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# Synthesis and Thermal Properties of Strontium and Calcium Peroxides

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# SYNTHESIS AND THERMAL PROPERTIES OF STRONTIUM AND CALCIUM PEROXIDES

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## SUMMARY

This report describes the synthesis and discusses some thermal properties of strontium and calcium peroxides ( $\text{SrO}_2$  and  $\text{CaO}_2$ ). Our interest in these peroxides is founded on their use in the preparation of the new high-temperature superconductors. In other reports we have demonstrated several advantages in substituting  $\text{BaO}_2$  for  $\text{BaCO}_3$  in the preparation of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  bulk superconductor. The required, high-purity  $\text{BaO}_2$  is easily made by heating  $\text{BaO}$  in dry  $\text{O}_2$ , and it is commercially available. However,  $\text{SrO}_2$  and  $\text{CaO}_2$ , which would be used in the newer superconductors, are best synthesized by first precipitating the peroxide octahydrate from a cold, aqueous ammoniacal Sr or Ca salt solution with dilute  $\text{H}_2\text{O}_2$ . Anhydrous  $\text{SrO}_2$  is conveniently prepared by heating the octahydrate at  $115^\circ\text{C}$  for 24 hr, and the less stable anhydrous  $\text{CaO}_2$  is best synthesized by drying the octahydrate at room temperature in a dry box containing an effective desiccant such as  $\text{P}_2\text{O}_5$ . The yields of anhydrous  $\text{SrO}_2$  and  $\text{CaO}_2$  by this method were about 66 percent based on the amount of Sr or Ca salt used. The yield of both peroxides may be increased to about 95 percent by adding a strong base, such as  $\text{NaOH}$ , which neutralizes the ammonium salt by-product.  $\text{SrO}_2$  is considerably more thermally stable and less susceptible to hydrolysis and  $\text{CO}_2$  pickup than  $\text{CaO}_2$ . In addition, we give a new x-ray diffraction pattern for  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  from which we calculated the lattice parameters  $a = 6.212830$  and  $c = 11.0090$  on the basis of the tetragonal crystal system.

## INTRODUCTION

In preparing the high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , we found that substituting barium peroxide,  $\text{BaO}_2$ , for the commonly used barium carbonate,  $\text{BaCO}_3$ , produced a better bulk superconductor in terms of greater sample homogeneity and density and improved reproducibility (ref. 1). Our success in using  $\text{BaO}_2$  as the barium source in the  $\text{YBa}_2\text{Cu}_2\text{O}_{7-x}$  formulation prompted us to investigate the synthesis and properties of strontium and calcium peroxides,  $\text{SrO}_2$  and  $\text{CaO}_2$ , for the preparation of the newer high-temperature superconductors involving these alkaline earth oxides.

The advantages of using alkaline earth metal peroxides ( $\text{BaO}_2$ ,  $\text{SrO}_2$ , and  $\text{CaO}_2$ ) in place of the corresponding carbonates are briefly outlined as follows:

(1) Less rigorous reaction conditions are required in preparing superconductors because the carbonates are considerably more stable than the corresponding peroxides.

(2) There is no carbon in the starting materials; thus, it should be possible to produce a carbonate-free superconductor. Deposits of nonconducting carbonate in the grain boundaries of bulk superconductors are believed to decrease the critical current.

(3) Peroxides provide an oxidizing media that favors the formation of higher oxidation states of metals, especially copper. In the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductor, the oxygen stoichiometry must be greater than that required for the normal valency if superconductivity is to take place (ref. 2).

(4) Decomposition of peroxides liberates oxygen instead of the carbon dioxide liberated during the decomposition of carbonates. With peroxides, processing becomes simpler: a muffle furnace can be used to fire compositions containing peroxides because it is not necessary to use flowing oxygen during firing to remove liberated  $\text{CO}_2$ . Liberated  $\text{CO}_2$  must not remain in the sample environment because it will be taken up by the material during cooling, resulting in carbonate formation. As stated before, carbonate deposits have a detrimental effect on superconducting properties.

(5) One desirable attribute of  $\text{BaO}_2$  is that it melts before it decomposes. This affords a liquid-solid phase reaction that is more efficient than the totally solid-solid phase reaction obtained with  $\text{BaCO}_3$ . The more efficient liquid-solid phase reaction with  $\text{BaO}_2$  may explain the greater homogeneity that we observed in the bulk  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductor when  $\text{BaO}_2$  was used instead of  $\text{BaCO}_3$  (ref. 1).

(6) The anhydrous peroxides  $\text{CaO}_2$ ,  $\text{SrO}_2$ , and  $\text{BaO}_2$  are less reactive and have better storage capabilities than their respective normal oxides  $\text{CaO}$ ,  $\text{SrO}$ , and  $\text{BaO}$ . The alkaline earth oxides are strong bases and, as such, tend to pick up acid gases in the atmosphere, such as  $\text{CO}_2$ , to form salts (e.g., carbonates). In addition, the oxides react vigorously with water to form hydroxides. On the other hand, the anhydrous peroxides, being less basic than the oxides, are practically inert toward  $\text{CO}_2$  pickup under ambient conditions. They also do not appreciably react with water at room temperature to produce hydroxides.

