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CHEMICAL STABILITY OF $BaCuO_2$ IN VARIOUS HUMID ATMOSPHERES

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ABSTRACT

The chemical stability of $BaCuO_2$ in various relative humidity conditions was studied at room temperature. $BaCuO_2$ is highly sensitive to water and moisture, and decomposes rapidly. In humid air $BaCuO_2$ decomposes to $BaCO_3$ and CuO, in O_2 saturated with water vapour to $Ba(OH)_2 \cdot 8H_2O$ and CuO, and in CO_2 saturated with water vapour to $BaCO_3$ and $CuCO_3 \cdot Cu(OH)_2$. The final decomposition products of $BaCuO_2$ were dependent on the atmosphere. But, in any humid environment, independent of the atmosphere, first $Ba(OH)_2$ and $Cu(OH)_2$ and then intermediate phase ("x"-phase) products were observed during the decomposition. It was also observed that $BaCuO_2$ is relatively stable in air of relatively low humidity and in dried CO_2 and O_2 at room temperature.

INTRODUCTION

The discovery of high-T_c ceramic superconductors in the La–Ba–Cu–O and Y–Ba–Cu–O systems [1–3] greatly stimulated interest in those oxides containing copper. In order to find new oxide superconductors of still higher T_c, extensive studies have been carried out, and $YBa_2Cu_3O_{7-x}$ ($T_c = 90$ K), $BiSrCaCu_2O_y$ [4] and $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ [5], with transition temperatures (T_c) above 100 K, have been found. An interesting common feature of these high-T_c oxide superconductors is the presence of alkaline earth metal elements such as Ba, Sr and Ca. Another interesting point is that $YBa_2Cu_3O_{7-x}$ containing only barium is moderately sensitive to humid atmospheres [6–9] whereas the single phase of the 100-K superconducting $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ was found to be extremely stable in water and moisture [4]. Furthermore, during preparation of pure high-T_c superconducting phases of the Tl–Ba–Ca–Cu–O system, first the compounds $BaCuO_2$ and Ca_2CuO_3 [10] or $BaCuO_2$ [11] formed, followed by the solid state reaction of $Tl_2O_3 + BaCuO_2 + Ca_2CuO_3$ to form the Tl–Ba–Ca–Cu–O superconductive compound. This suggests that it is important to clarify the

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properties of compounds in the Ba–Cu–O, Sr–Cu–O and Ca–Cu–O systems.

In the Ba–Cu–O system, four compounds have been reported, i.e. $BaCuO_2$, Ba_2CuO_3, Ba_2CuO_4 and $BaCu_2O_2$. Ba_2CuO_3 and Ba_3CuO_4 have been described as hydroscopic and are said to decompose above 850 ° C, but no one has prepared them successfully [12–13]. $BaCu_2O_2$ is apparently unstable in air [14]. $BaCuO_2$ is relatively better known [15] than the other three compounds and has cubic symmetry, *I*432, with $a = 18.26$ Å. It takes in oxygen to a value of $BaCuO_{2.1}$ between 350 and 600 ° C, and under higher oxygen pressure, $BaCuO_{2.5}$ and $BaCuO_{2.63}$ can be obtained but its chemical properties are little known. In this paper, the stability of a pure single phase of $BaCuO_2$ was studied in various humid atmospheres.

EXPERIMENTAL

Sample preparation

Samples were prepared by solid state reaction. High purity $BaCO_3$ and CuO, obtained by heating Cu_2O at 900 ° C for 5 h in air, were mixed, pressed into pellets 20 mm in diameter, calcined at 850 ° C for 24 h in air, and quenched to room temperature. One of the common problems associated with preparation by solid state reaction is the incomplete reaction between powders. The calcined and quenched specimens were then ground, pressed into pellets, fired at 900 ° C for 24 h and quenched to room temperature, for at least three times, in order to obtain a completely reacted, homogeneous sample. X-ray diffractometry (XRD) and differential thermal gas analysis (DTGA) [16] were used to confirm the formation of a pure single phase compound, $BaCuO_2$, and the complete absence of $BaCO_3$. Using DTGA and thermogravimetry (TG) measurements, it was also observed that a sample prepared by quenching to room temperature in air is oxygen deficient and takes up oxygen at about 350 ° C, and then loses oxygen again from about 450 to 800 ° C. Detailed results concerning the oxygen deficiency of $BaCuO_2$ will be reported elsewhere. In order to obtain a sample without oxygen deficiency for these studies, the samples prepared by the method mentioned above were annealed at 900 ° C for 10 h in dry, CO_2-free O_2, and cooled to room temperature at a cooling rate of 5 ° C min^{-1}. The samples were placed in a vacuum desiccator as soon as possible to prevent reaction with water vapour. The $BaCuO_2$ used for this study was a pure single phase with no oxygen deficiency.

