

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 $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and CuO , and in CO_2 saturated with water vapour to BaCO_3 and $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. The final decomposition products of BaCuO_2 were dependent on the atmosphere. But, in any humid environment, independent of the atmosphere, first $\text{Ba}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T_c = 90$ K), $\text{BiSrCaCu}_2\text{O}_y$ [4] and $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ [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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ containing only barium is moderately sensitive to humid atmospheres [6–9] whereas the single phase of the 100-K superconducting $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ 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 $\text{Tl}_2\text{O}_3 + \text{BaCuO}_2 + \text{Ca}_2\text{CuO}_3$ to form the Tl–Ba–Ca–Cu–O superconductive compound. This suggests that it is important to clarify the

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 hygroscopic 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, $I432$, with $a = 18.26 \text{ \AA}$. It takes in oxygen to a value of $\text{BaCuO}_{2.1}$ between 350 and 600°C , and under higher oxygen pressure, $\text{BaCuO}_{2.5}$ and $\text{BaCuO}'_{2.63}$ 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) O₂ (30 ml min⁻¹) saturated with water vapour, and (4) CO₂ (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 CO₂.

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 O₂ saturated with water vapour for 72 h were observed with a scanning electron microscope.

RESULTS AND DISCUSSIONS

Stability in air

It was found that BaCuO₂ 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 BaCuO₂ 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 YBa₂Cu₃O₇ [8]. After formation of "x"-phase, peaks of poorly crystalline BaCO₃ 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 BaCO₃ phase. When exposed more than 8 days, only BaCO₃ 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 BaCO₃, was observed. This demonstrated that after a

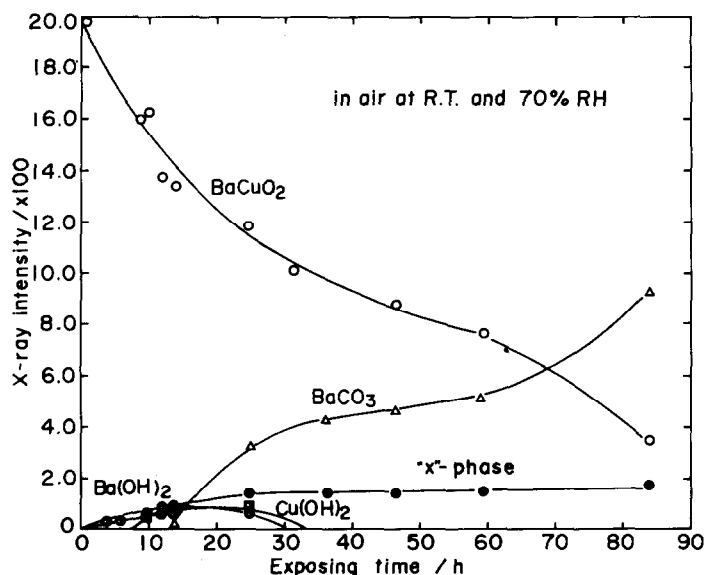
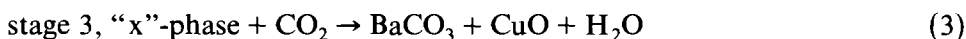
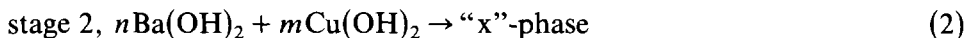
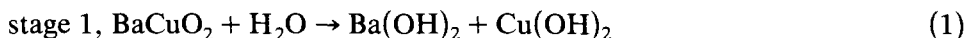


Fig. 1. Relation between the X-ray diffraction intensity of each constituent in samples exposed in air of 70% relative humidity at room temperature and the exposure time.

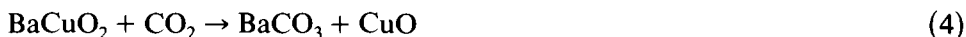
long period of exposure in humid air, BaCuO_2 is nearly completely decomposed to BaCO_3 and CuO . The decomposition product CuO was believed to exist in an amorphous form, because its X-ray pattern was not observed.