Alkaline earth peroxides undergo three general reactions as shown. With calcium peroxide used to illustrate these reactions, they are as follows:

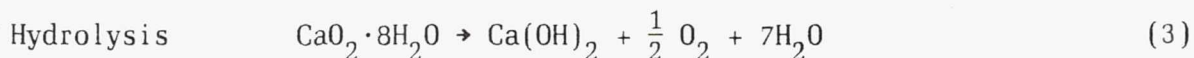
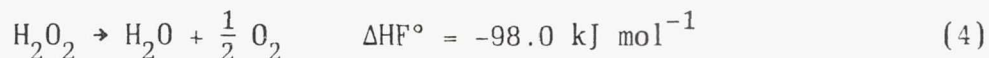


Table I gives the calculated standard enthalpy of reaction  $\Delta\text{HF}^\circ$  from the National Bureau of Standards Tables (ref. 3). Unfortunately, the free energy of formation  $\Delta\text{GF}^\circ$  data for the alkaline earth peroxides and their octahydrates are not available; thus  $\Delta\text{HF}^\circ$  values are used instead to explain reaction trends. For all three of the peroxides and their octahydrates, the decomposition, dehydration, and hydrolysis reactions are endothermic - unlike some peroxides, which can decompose exothermically to form the oxide, for example, hydrogen peroxide

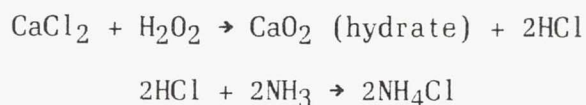




The thermodynamic data for the anhydrous peroxides indicate that they are more stable than the corresponding oxides. Thus these peroxides may be stored safely without danger of violent decomposition.

There are two general methods for synthesizing peroxides (ref. 4). The first involves heating the oxide in a stream of pure, CO<sub>2</sub>-free dry oxygen. This method is favored for making peroxides that are considerably more stable than the corresponding oxide - for example, for the preparation of BaO<sub>2</sub>. In fact, BaO<sub>2</sub> is commercially made by heating BaO at 500 °C in flowing, pure oxygen. The synthesis of the less stable SrO<sub>2</sub> requires more drastic conditions, namely heating the oxide at a temperature of 350 °C in a bomb containing high-pressure oxygen (250 atm). Finally, CaO<sub>2</sub>, the least stable of the three, cannot be conveniently synthesized by direct combination of oxide with oxygen.

The second technique, which is more suitable for the preparation of less stable peroxides involves precipitating the insoluble peroxide from aqueous solution by adding H<sub>2</sub>O<sub>2</sub> to a basic solution of the metal salt. Again using CaO<sub>2</sub> as the example,



Addition of aqueous ammonia to neutralize the HCl, forces the reaction to favor the precipitation of the peroxide hydrate.

This report presents various aspects of the preparation of both the hydrated and anhydrous calcium and strontium peroxides using the second synthesis technique. Since the chemistry of CaO<sub>2</sub> is more complicated because it is less stable than SrO<sub>2</sub>, it was studied in greater detail.

The thermal decomposition properties of SrO<sub>2</sub> and CaO<sub>2</sub> were also investigated. A new x-ray diffraction powder pattern was determined for CaO<sub>2</sub>·8H<sub>2</sub>O, and lattice parameters were calculated from it. Because BaO<sub>2</sub> is commercially available as a pure anhydrous powder, no effort was made to investigate the synthesis and chemical properties of this compound.

#### EXPERIMENTAL PROCEDURE

The synthesis of strontium and calcium peroxides was accomplished by a modification of the method outlined in Brauer's Handbook of Preparative Chemistry (ref. 4). Calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O) or strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub> (0.4 mol)) was dissolved in 1.5 liters of deionized water. An excess of aqueous ammonia (ammonium hydroxide, NH<sub>4</sub>OH), 2 mol in 600 ml water, was added to the stirred salt solution. No precipitated Ca or Sr salts (carbonates) were observed. In all of our cases, the solution remained clear. The solution was adjusted to the desired temperature by either heating it in a water bath or cooling it in an ice bath. Because of the ease with which the CaO<sub>2</sub>·8H<sub>2</sub>O loses water even under water, the octahydrate was precipitated in ice