Atmosphere treatment

A pellet sample taken from the desiccator was ground to powder as rapidly as possible, and then exposed to various conditions of ambient relative humidity. In this study, four different relative humidity environments were employed. They were: (1) air of about 35% relative humidity, (2) air of about 70% relative humidity, (3) O_2 (30 ml min^{-1}) saturated with water vapour, and (4) CO_2 (30 ml min^{-1}) saturated with water vapour. In the case of (3) and (4), about 200 mg of powdered sample was loosely packed in an alumina boat. The distilled water used was boiled for 30 min to eliminate dissolved CO_2.

XRD, DTA, DTGA and SEM measurements

After a sample had been exposed to the various humid atmospheres for a desired time, the DTA, DTGA and XRD measurements were immediately carried out to confirm the decomposition products. About 30 mg samples were used for the DTA and DTGA measurements. All of the DTA measurements were carried out in static air and the DTGA was determined in a flow of He (20 ml min^{-1}) at a heating rate of 10 °C min^{-1}. Samples from before and after being exposed to O_2 saturated with water vapour for 72 h were observed with a scanning electron microscope.

RESULTS AND DISCUSSIONS

Stability in air

It was found that $BaCuO_2$ powder decomposed by exposing it to air of about 70% relative humidity at room temperature.

Figure 1 shows the X-ray diffraction intensity change of each constituent present in the sample with exposure time. A weight gain was observed in the sample during exposure in humid air, as shown in Fig. 2a. After 2 h, the X-ray diffraction intensity of $BaCuO_2$ was considerably weakened. When the weight gain was larger than 1%, weak X-ray diffraction patterns of $Ba(OH)_2$ and $Cu(OH)_2$ began to be detected (although the strongest peak of the $Ba(OH)_2$ pattern was missing). Then, with increasing weight gain, the XRD pattern of the "x"-phase was observed; this has also been observed in the decomposition of the superconducting oxide $YBa_2Cu_3O_7$ [8]. After formation of "x"-phase, peaks of poorly crystalline $BaCO_3$ began to appear, and simultaneously the peak intensities of $Ba(OH)_2$ and $Cu(OH)_2$ became weak. When the weight gain was larger than 4%, the XRD patterns of $Ba(OH)_2$ and $Cu(OH)_2$ had completely disappeared, and further exposure caused an increase in the $BaCO_3$ phase. When exposed more than 8 days, only $BaCO_3$ could be observed from the XRD measurement. Furthermore, in the DTA curve of the sample exposed in air of 70% relative humidity at room temperature for 8 days, only a large endothermic peak (812 °C), caused by the transformation of $BaCO_3$, was observed. This demonstrated that after a

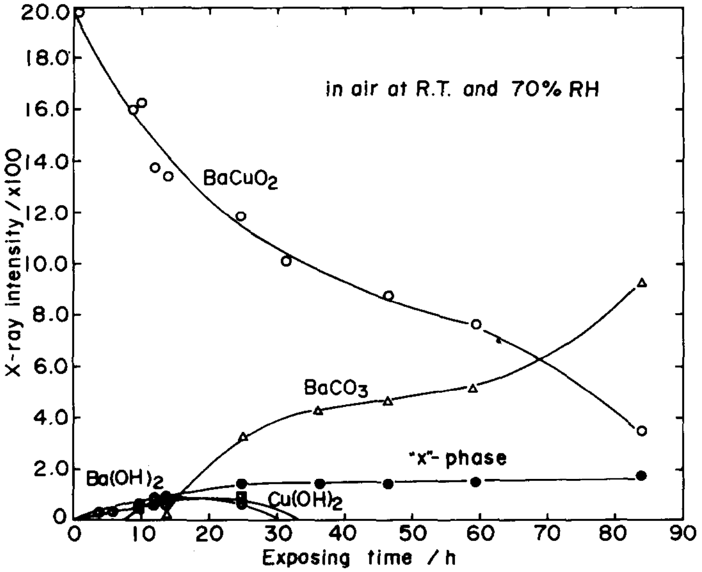


Fig. 1. Relation between the X-ray diffraction intensity of each constituent in samples exposed in air of 70% relative humidity at room temperature and the exposure time.

long period of exposure in humid air, $BaCuO_2$ is nearly completely decomposed to $BaCO_3$ and CuO. The decomposition product CuO was believed to exist in an amorphous form, because its X-ray pattern was not observed.