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



and the overall decomposition may be written as



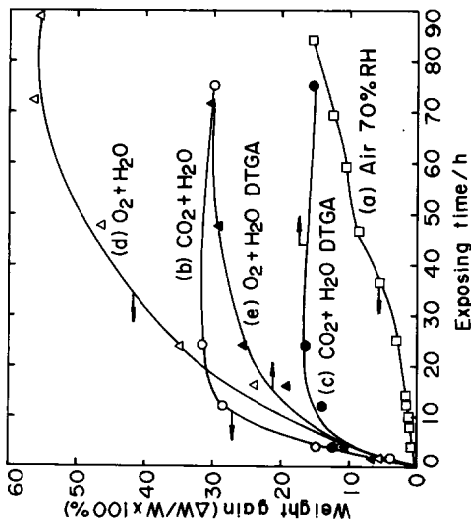


Fig. 2. The weight change of samples exposed in (1) air of 70% relative humidity; (2) CO_2 (30 ml min^{-1}) saturated with water vapour; and (3) O_2 (30 ml min^{-1}) saturated with water vapour at room temperature and after differential thermal gas analysis (DTGA) measurement in He (20 ml min^{-1}) to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

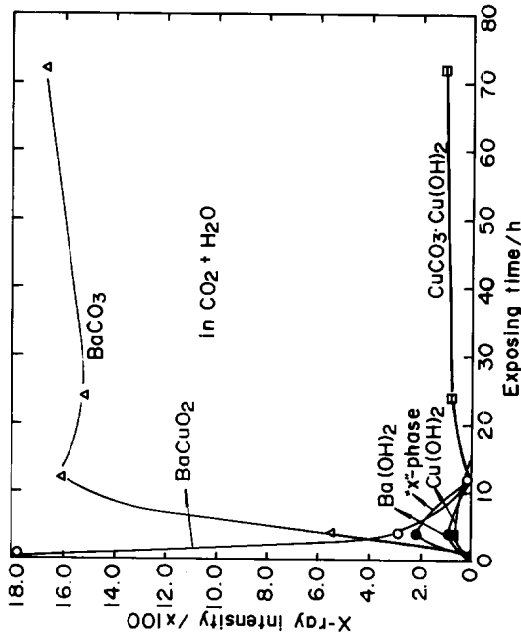


Fig. 3. Relation between the X-ray diffraction intensity of each constituent in samples exposed in CO_2 (30 ml min^{-1}) saturated with water vapour and the exposure time.

Decomposition in CO₂ saturated with water vapour

Samples were exposed in CO₂ 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 BaCuO₂ 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 BaCuO₂ had decomposed to form BaCO₃, “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 endothermic peaks were observed respectively. The endothermic 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 BaCO₃ 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 BaCO₃ increases. Following exposure for 12 h, only the pattern of BaCO₃ 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 BaCuO₂. Up to this 12 h exposure time, the decomposition behaviour of BaCuO₂ in CO₂ 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 · nH₂O), because crystalline Cu(OH)₂ loses water at about 185 °C.

An interesting difference between the decomposition in humid air and in CO₂ saturated with water vapour was the formation of CuCO₃ · Cu(OH)₂ (Fig. 4) by exposing the sample longer than 12 h. CuCO₃ · Cu(OH)₂ decom-