cold solution. To maintain the solution temperature at close to 0 °C, the ammoniacal  $\text{CaCl}_2$  solution was kept in the freezer until some ice formed. To the well-stirred, cold solution, ice cold 3 percent  $\text{H}_2\text{O}_2$  containing a slight excess of  $\text{H}_2\text{O}_2$  (0.45 mol) was added at a rate of about two drops per second. The pearly white, crystalline hydrated peroxide was allowed to settle, and excess solution was removed via decantation. The crystals were filtered using a suction flask, sucked as dry as possible, washed with about 200 ml water containing several milliliters of  $\text{NH}_4\text{OH}$ , and then, again, sucked as dry as possible. After the peroxide was removed from the filter, it was either air dried by allowing it to stand at ambient conditions in the laboratory or dried under specified conditions (see tables II and IV). The  $\text{SrO}_2$  and the other  $\text{CaO}_2$  preparations were synthesized in the same way except at different temperatures. For these preparations, the  $\text{Sr}(\text{NO}_3)_2$  or  $\text{CaCl}_2$  solution was maintained at the indicated temperature while the  $\text{H}_2\text{O}_2$  solution was added at room temperature.

We took special care to prevent the  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  from dehydrating so that we could generate a new x-ray powder diffraction pattern of this compound. It was important that  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  remain as the pure octahydrate throughout the manipulation to ensure that the pattern was a true representation of the octahydrate. After filtration, the  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  crystals were kept moist. The moist peroxide was stored in a tightly capped plastic bottle that was kept cold in a freezer. The diffraction pattern of the wet crystals was recorded immediately after the octahydrate was removed from the freezer.

In other experiments involving  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ , the moist crystals were removed from the filter and treated as indicated in the Results section. In most cases, further treatment involved heating the crystals at various temperatures in a drying oven or drying them in a flowing-nitrogen dry box containing  $\text{P}_2\text{O}_5$  drying agent in a dish.

The peroxide yield was considerably less than stoichiometric based on the limiting reagent  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , thus indicating some reverse reaction with the  $\text{NH}_4\text{Cl}$  by-product. We found that adding a strong base (NaOH solution) to increase pH, increased the yield to near stoichiometric. This was accomplished by the dropwise addition of 500 ml of a solution containing 0.75 mol of NaOH to the well-stirred precipitated peroxide suspension just following the addition of  $\text{H}_2\text{O}_2$ . Slightly less than the stoichiometric amount of NaOH was added so as to prevent the precipitation of calcium compounds other than  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ , namely  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ . If sodium contamination presents a problem, an organic strong base such as tetramethylammonium hydroxide ( $(\text{CH}_3)_4\text{NOH}$ ) may be substituted for NaOH.

The anhydrous  $\text{CaO}_2$  was also directly precipitated from aqueous solution. The previously described method was employed except that it was done at higher solution temperature (e.g., 70 °C).

$\text{SrO}_2 \cdot 8\text{H}_2\text{O}$  was synthesized in a fashion similar to that for  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ . However, because of its lesser tendency to dehydrate, it was unnecessary to keep the  $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$  moist and cold. The diffraction pattern was taken on the dried and heat treated samples and compared with the known patterns for the octahydrate and anhydrous  $\text{SrO}_2$ .



We determined the purity and degree of hydration of both peroxides by firing them for 12 hr at 1000 °C in air, thereby converting the strontium and calcium compounds to their normal oxides, SrO and CaO. X-ray diffraction was used to identify various components resulting from different runs. These components include peroxides, hydroxides, carbonates, and oxides. Particle morphology was investigated with scanning electron microscope (SEM) and optical photomicrographs. Thermogravimetric analysis (TGA) runs in helium (30 cm<sup>3</sup>/min) at a heating rate of 10 °C/min established the decomposition temperatures of anhydrous SrO<sub>2</sub> and CaO<sub>2</sub>.

## RESULTS

### Synthesis of SrO<sub>2</sub>

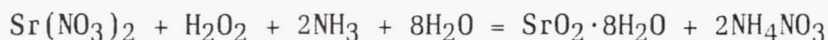
Addition of H<sub>2</sub>O<sub>2</sub> to ammoniacal Sr(NO<sub>3</sub>)<sub>2</sub> solution (as described in the experimental section) produced pearly white, crystalline SrO<sub>2</sub>·8H<sub>2</sub>O. The crystals settled rapidly and were readily isolated by filtration. The theoretical yield was about 66 percent based on the amount of Sr(NO<sub>3</sub>)<sub>2</sub> starting material. Table II gives the effects of various treatments on the degree of hydration of SrO<sub>2</sub>·XH<sub>2</sub>O. The value of X in the table corresponds to the degree of hydration, X = moles H<sub>2</sub>O/moles SrO<sub>2</sub>. This value is calculated from the weight loss when SrO<sub>2</sub>·XH<sub>2</sub>O is fired to SrO. Values of X less than 8 probably represent a mixture of SrO<sub>2</sub>·8H<sub>2</sub>O and anhydrous SrO<sub>2</sub> rather than the presence of a definite hydrated peroxide with less than eight waters of hydration.