However, in air of 35% humidity, even exposing $BaCuO_2$ for 100 days at room temperature, no observable weight gain, and no major change could be detected in either the X-ray diffraction pattern or the DTA curve.

This suggested that the decomposition of $BaCuO_2$ was caused by the water in the humid air. According to the XRD results, its decomposition may be manifested in three stages. In stage 1, the crystallinity of $BaCuO_2$ decreases due to the absorption of water, resulting in a lowering of the X-ray diffraction intensity; then $BaCuO_2$ reacts with the absorbed water to form crystalline $Ba(OH)_2$ and $Cu(OH)_2$. In stage 2, the $Ba(OH)_2$ formed reacts with $Cu(OH)_2$ to produce "x"-phase, and finally in stage 3, the reaction between "x"-phase and CO_2 in the atmosphere occurs to form crystalline $BaCO_3$. These decompositions may be written as

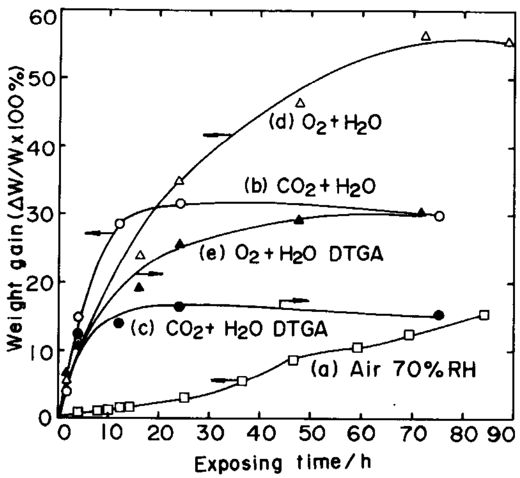
$$\text{stage 1, } BaCuO_2 + H_2O \rightarrow Ba(OH)_2 + Cu(OH)_2 \tag{1}$$

$$\text{stage 2, } n Ba(OH)_2 + m Cu(OH)_2 \rightarrow \text{“x”-phase} \tag{2}$$

$$\text{stage 3, “x”-phase} + CO_2 \rightarrow BaCO_3 + CuO + H_2O \tag{3}$$

and the overall decomposition may be written as

$$BaCuO_2 + CO_2 \rightarrow BaCO_3 + CuO \tag{4}$$



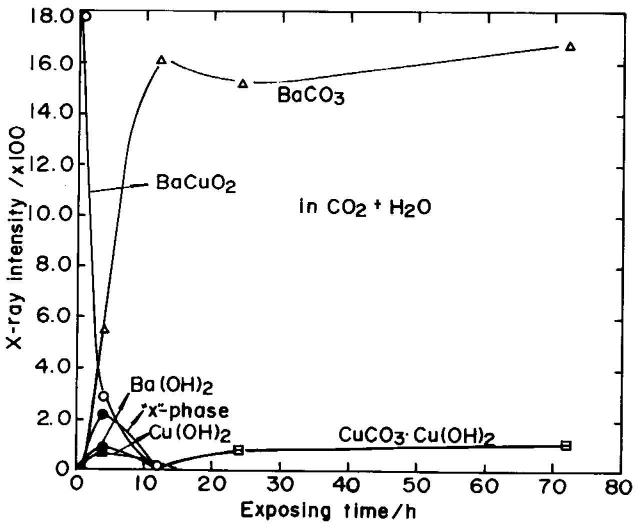


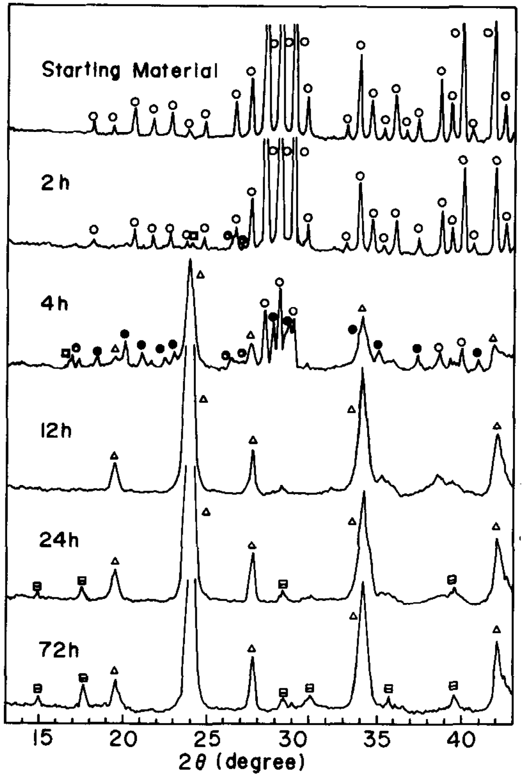
Fig. 2. The weight change of samples exposed in (1) air of 70% relative humidity; (2) CO_2 (30 ml min^{-1}) saturated with water vapour; and (3) O_2 (30 ml min^{-1}) saturated with water vapour at room temperature and after differential thermal gas analysis (DTGA) measurement in He (20 ml min^{-1}) to 900 °C at 10 °C min^{-1}: a, weight gain for samples exposed in (1); b, weight gain for samples exposed in (2); c, weight loss after DTGA for samples exposed in (2); d, weight gain for samples exposed in (3); e, weight loss after DTGA for samples exposed in (3).