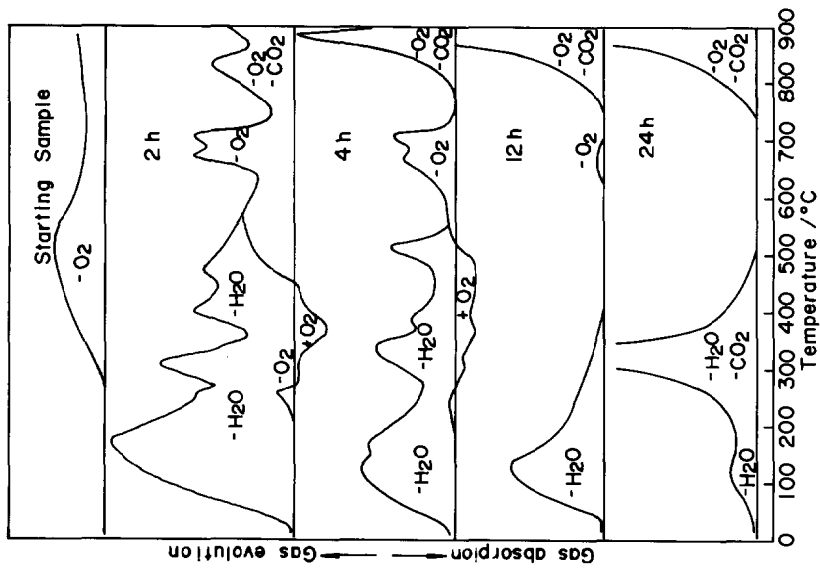


Fig. 4. X-ray diffraction patterns of samples exposed in CO_2 (30 ml min^{-1}) saturated with water vapour at room temperature: \circ , BaCuO_2 ; Δ , BaCO_3 ; \bullet , "x"-phase; \bullet , Ba(OH)_2 ; \square , Cu(OH)_2 ; \square , $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$.

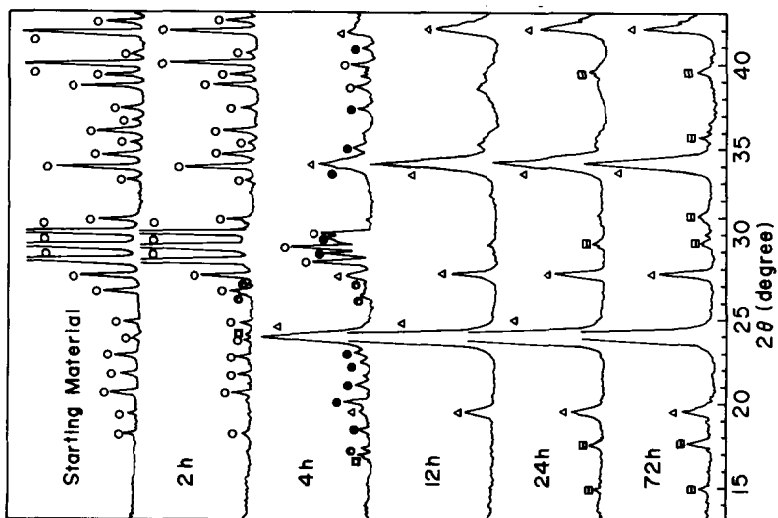


Fig. 5. DTGA curves of samples exposed in CO_2 (30 ml min^{-1}) saturated with water vapour (heating rate, $10^\circ \text{ C min}^{-1}$).