Freshly precipitated SrO<sub>2</sub>·8H<sub>2</sub>O loses water of hydration gradually when it sits in a crystallizing dish at ambient laboratory conditions (about 21 °C). After 2 days the value of X drops from 8.00 to the range 7.05 to 7.70. The x-ray diffraction pattern, however, showed only the presence of the octahydrate. When freshly precipitated SrO<sub>2</sub>·8H<sub>2</sub>O is placed in a dry box at ambient temperature with flowing dry nitrogen and with P<sub>2</sub>O<sub>5</sub> drying agent, water of crystallization is gradually lost. After 5 days the degree of hydration decreases to 0.29, and, according to x-ray diffraction, anhydrous SrO<sub>2</sub> becomes the major component. On drying in air at 100 °C for 24 hr, only a small amount of water (X = 0.14) remains, and at 115 °C for 24 hr, pure anhydrous SrO<sub>2</sub> is produced. Up to this point, no decomposition products (Sr(OH)<sub>2</sub> or SrO) were observed. And, at this point, x-ray diffraction showed anhydrous SrO<sub>2</sub> as the sole component of the material. Chemical analysis gave 86.94 percent SrO (86.62 percent is the theoretical value), and the results of atomic adsorption analysis were also in good agreement: 73 percent Sr (whereas the theoretical value is 73.25 percent Sr). For superconductor formulations where a pure SrO<sub>2</sub> of known composition is required, we recommend drying the freshly precipitated hydrated SrO<sub>2</sub> in air at 115 °C for 24 hr. Raising the drying temperature to 125 °C resulted in a calculated negative value of X = -0.15. This denotes that in addition to complete dehydration, possibly a small amount of the normal oxide SrO was present probably because of a slight decomposition of the peroxide. TGA analysis indicated that anhydrous SrO<sub>2</sub> begins rapid decomposition at about 400 °C.

The theoretical yield of SrO<sub>2</sub> was increased from 66 percent to about 95 percent by neutralizing most (about 94 percent) of the NH<sub>4</sub>NO<sub>3</sub> reaction byproduct with the strong base, NaOH, thereby increasing the pH of the solution:



We expect an increase in pH to drive the overall  $\text{SrO}_2$ -producing reaction to the right, thereby favoring the  $\text{SrO}_2$  yield:



Neutralization with NaOH was not investigated further.

### Synthesis of $\text{CaO}_2$

The relative instability of  $\text{CaO}_2$ , especially when compared with  $\text{SrO}_2$ , warranted a more extensive investigation into the chemistry of  $\text{CaO}_2$ . It is the least stable of the alkaline earth peroxides, especially with regard to hydrolysis, decomposition, and loss of water of hydration.

Table III lists the degree of hydration (value of X in the formula  $\text{CaO}_2 \cdot X\text{H}_2\text{O}$ ) when the peroxide is precipitated at various solution temperatures. It is evident that the average degree of hydration of the precipitated  $\text{CaO}_2$  depends on the solution temperature. When the precipitation is carried out at 0 °C, pearllike crystals of the octahydrate form. Like the  $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$  precipitate, the insoluble, hydrated  $\text{CaO}_2$  crystals settle rapidly and are easily filtered. At this time, we attribute the unknown x-ray diffraction pattern to  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ . In a later part of this report, this supposition is further substantiated. As the precipitation temperature is increased, especially above 50 °C, the beige-colored anhydrous peroxide precipitates. The insoluble anhydrous peroxide is less crystalline and is more difficult to filter. For precipitation above 50 °C, the x-ray diffraction pattern shows only the presence of the anhydrous peroxide. On the basis of the value of X, practically pure anhydrous  $\text{CaO}_2$  is precipitated directly at the maximum temperature of our experiments, 70 °C. An important aspect to be considered in the synthesis of  $\text{CaO}_2$  is that the peroxide yield decreases with increasing precipitation temperature; this yield is calculated from the amount of  $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$  used as the limiting reagent. The yield ranges from 67.3 percent at 0 °C to 51.0 percent at 70 °C. As was the case with the deposition of  $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$  described earlier, increasing the pH of the solution by neutralizing 90 percent of the  $\text{NH}_4\text{Cl}$  by-product with aqueous NaOH increased the calcium peroxide yield in cold solution to about 95 percent of theoretical based on the amount of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  starting material. Again, the results of neutralization experiments were not studied further.

Figure 1 presents micrographs of the octahydrate and anhydrous calcium peroxide. Parts (a) and (b) show the octahedral crystal plates of freshly precipitated  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  from cold solution (0 °C). Figure 1(a) shows transparent octahedral crystals; figure 1(b) shows the same material at higher magnification. More detail can be seen of the morphology of the eight-sided plates of  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ . Parts (c) and (d) show the  $\text{CaO}_2$  that was precipitated from hot solution (70 °C). It was surprising that the  $\text{CaO}_2$  precipitated in the form of spheres instead of well-defined crystals. Such a phenomenon suggests that when the  $\text{H}_2\text{O}_2$  solution was added to the hot ammoniacal  $\text{CaCl}_2$  solution, the octahydrate  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  formed first, then melted in its own water of crystallization with the formation of small suspended spherical droplets. As the hydrated water was lost, the liquid droplets solidified into spheres of anhydrous  $\text{CaO}_2$ .