Fig. 3. Relation between the X-ray diffraction intensity of each constituent in samples exposed in CO_2 (30 ml min^{-1}) saturated with water vapour and the exposure time.

Decomposition in CO_2 saturated with water vapour

Samples were exposed in CO_2 saturated with water vapour for 2–75 h. The relative X-ray diffraction intensity change of each constituent in the exposed samples with the exposure time is shown in Fig. 3, and the X-ray diffraction patterns are given in Fig. 4. Figure 5 and 6 are the DTGA and DTA curves of the corresponding exposed samples respectively. Under these exposure conditions, the decomposition of $BaCuO_2$ was quite fast. An initial 2 h exposure caused as 4% weight gain to form $Ba(OH)_2$ and $Cu(OH)_2$. When the sample had gained 15% weight (4 h exposure) (Fig. 2b), about 70% of the $BaCuO_2$ had decomposed to form $BaCO_3$, "x"-phase, $Ba(OH)_2$ and $Cu(OH)_2$ (Figs. 3 and 4). In other words, at this moment, there was a coexistence of five phases. In the DTGA and DTA curves (Figs. 5 and 6) of samples exposed for 2 and 4 h, several peaks due to loss of water and endothermal peaks were observed respectively. The endothermal peaks at about 120, 310 and 360 °C were considered to be most probably caused by water loss and decomposition of "x"-phase, because it is known that $Ca(OH)_2$ loses water at about 180 °C, $Ba(OH)_2$ has a transformation at about 390 °C and loses water at about 700 °C, and $BaCO_3$ has a transformation at about 810 °C. But it was not clear which oxygen evolution (at 200–250 °C and 500–730 °C) or oxygen absorption (at 250–500 °C) peaks, observed in the DTGA curves (Fig. 5), were caused by which of the coexisting five phases. From Figs. 3 and 4, it can be seen that with increasing exposure time, the X-ray peaks of $Ba(OH)_2$, $Cu(OH)_2$ and "x"-phase become weak and eventually disappear, while that of $BaCO_3$ increases. Following exposure for 12 h, only the pattern of $BaCO_3$ could be obtained (Fig. 4) and the endothermic peaks (at about 310 and 360 °C) of "x"-phase had disappeared. This showed that in this situation, the 12 h exposure had led to the complete decomposition of $BaCuO_2$. Up to this 12 h exposure time, the decomposition behaviour of $BaCuO_2$ in CO_2 saturated with water vapour was identical to that in air of 70% relative humidity, except in the more rapid decomposition of the latter. The difference from that in humid air was that no trace of $Cu(OH)_2$ could be observed in the X-ray diffraction pattern of the sample exposed for 12 h (Fig. 4). It is believed that the product formed from the decomposition of "x"-phase must be $Cu(OH)_2$ which may be amorphous, not CuO, because on the DTGA curves (Fig. 5) of sample exposed for 12 h, the peak for water vapour evolution occurs at temperatures lower than 150 °C, and on the DTA curves (Fig. 6), there is an endothermic peak at about 120 °C. These are believed to be caused by $Cu(OH)_2$ (or $CuO \cdot nH_2O$), because crystalline $Cu(OH)_2$ loses water at about 185 °C.

An interesting difference between the decomposition in humid air and in CO_2 saturated with water vapour was the formation of $CuCO_3 \cdot Cu(OH)_2$ (Fig. 4) by exposing the sample longer than 12 h. $CuCO_3 \cdot Cu(OH)_2$ decom-