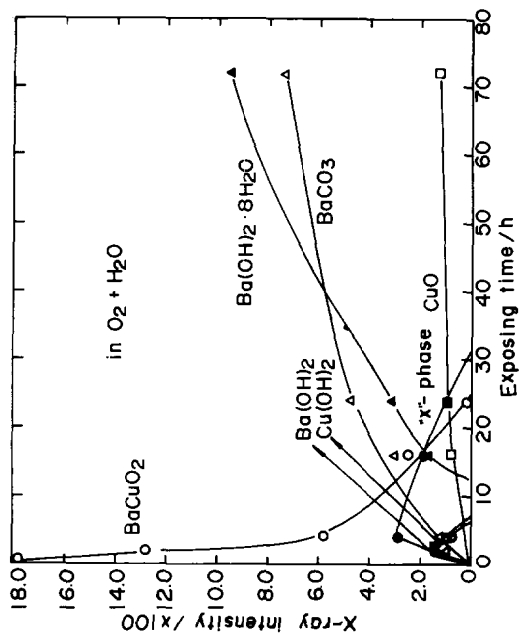
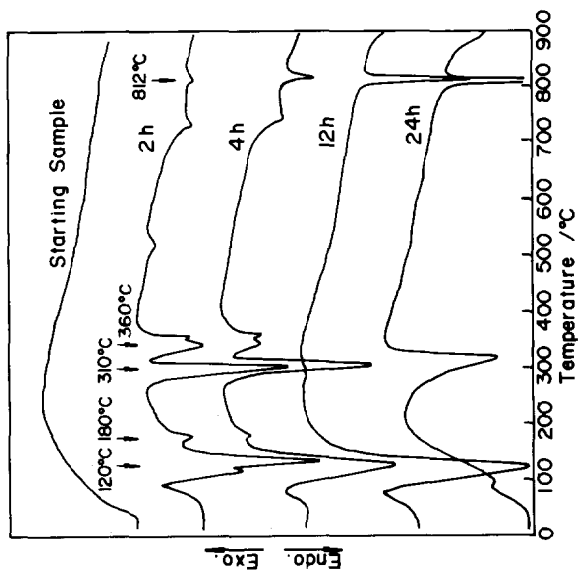
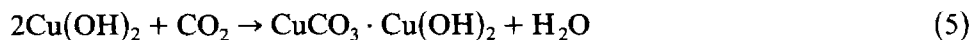


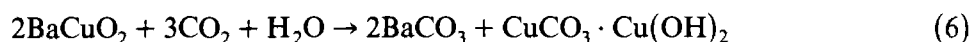
Fig. 6. The DTA curves of samples exposed in CO_2 (30 ml min⁻¹) saturated with water vapour. The DTA measurement was carried out in static air. The heating rate was 10 °C min⁻¹.

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.

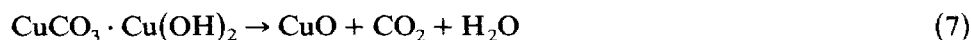
poses to CuO with loss of H₂O and CO₂ at about 360 °C, which can be seen from the results of the DTGA (Fig. 5) and DTA (Fig. 6) of samples exposed for 24 h and 75 h. The formation of CuCO₃ · Cu(OH)₂ can be written



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 BaCuO₂ were BaCO₃ and CuCO₃ · Cu(OH)₂, and this decomposition process was complete after 24 h exposure. So, the total decomposition reaction can be written



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 Cu₂O 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 BaCO₃, CuO and a little BaCuO₂ were produced. So, during these two heating stages, the main reaction may be written



where the weight loss was mainly caused by the CuCO₃ · Cu(OH)₂. Theoretically, according to eqn. (7) if only the decomposition of CuCO₃ · 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 BaCO₃ to form BaCuO₂ and the partial reduction of CuO to Cu₂O, because a big peak caused by the evolution of CO₂ (from the decomposition of BaCO₃) and of O₂ (from the reduction of CuO) is observed on the DTGA curves (Fig. 5) above 750 °C.

Decomposition in flowing O₂ saturated with water vapour

In O₂ saturated with water vapour, the initial decomposition behaviour was observed to be similar to that in humid air and in CO₂ 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