A liquid phase was observed when the octahydrate was heated to 90 °C in the oven prior to thermal dehydration to the anhydrous peroxide. It is apparent that this liquid phase is molten hydrated  $\text{CaO}_2$ .

The final investigation into calcium peroxide chemistry concerned its thermal decomposition. The results (table IV) illustrate the ease with which hydrated  $\text{CaO}_2$  loses water of hydration. It is difficult to obtain the pure octahydrate because attempts to remove excess absorbed water from wet, freshly prepared  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  resulted in some dehydration. The original sample used in the thermal decomposition studies was octahydrate freshly precipitated from cold solution at 0 °C and dried at room temperature overnight. The composition of this material was  $\text{CaO}_2 \cdot 7.4\text{H}_2\text{O}$ . To illustrate the ease with which this material loses water, we left a sample of  $\text{CaO}_2 \cdot 7.4\text{H}_2\text{O}$  standing for 5 days on a lab bench. It lost most of its water of hydration, and the x-ray diffraction pattern showed only the presence of anhydrous  $\text{CaO}_2$ . The same material when placed in a flowing-nitrogen dry box containing  $\text{P}_2\text{O}_5$  drying agent for 48 hr at room temperature lost practically all of its hydrated water (table IV,  $X = 0.11$ ). Thus, it is not surprising that thermal dehydration takes place at elevated temperatures (table IV). Above 100 °C some decomposition (eq. (3)) takes place as indicated by  $\text{Ca}(\text{OH})_2$  showing as a minor component. At the highest drying temperature in the table, 120 °C, decomposition of the hydrated peroxide to  $\text{Ca}(\text{OH})_2$  followed by  $\text{CO}_2$  pickup from the atmosphere becomes important. These reactions are indicated by  $\text{CaCO}_3$  showing as a minor phase in the x-ray diffraction pattern. From these results, it is apparent that  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  should be dehydrated in a dry,  $\text{CO}_2$ -free atmosphere at a relatively low temperature to obtain pure, anhydrous  $\text{CaO}_2$ .

Thermal decomposition data for  $\text{CaO}_2$  and  $\text{SrO}_2$  are summarized in table V. However, these decomposition temperatures are for the pure compounds. When mixed with copper oxide ( $\text{CuO}$ ), the decomposition temperatures are probably considerably lower.

The last aspect of this report concerns the new x-ray diffraction pattern attributed to calcium peroxide octahydrate,  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ . We were unable to verify an exact stoichiometry for the octahydrate because of the ease with which dehydration took place during attempts to remove excess water from the freshly precipitated compound. Because of the isostructural similarity of the unknown  $\text{CaO}_2 \cdot X\text{H}_2\text{O}$  with tetragonal octahydrates of other alkaline earth peroxides,  $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ , we attributed our new x-ray powder pattern (table VI) to  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ . The isostructuralism was confirmed through a lattice parameter program with a diffractometer extrapolation function. Photomicrographs of the  $\text{CaO}_2$  hydrate show that its platelet morphology is similar to that described for  $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$  (JCPDS 25-905). This platelet morphology supports the conclusion of preferred orientation occurring and explains the well-defined, integrated-intensity results for the low index (0.0.1) planes. As expected, the lattice parameters of  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  would be smaller than those for  $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$  because the Ca atom is smaller than the Sr and Ba atoms.

## CONCLUSIONS

The most important practical aspect of our experimental results is the development of a simple synthesis for pure  $\text{CaO}_2$  and  $\text{SrO}_2$ . The peroxides are of



particular interest as replacements for the corresponding alkaline earth carbonates for the synthesis of the new high-temperature superconductors. Their use in BiCaSrCuO and the most recent TlBaCaCuO systems should offer the same advantages as we found when BaO<sub>2</sub> was substituted for BaCO<sub>3</sub> in the preparation of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> superconductor. Furthermore, CaO<sub>2</sub> and SrO<sub>2</sub> may be generally useful when an oxidizing alkaline fusion media is required to synthesize compounds other than superconductors.