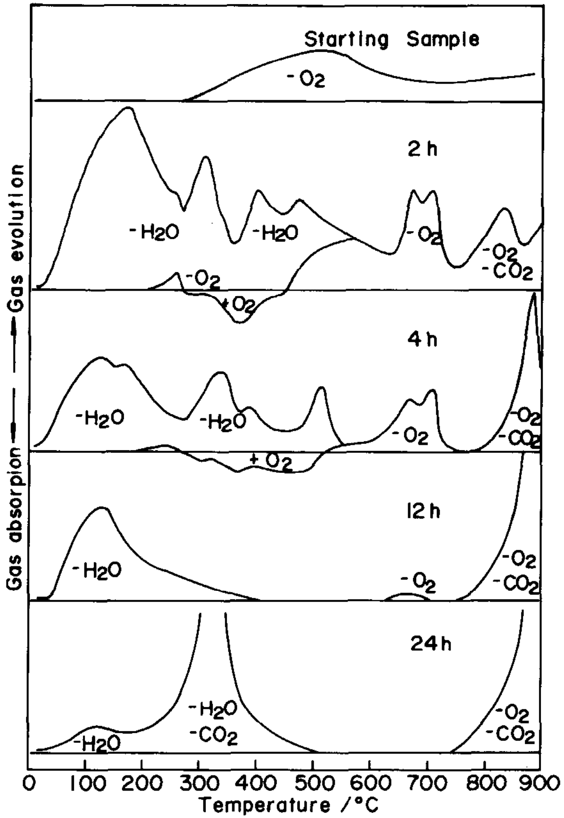
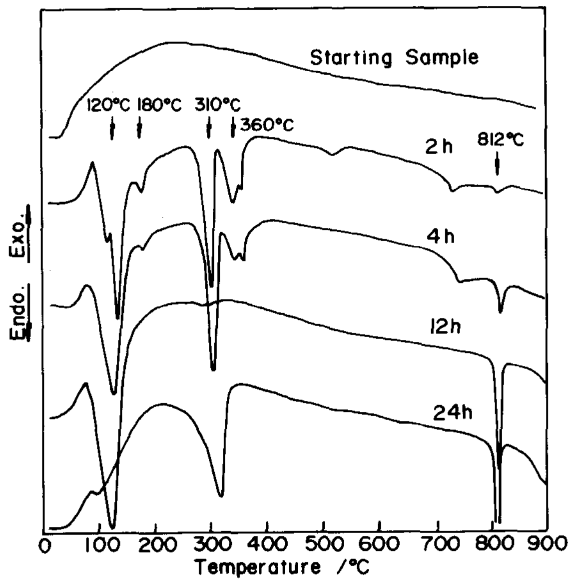


Fig. 4. X-ray diffraction patterns of samples exposed in CO_2 (30 ml min^{-1}) saturated with water vapour at room temperature: ○, $BaCuO_2$; △, $BaCO_3$; ●, "x"-phase; ◉, $Ba(OH)_2$; □, $Cu(OH)_2$; ⊟, $CuCO_3 \cdot Cu(OH)_2$.

Fig. 5. DTGA curves of samples exposed in CO_2 (30 ml min^{-1}) saturated with water vapour (heating rate, 10 °C min^{-1}).



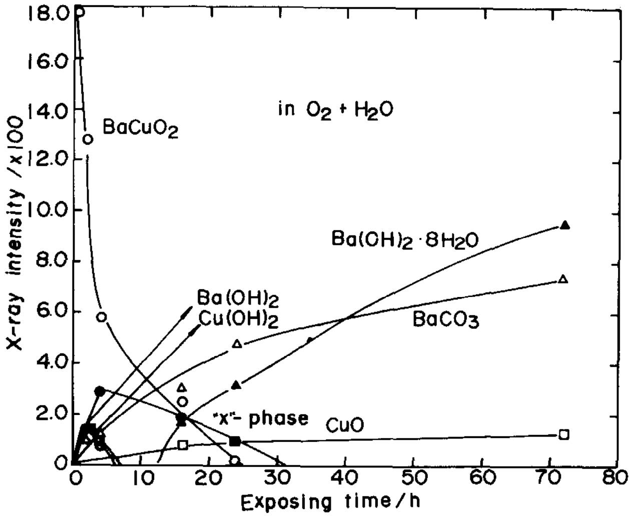


Fig. 6. The DTA curves of samples exposed in CO_2 (30 ml min^{-1}) saturated with water vapour. The DTA measurement was carried out in static air. The heating rate was 10 °C min^{-1}.