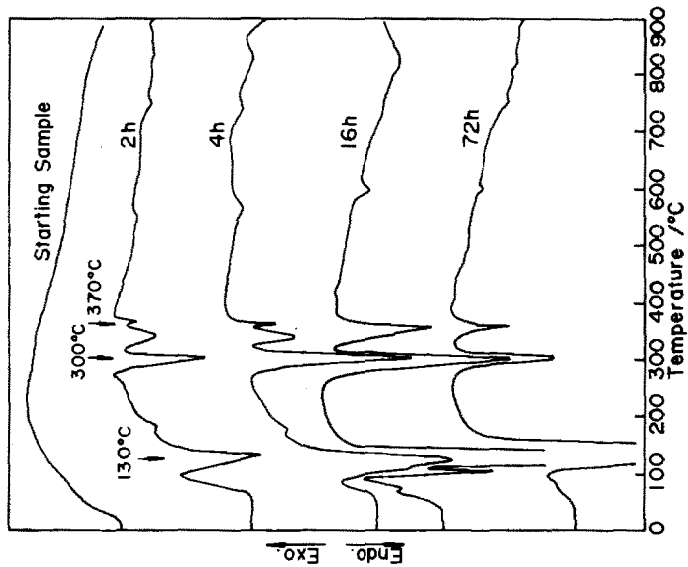


Fig. 8. X-ray diffraction patterns of samples exposed in O_2 (30 ml min^{-1}) saturated with water vapour at room temperature: \circ , $BaCuO_2$; Δ , $BaCO_3$; \bullet , $Ba(OH)_2$; \square , $Cu(OH)_2$; \blacktriangle , "x"-phase; \blacklozenge , $Ba(OH)_2 \cdot 8H_2O$; \square , CuO .

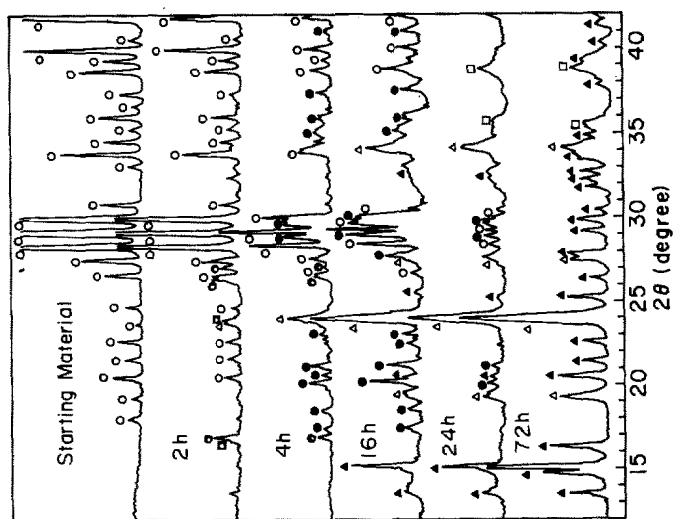
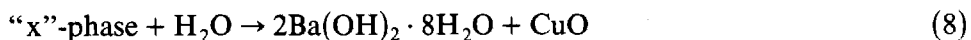
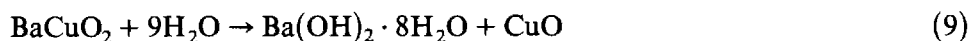


Fig. 9. The DTA curves of samples exposed in O_2 (30 ml min^{-1}) saturated with water vapour at room temperature.

“x”-phase existed only as an intermediate compound and decomposed easily. But in this situation, because of the absence of CO₂, “x”-phase reacted with water vapour to form Ba(OH)₂·8H₂O and CuO (poorly crystalline) (Figs. 7–9). This reaction can be written



From Fig. 8, it can be seen that after a 16 h exposure, a strong X-ray diffraction pattern of Ba(OH)₂·8H₂O is observed. With increasing exposure time, the X-ray intensity of Ba(OH)₂·8H₂O increased and the peak intensity of the “x”-phase simultaneously decreased. In a sample exposed for 72 h, only Ba(OH)₂·8H₂O and BaCO₃ could be observed. In this situation, the BaCO₃ observed in the XRD pattern was believed to be due to the reaction between Ba(OH)₂·8H₂O and the CO₂ 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 BaCO₃ became. From the above results, the total decomposition reaction may be as follows



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 BaCuO₂

A sample of BaCuO₂ was also exposed to dried CO₂ and to O₂ (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 BaCuO₂ 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 BaCuO₂ greatly depend on the atmosphere. The decomposition products of BaCuO₂ in various humid atmospheres are listed in Table 1.