In view of our experimental results, we recommend the following procedure for the practical synthesis of pure SrO<sub>2</sub> and CaO<sub>2</sub>. For both peroxides, the first step involves precipitation of the octahydrate by dropwise addition of H<sub>2</sub>O<sub>2</sub> to a cold solution (about 0 °C) of ammoniacal Sr(NO<sub>3</sub>)<sub>2</sub> or CaCl<sub>2</sub>. The best way to prepare anhydrous SrO<sub>2</sub> is to dry the freshly prepared octahydrate for 24 hr at 115 °C, preferably in a CO<sub>2</sub>-free atmosphere. In the case of the less stable CaO<sub>2</sub>, the freshly precipitated octahydrate is best dehydrated at room temperature for at least 24 hr in a CO<sub>2</sub>-free drybox containing an efficient desiccant such as P<sub>2</sub>O<sub>5</sub>. The octahydrates of both peroxides are crystalline precipitates that tend to settle out rapidly, thereby allowing most of the mother liquor to be removed by decantation. The crystalline octahydrates are easy to recover by filtration and have little tendency to peptize during filtration and washing. If peroxide yield is important, it can be increased by neutralizing most of the ammonium salt byproduct with a strong base such as NaOH. If sodium contamination is to be avoided, a strong organic base such as tetramethylammonium hydroxide (CH<sub>3</sub>)<sub>4</sub>NOH may be used instead.

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TABLE I. - CALCULATED STANDARD ENTHALPY OF REACTION ( $\Delta H_f^\circ$ ) FOR DECOMPOSITION, DEHYDRATION, AND HYDROLYSIS OF THE ALKALINE EARTH PEROXIDES

[From National Bureau of Standards Tables (ref. 3).]

| Reaction      | Equation | $\Delta H_f^\circ$ , kJ-mol <sup>-1</sup> |                  |                  |
|---------------|----------|---|------------------|------------------|
|               |          | CaO <sub>2</sub>                          | SrO <sub>2</sub> | BaO <sub>2</sub> |
| Decomposition | (1)      | 17.6                                      | 41.5             | 80.8             |
| Dehydration   | (2)      | 65.6                                      | 103.3            | 85.7             |
| Hydrolysis    | (3)      | 18.0                                      | 63.6             | 61.1             |

TABLE II. - EFFECT OF VARIOUS TREATMENTS ON SrO<sub>2</sub>·XH<sub>2</sub>O

| Treatment  | $\frac{\text{moles H}_2\text{O}}{\text{moles SrO}_2}, X$ | Composition (from x-ray diffraction analysis)                         |
|--|--|---|
| Air dried, room temperature, 2 days  | 7.05 to 7.70   | SrO <sub>2</sub> ·8H <sub>2</sub> O                                   |
| Dried in dry box over P <sub>2</sub> O <sub>5</sub> , room temperature, 5 days | 0.29   | Major: SrO <sub>2</sub><br>Minor: SrO <sub>2</sub> ·8H <sub>2</sub> O |
| Air dried, 100 °C, 24 hr   | 0.14   | SrO <sub>2</sub>  |
| Air dried, 115 °C, 24 hr <sup>a</sup>  | 0  | SrO <sub>2</sub>  |
| Air dried, 125 °C, 24 hr   | -0.15  | SrO <sub>2</sub>  |

<sup>a</sup>X-ray diffraction analysis: SrO<sub>2</sub> is the only phase.

Chemical analysis: 86.94 percent SrO (86.62 percent theoretical).

Atomic adsorption analysis: 73 percent Sr (73.25 percent theoretical).

TABLE III. - SYNTHESIS OF CaO<sub>2</sub>·XH<sub>2</sub>O

| Precipitation temperature, °C | $\frac{\text{moles H}_2\text{O}}{\text{moles CaO}_2}, X$ | Composition (from x-ray diffraction analysis) | Yield, percent <sup>a</sup> |
|-------------------------------|--|---|-----------------------------|
| 0                             | 7.4  | (b)   | 67.32                       |
| 5                             | 6.3  | (b)   | -----                       |
| 10                            | 5.1  | (b)   | 64.23                       |
| 50                            | .42  | CaO <sub>2</sub>                              | -----                       |
| 60                            | .13  | CaO <sub>2</sub>                              | -----                       |
| 65                            | .10  | CaO <sub>2</sub>                              | 54.09                       |
| 70                            | .09  | CaO <sub>2</sub>                              | 51.03                       |

<sup>a</sup>Based on amount of CaCl<sub>2</sub>·2H<sub>2</sub>O (limiting reagent) used.

<sup>b</sup>Attributed to CaO<sub>2</sub>·8H<sub>2</sub>O.