Fig. 7. Relation between X-ray diffraction intensity of each constituent in samples exposed in O_2 (30 ml min^{-1}) saturated with water vapour and the exposure time.

poses to CuO with loss of H_2O and CO_2 at about 360 °C, which can be seen from the results of the DTGA (Fig. 5) and DTA (Fig. 6) of samples exposed for 24 h and 75 h. The formation of $CuCO_3 \cdot Cu(OH)_2$ can be written

$$2Cu(OH)_2 + CO_2 \rightarrow CuCO_3 \cdot Cu(OH)_2 + H_2O \qquad (5)$$

From Fig. 2b, it can be seen that an exposure time longer than 24 h did not increase the weight gain of the sample. Therefore, the sample exposed for 75 h had the same weight loss as that for 24 h during the DTGA (Fig. 2c) and DTA. This showed that in this situation, the final decomposition products of $BaCuO_2$ were $BaCO_3$ and $CuCO_3 \cdot Cu(OH)_2$, and this decomposition process was complete after 24 h exposure. So, the total decomposition reaction can be written

$$2BaCuO_2 + 3CO_2 + H_2O \rightarrow 2BaCO_3 + CuCO_3 \cdot Cu(OH)_2 \qquad (6)$$

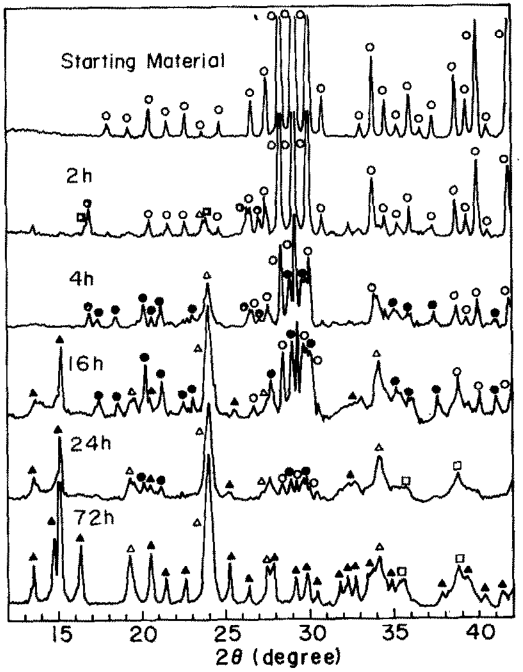
According to this reaction, the sample should have a weight gain of 32.2%, which was in good agreement with the measured value 31.7% (Fig. 2b) for a sample exposed for 24 h and 75 h. On the other hand, the XRD results showed that after measurement of DTGA, during which part of the CuO was reduced to Cu_2O because of the low oxygen pressure in the helium (10^{-3} atm), and DTA heating to 900 °C at 10 °C min^{-1} in the samples exposed for 24 h and 75 h, crystalline $BaCO_3$, CuO and a little $BaCuO_2$ were produced. So, during these two heating stages, the main reaction may be written

$$CuCO_3 \cdot Cu(OH)_2 \rightarrow CuO + CO_2 + H_2O \qquad (7)$$

where the weight loss was mainly caused by the $CuCO_3 \cdot Cu(OH)_2$. Theoretically, according to eqn. (7) if only the decomposition of $CuCO_3 \cdot Cu(OH)_2$ occurs, the heating process should have a weight loss of 10.3%. The practical weight loss, however, was 16.7% after DTGA (Fig. 2c) and 13.49% after DTA. The net weight loss difference was believed to be caused by the partial decomposition of $BaCO_3$ to form $BaCuO_2$ and the partial reduction of CuO to Cu_2O, because a big peak caused by the evolution of CO_2 (from the decomposition of $BaCO_3$) and of O_2 (from the reduction of CuO) is observed on the DTGA curves (Fig. 5) above 750 °C.

Decomposition in flowing O_2 saturated with water vapour

In O_2 saturated with water vapour, the initial decomposition behaviour was observed to be similar to that in humid air and in CO_2 saturated with water vapour. The X-ray diffraction intensity change of each constituent in samples exposed for different times and the corresponding X-ray diffraction patterns are given in Figs. 7 and 8. In a sample exposed for 2 h, the formation of $Ba(OH)_2$ and $Cu(OH)_2$ was first detected; then the "x"-phase was detected in a sample exposed for 4 h (Fig. 8). As mentioned above, the



