Cu_3O_{7-x}$

$YBa_2Cu_3O_{7-x}$ did not react with desiccated CO_2, O_2 and N_2 gases at room temperature. In the $CO_2 + H_2O$ atmosphere it seemed to be almost unchanged, and the amount of gas evolved slightly increased with exposure time. In contrast, it was very reactive in the $O_2 + H_2O$ and $N_2 + H_2O$ atmospheres. $BaCO_3$ and $Ba(OH)_2 \cdot 8H_2O$ were formed at 20 ° C, and $BaCO_3$, $Ba(OH)_2 \cdot 8H_2O$, $Y(OH)_3$ and CuO coexisted in the bulk of the sintered specimen exposed to air saturated with H_2O at 40 ° C. From these results, the decomposition reactions of $YBa_2Cu_3O_{7-x}$ in H_2O-containing air are shown in the following two steps.

$$YBa_2Cu_3O_{7-x} + 23/2\ H_2O$$
$$\rightarrow 2Ba(OH)_2 \cdot 8H_2O + Y(OH)_3 + 3CuO + (0.5 - x)/2O_2 \tag{1}$$

$$Ba(OH)_2 \cdot 8H_2O + CO_2 \rightarrow BaCO_3 + 9H_2O \tag{2}$$

These reactions require O_2 or N_2 as well as H_2O and CO_2. The reason that $YBa_2Cu_3O_{7-x}$ hardly decomposed in $CO_2 + H_2O$ is now being investigated. However, it has been reported [3] that $YBa_2Cu_3O_{7-x}$ decomposes strongly in $CO_2 + H_2O$ at 200–300 ° C.

CONCLUSION

The chemical stability of $YBa_2Cu_3O_{7-x}$ in various gases (O_2, CO_2, $N_2 + H_2O$, $O_2 + H_2O$ and $CO_2 + H_2O$ at room temperature and H_2O + air at 40 ° C) was examined by detecting the evolution and/or absorption gases. There were hardly any changes in desiccated O_2 and CO_2 gases. $YBa_2Cu_3O_{7-x}$ was fairly stable in the $CO_2 + H_2O$ atmosphere compared with $O_2 + H_2O$ and $N_2 + H_2O$. In $CO_2 + H_2O$ a slight evolution of H_2O and CO_2 was detected, but the amount of these gases only increased slowly even for a long period of exposure (40 h). $YBa_2Cu_3O_{7-x}$ reacted strongly with H_2O to form $Ba(OH)_2 \cdot 8H_2O$ and $BaCO_3$ in $N_2 + H_2O$ and $O_2 + H_2O$, and decomposed to $BaCO_3$, $Ba(OH)_2 \cdot 8H_2O$, $Y(OH)_3$ and CuO at 40 ° C in air saturated with H_2O.

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