TABLE IV. - EFFECT OF HEAT TREATMENT ON MOLES H<sub>2</sub>O/MOLES CaO<sub>2</sub>  
 [Starting material: 7.4 mol H<sub>2</sub>O/mol CaO<sub>2</sub>. Hydrated CaO<sub>2</sub> tends to dehydrate; reacts with ambient CO<sub>2</sub> to form CaCO<sub>3</sub>.]

| Temperature, °C  | Duration, hr | $\frac{\text{moles H}_2\text{O}}{\text{moles CaO}_2}$ | Composition (from x-ray diffraction analysis)         |
|------------------|--------------|---|---|
| 90               | 24           | 0.15  | CaO <sub>2</sub>                                      |
| 100              | ↓            | .13   | Major: CaO <sub>2</sub><br>Minor: Ca(OH) <sub>2</sub> |
| 107              |              | .098  | Major: CaO <sub>2</sub><br>Minor: Ca(OH) <sub>2</sub> |
| 120              |              | .18   | Major: CaO <sub>2</sub><br>Minor: CaCO <sub>3</sub>   |
| Room temperature | 48           | .11   | CaO <sub>2</sub>                                      |

TABLE V. - DECOMPOSITION TEMPERATURES TO FORM OXIDES (ref. 5)

| $2\text{MO}_2 \rightarrow 2\text{MO} + \text{O}_2$ |                               | $2\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2$ |                               |
|--|-------------------------------|---|-------------------------------|
| Compound   | Decomposition temperature, °C | Compound  | Decomposition temperature, °C |
| BaO <sub>2</sub>                                   | <sup>a</sup> 800              | BaCO <sub>3</sub>                                   | 1450                          |
| SrO <sub>2</sub>                                   | <sup>b</sup> 400              | SrCO <sub>3</sub>                                   | 1340                          |
| CaO <sub>2</sub>                                   | <sup>b</sup> 330              | CaCO <sub>3</sub>                                   | 899                           |

<sup>a</sup>Melting point, 450 °C.

<sup>b</sup>Determined from our own TGA data.

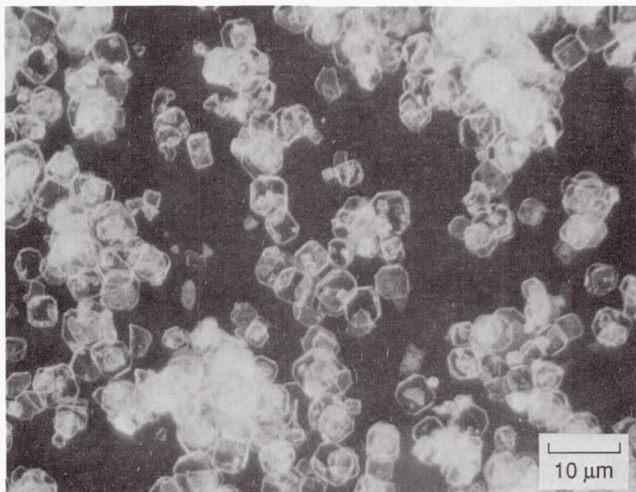
TABLE VI. - X-RAY POWDER DATA FOR



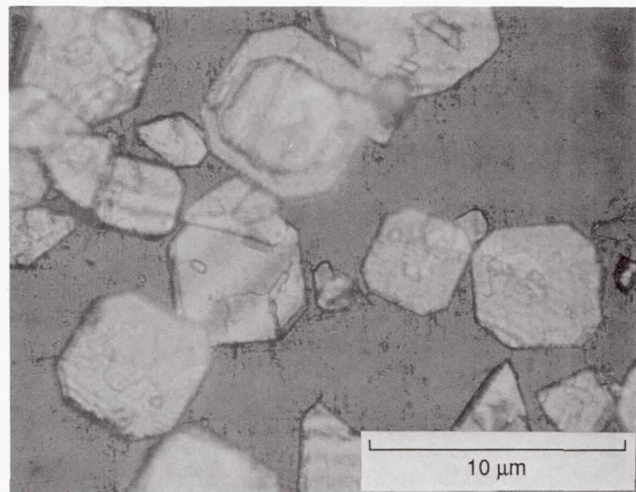
[Crystal system: tetragonal lattice parameters ( $\text{\AA}$ );  $a = 6.212830 \pm 7.628441 \times 10^{-3}$ ;  $c = 11.00990 \pm 1.083599 \times 10^{-2}$ ; all peaks attributed to  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ ; no known impurity peaks for  $\text{CaO}_2$ ,  $\text{CaCO}_3$ , and  $\text{Ca}(\text{OH})_2$  were observed.]