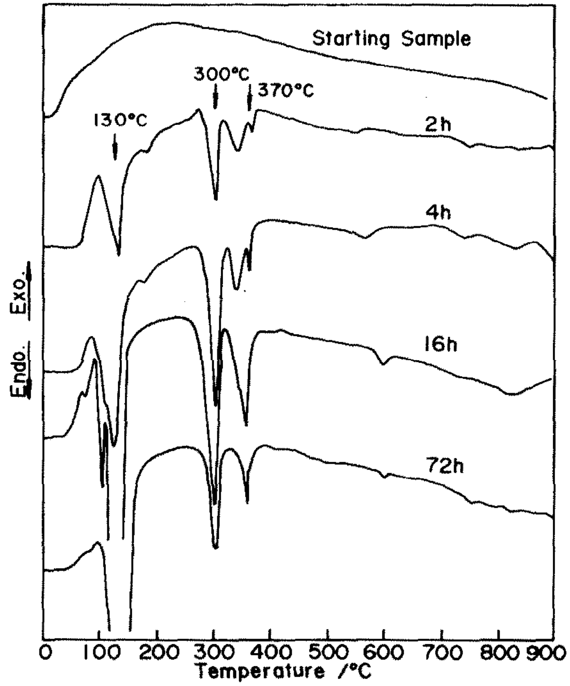


Fig. 8. X-ray diffraction patterns of samples exposed in O_2 (30 ml min^{-1}) saturated with water vapour at room temperature: ○, $BaCuO_2$; △, $BaCO_3$; ⊙, $Ba(OH)_2$; ▣, $Cu(OH)_2$; ●, "x"-phase; ▲, $Ba(OH)_2 \cdot 8H_2O$; □, CuO.

Fig. 9. The DTA curves of samples exposed in O_2 (30 ml min^{-1}) saturated with water vapour at room temperature.

"x"-phase existed only as an intermediate compound and decomposed easily. But in this situation, because of the absence of CO_2, "x"-phase reacted with water vapour to form $Ba(OH)_2 \cdot 8H_2O$ and CuO (poorly crystalline) (Figs. 7–9). This reaction can be written

$$\text{"x"-phase} + H_2O \rightarrow 2Ba(OH)_2 \cdot 8H_2O + CuO \tag{8}$$

From Fig. 8, it can be seen that after a 16 h exposure, a strong X-ray diffraction pattern of $Ba(OH)_2 \cdot 8H_2O$ is observed. With increasing exposure time, the X-ray intensity of $Ba(OH)_2 \cdot 8H_2O$ increased and the peak intensity of the "x"-phase simultaneously decreased. In a sample exposed for 72 h, only $Ba(OH)_2 \cdot 8H_2O$ and $BaCO_3$ could be observed. In this situation, the $BaCO_3$ observed in the XRD pattern was believed to be due to the reaction between $Ba(OH)_2 \cdot 8H_2O$ and the CO_2 in the air when the sample was exposed in air for weighting and XRD measurement, because the longer this sample was in contact with air, the stronger the X-ray intensity of $BaCO_3$ became. From the above results, the total decomposition reaction may be as follows

$$BaCuO_2 + 9H_2O \rightarrow Ba(OH)_2 \cdot 8H_2O + CuO \tag{9}$$

which seems to be complete after 72 h of exposure because a longer exposure did not result in any further weight gain (Fig. 2d).

Effect of atmosphere on the decomposition products of $BaCuO_2$

A sample of $BaCuO_2$ was also exposed to dried CO_2 and to O_2 (30 ml min^{-1}) at room temperature for 9 h and 12 h, respectively. In both cases, as was found in air of low humidity (35% RH), no change could be detected either from weight measurement or from DTA, DTGA and XRD. This suggests that under the three different exposure conditions mentioned above, it is the water vapour that makes $BaCuO_2$ decompose. According to the results of the XRD, DTA and DTGA, in any humid atmosphere, first $Ba(OH)_2$ and $Cu(OH)_2$ are formed, and then the "x"-phase is produced as an intermediate compound, but the final decomposition products of $BaCuO_2$ greatly depend on the atmosphere. The decomposition products of $BaCuO_2$ in various humid atmospheres are listed in Table 1.

With the three atmospheres used in the present study, $BaCuO_2$ first absorbs water vapour and reacts with H_2O to form $Ba(OH)_2$ and $Cu(OH)_2$, and then the "x"-phase is formed; both of these processes seems to be independent of the atmosphere. The "x"-phase, which was also observed during the decomposition of the superconducting oxide $YBa_2Cu_3O_{7-x}$ [8] and is said to be $Ba_2Cu(OH)_6$ [6], was quite unstable and decomposed easily. Its decomposition product was strongly dependent on the presence or absence of CO_2 and/or H_2O. In higher relative humidity, if no CO_2 is present, as in O_2 saturated with water vapour, the "x"-phase will react with

TABLE 1

Decomposition products of $BaCuO_2$ in various humid atmospheres

Atmosphere	1st step	2nd step	3rd step	Final products
Air, 70% RH	$Ba(OH)_2$ $Cu(OH)_2$	"x"-phase		$BaCO_3$ CuO (am)
CO_2 + H_2O (g)	$Ba(OH)_2$ $Cu(OH)_2$	"x"-phase	$BaCO_3$ $CuO \cdot H_2O$	$BaCO_3$ $CuCO_3 \cdot Cu(OH)_2$
O_2 + H_2O (g)	$Ba(OH)_2$ $Cu(OH)_2$	"x"-phase		$Ba(OH)_2 \cdot 8H_2O$ CuO

water to decompose to $Ba(OH)_2 \cdot 8H_2O$ and CuO. But in the presence of CO_2, with low P_{CO_2} and low relative humidity, as in humid air, it reacts with CO_2 to decompose to $BaCO_3$ and CuO (amorphous); if both the pressure of