With the three atmospheres used in the present study, BaCuO₂ first absorbs water vapour and reacts with H₂O 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 YBa₂Cu₃O_{7-x} [8] and is said to be Ba₂Cu(OH)₆ [6], was quite unstable and decomposed easily. Its decomposition product was strongly dependent on the presence or absence of CO₂ and/or H₂O. In higher relative humidity, if no CO₂ is present, as in O₂ 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 + $\text{H}_2\text{O (g)}$	Ba(OH)_2 Cu(OH)_2	“x”-phase	BaCO_3 $\text{CuO} \cdot \text{H}_2\text{O}$	BaCO_3 $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
O_2 + $\text{H}_2\text{O (g)}$	Ba(OH)_2 Cu(OH)_2	“x”-phase		$\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ CuO

water to decompose to $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ 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

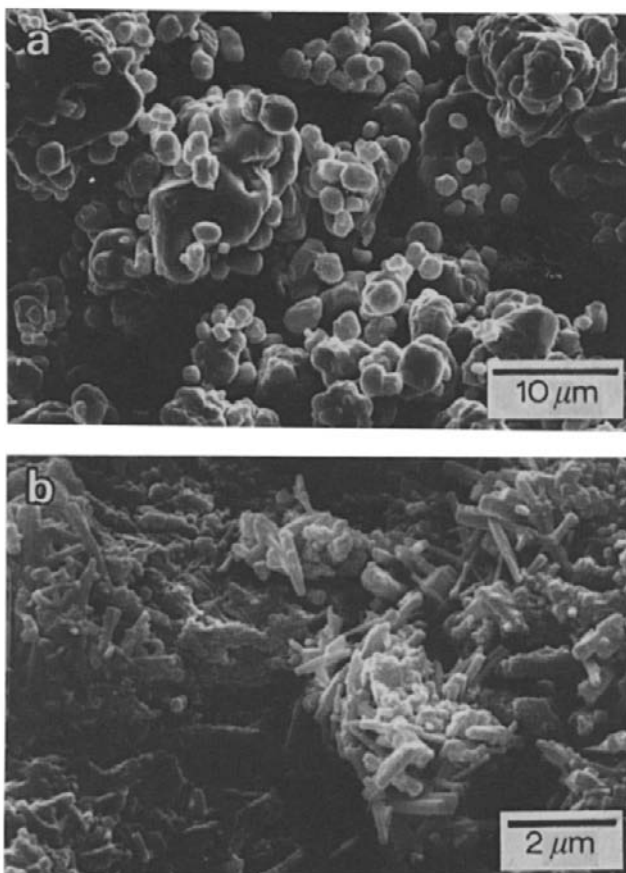


Fig. 10. Scanning electron micrographs of BaCuO_2 : (a) starting sample, and (b) after exposure for 72 h in O_2 saturated with water vapour.

CO₂ and the relative humidity are higher, as with CO₂ saturated with water vapour, it decomposes to BaCO₃ and CuO · H₂O (amorphous), and then CuO · H₂O reacts with CO₂ to produce CuCO₃ · Cu(OH)₂. The resultant CuCO₃ · Cu(OH)₂ is crystalline and stable under atmospheric conditions. But the Ba(OH)₂ · 8H₂O produced in O₂ with water vapour was unstable in air and rapidly reacted with CO₂ from the air to give BaCO₃. The freshly produced BaCO₃ 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 O₂ saturated with water vapour for 72 h, at which point the growing microcrystals of BaCO₃ 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 · 8H₂O, and CuO easily react with each other to become BaCuO₂ again.

CONCLUSIONS

BaCuO₂ is very sensitive to water, and it decomposes in humid environments. Its decomposition behaviour is quite similar to that of the superconducting oxide YBa₂Cu₃O_{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 O₂ saturated with water vapour, and in four stages in CO₂ 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 · 8H₂O and CuO (with higher relative humidity and in the absence of CO₂), and the formation of BaCO₃ and Cu(OH)₂ (with higher relative humidity and lower P_{CO₂}); and (4) the formation of CuCO₃ · Cu(OH)₂ (with higher relative humidity and higher P_{CO₂}). The "x"-phase must be a mixed hydroxide of barium and copper.

In dried pure CO₂ and O₂, or in fairly dry air (relative humidity lower than 40%), BaCuO₂ may be relatively stable.

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