| 2-theta (obs) | d( $\text{\AA}$ ) | hkl | I/I <sub>0</sub> |
|---------------|-------------------|-----|------------------|
| 14.287        | 6.1993            | 100 | 1                |
| 16.182        | 5.4774            | 002 | 100              |
| 20.295        | 4.3758            | 110 | 1                |
| 21.656        | 4.1037            | 102 | 2                |
| 26.003        | 3.4268            | 112 | 13               |
| 28.759        | 3.1043            | 200 | 1                |
| 32.601        | 2.7467            | 004 | 63               |
| 33.188        | 2.6994            | 211 | 11               |
| 35.724        | 2.5134            | 104 | 7                |
| 36.250        | 2.4782            | 212 | 1                |
| 38.695        | 2.3270            | 114 | 23               |
| 40.765        | 2.2135            | 213 | 11               |
| 41.118        | 2.1953            | 220 | 1                |
| 44.017        | 2.0572            | 204 | 11               |
| 44.407        | 2.0400            | 222 | 2                |
| 46.182        | 1.9657            | 310 | 5                |
| 46.496        | 1.9532            | 214 | 10               |
| 47.003        | 1.9333            | 302 | 1                |
| 49.248        | 1.8503            | 312 | 3                |
| 52.029        | 1.7577            | 106 | 18               |
| 53.111        | 1.7244            | 215 | 5                |
| 54.232        | 1.6914            | 116 | 2                |
| 55.532        | 1.6549            | 304 | 1                |
| 58.495        | 1.5779            | 206 | 1                |
| 60.502        | 1.5290            | 216 | 8                |
| 60.715        | 1.5279            | 216 | 4                |
| 62.120        | 1.4942            | 410 | 1                |
| 63.528        | 1.4645            | 324 | <1               |
| 66.032        | 1.4149            | 332 | <1               |
| 67.323        | 1.3909            | 420 | 1                |
| 68.215        | 1.3737            | 306 | 6                |
| 68.602        | 1.3669            | 217 | 6                |
| 68.831        | 1.3663            | 217 | 3                |
| 69.467        | 1.3531            | 404 | 2                |
| 70.083        | 1.3416            | 108 | 10               |
| 70.333        | 1.3407            | 108 | 5                |
| 71.328        | 1.3223            | 118 | <1               |
| 73.186        | 1.2922            | 334 | 1                |
| 75.708        | 1.2563            | 326 | 1                |
| 77.422        | 1.2317            | 218 | 2                |
| 77.750        | 1.2304            | 218 | 1                |

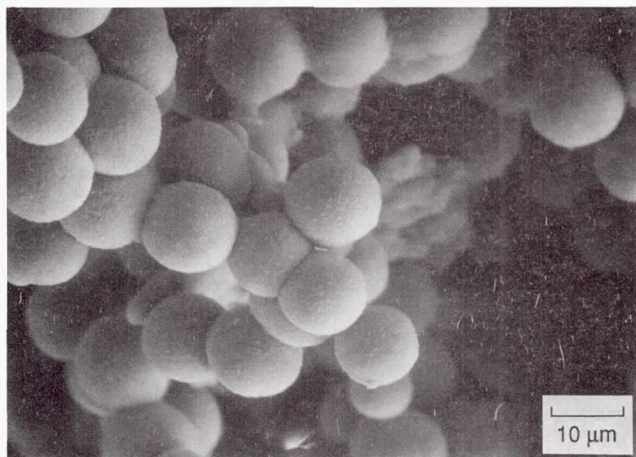




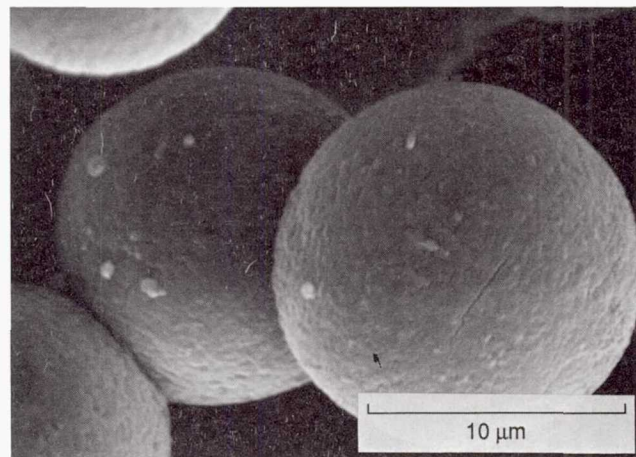
(a)  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  precipitated from 0 °C solution.



(b) Enlarged view of  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  precipitated from 0 °C solution.



(c) Anhydrous  $\text{CaO}_2$  precipitated from 70 °C solution.



(d) Enlarged view of  $\text{CaO}_2$  precipitated from 70 °C solution.

Figure 1.—Optical photomicrographs of precipitated anhydrous and octahydrate calcium peroxide.



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## Report Documentation Page

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| 16. Abstract<br><p>A practical synthesis and a discussion of some chemical properties of pure strontium peroxide and calcium peroxide are presented. The general synthesis of these peroxides involves precipitation of their octahydrates by addition of <math>H_2O_2</math> to aqueous ammoniacal <math>Sr(NO_3)_2</math> or <math>CaCl_2</math>. The octahydrates are converted to the anhydrous peroxides by various dehydration techniques. A new x-ray diffraction powder pattern for <math>CaO_2 \cdot 8H_2O</math> is given from which lattice parameters <math>a = 6.212830</math> and <math>c = 11.0090</math> were calculated on the basis of the tetragonal crystal system.</p> |  |  |                   |
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