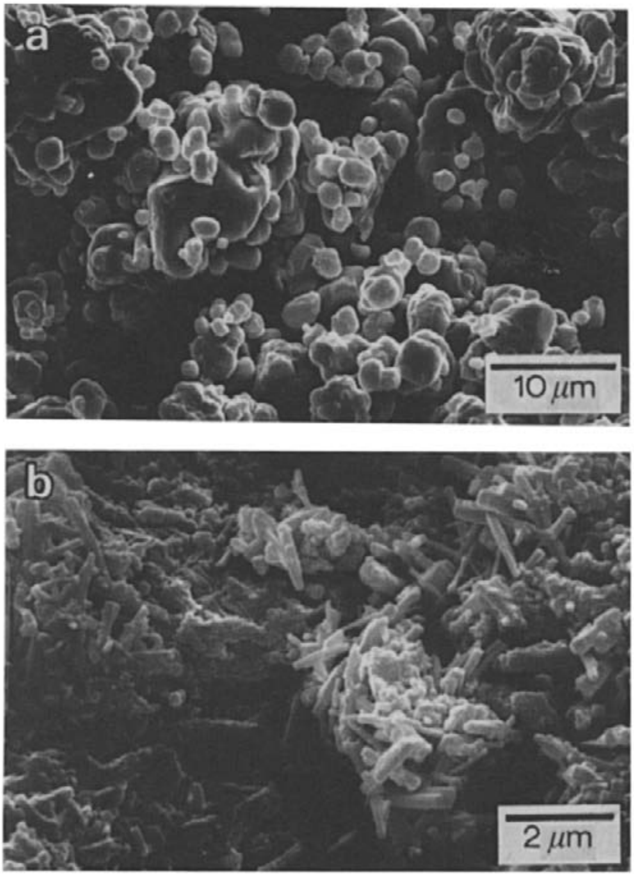


Fig. 10. Scanning electron micrographs of $BaCuO_2$: (a) starting sample, and (b) after exposure for 72 h in O_2 saturated with water vapour.

CO_2 and the relative humidity are higher, as with CO_2 saturated with water vapour, it decomposes to $BaCO_3$ and $CuO \cdot H_2O$ (amorphous), and then $CuO \cdot H_2O$ reacts with CO_2 to produce $CuCO_3 \cdot Cu(OH)_2$. The resultant $CuCO_3 \cdot Cu(OH)_2$ is crystalline and stable under atmospheric conditions. But the $Ba(OH)_2 \cdot 8H_2O$ produced in O_2 with water vapour was unstable in air and rapidly reacted with CO_2 from the air to give $BaCO_3$. The freshly produced $BaCO_3$ was in the form of micrometer-sized needle-like crystals. Figure 10 shows the scanning electron microscope image taken (a) before and (b) after exposure in O_2 saturated with water vapour for 72 h, at which point the growing microcrystals of $BaCO_3$ can just be observed in some places. The XRD results of samples after DTA and DTGA indicated that only during the DTA heating (900 °C, 10 °C min^{-1}) could the decomposition products $Ba(OH)_2 \cdot 8H_2O$, and CuO easily react with each other to become $BaCuO_2$ again.

CONCLUSIONS

$BaCuO_2$ is very sensitive to water, and it decomposes in humid environments. Its decomposition behaviour is quite similar to that of the superconducting oxide $YBa_2Cu_3O_{7-x}$. The higher the humidity the faster the decomposition at room temperature. The decomposition behaviour can be manifested in three stages in humid air and in O_2 saturated with water vapour, and in four stages in CO_2 saturated with water vapour.

These stages are: (1) the formation of $Ba(OH)_2$ and $Cu(OH)_2$; (2) the formation of "x"-phase; (3) the decomposition of "x"-phase and formation of $Ba(OH)_2 \cdot 8H_2O$ and CuO (with higher relative humidity and in the absence of CO_2), and the formation of $BaCO_3$ and $Cu(OH)_2$ (with higher relative humidity and lower P_{CO_2}); and (4) the formation of $CuCO_3 \cdot Cu(OH)_2$ (with higher relative humidity and higher P_{CO_2}). The "x"-phase must be a mixed hydroxide of barium and copper.

In dried pure CO_2 and O_2, or in fairly dry air (relative humidity lower than 40%), $BaCuO_2$ may be relatively stable.

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