

## Effect of Mechanical Treatment on the Structure of Barium Peroxide

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### Abstract

The result of structural investigation of BaO<sub>2</sub> powder samples exposed to intensive mechanical treatment in the disintegrator are presented. X-ray patterns of the powders under study displayed features involving significant broadening and changes in positions of X-ray peaks at the certain stage of treatment. The structural instability which manifested in discontinuous jump of lattice parameters, is observed. Assumptions of the reasons causing a sharp leap of lattice parameters and broadening of X-ray lines have been made. Correlation between structural instability and solubility of BaO<sub>2</sub> has been established.

### INTRODUCTION

The increasing interest to mechanically activated powders is caused by the possibility of using their unusual (higher reactivity, solubility etc.) properties in material science, powder technology and raw material processing [1, 2]. Barium peroxide is used successfully in various technological processes as source of chemically bonded oxygen, yet easily emitting at high temperature. A differential thermal analysis and thermal gravimetry in air atmosphere of mechanically activated BaO<sub>2</sub> have been carried out in [3, 4]. Exothermic peaks and weight loss in the range of 150–350 °C for activated BaO<sub>2</sub> were found. The nonlinear dependencies of exothermic peaks intensities and weight losses as functions of the treatment duration were recognized. This work presents the dependencies of powder unit cell parameters and integral width of X-ray reflections on the degree of mechanical treatment. This results were compared with the thermal data from [3, 4].

### METHODS

The samples were prepared by grinding in disintegrator DEZI-1420 of chemically pure

BaO<sub>2</sub>. The powder particles in disintegrator are underwent several powerful impacts and then leave it. According to [5], the particles pass through the disintegrator in time about 0.01 s. Six activated samples were obtained by repeated mechanical treatment in disintegrator. All samples were numbered so as the number of sample  $N$  and time of treatment  $t$  were connected by the relation  $t = 0.01N$ .

The sedimentometric analysis was carried out using centrifugal sedimentometer SV-3 by continuous registration of powder sedimentation process in centrifugal field. X-ray data are obtained by diffractometer DRON-4.0 with CuK<sub>α</sub> radiation. The least square method was used to calculate unit cell parameters.

### RESULTS AND DISCUSSION

The particle size distribution has been calculated from sedimentometric data and showed that the maximum value of particle sizes of initial powder is equal 20 mm. It was established that the grinding stage was completed after two acts of treatment, as a result of which the particle sizes did not exceed 5 mm.

X-ray data obtained for initial and treated samples showed expected lines for tetragonal

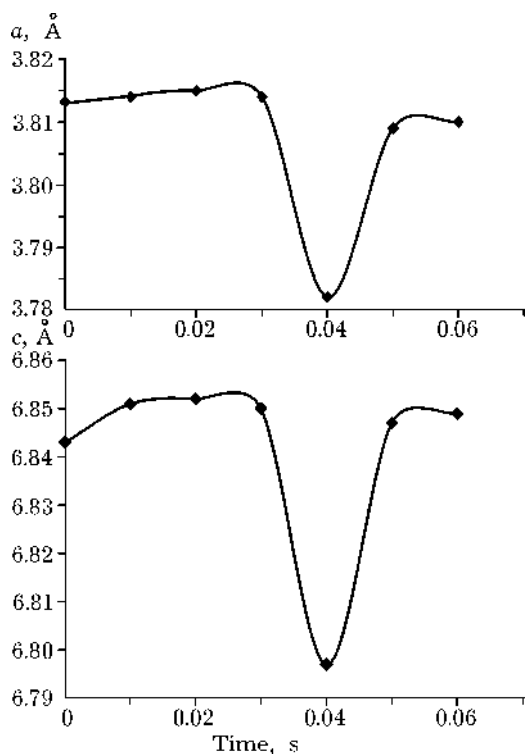


Fig. 1. Dependence of lattice parameters on mechanical treatment duration of  $\text{BaO}_2$  samples.

$\text{BaO}_2$  lattice. The comparison of untreated sample lattice parameters ( $a = 3.806(4) \text{ Å}$ ,  $c = 6.843(6) \text{ Å}$ ) with those from ICDD library ( $a = 3.807 \text{ Å}$ ,  $c = 6.841 \text{ Å}$ ) showed that they were in good agreement. Our  $a$  and  $c$  values as a function of treatment time for the treated samples are presented in Fig. 1. As can be seen, there are no essential changes in lattice parameter for No. 1–3 samples. However, the sharp decrease of both parameters ( $a = 3.782(4) \text{ Å}$ ,  $c = 6.797(5) \text{ Å}$ ) for the fourth sample is observed. Modified state of crystal lattice obtained was stable at room

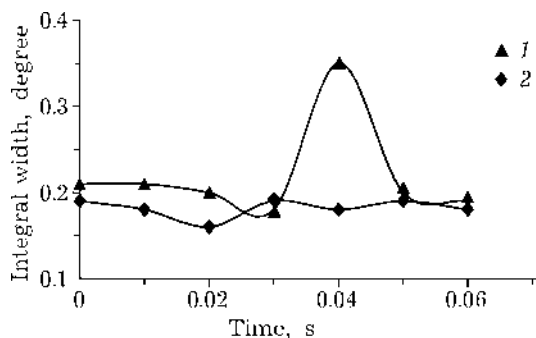


Fig. 2. Dependence integral width on mechanical treatment duration of  $\text{BaO}_2$  samples: 1 and 2 – (004) and (002) lines, respectively.

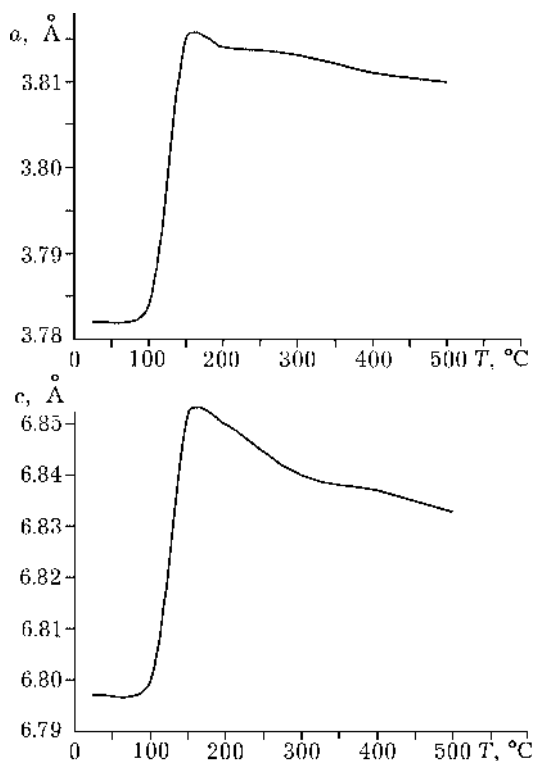


Fig. 3. Dependence of  $\text{BaO}_2$  lattice parameters on annealing temperatures.

temperature. Further mechanical treatment of this sample resulted in the lattice parameters reversal to the previous values. It is necessary to say that the relation  $c/a = 1.80$  for all the specimens was invariable.

The formation of modified state of crystal lattice (sample No. 4) is accompanied by the increase of integral width parameter for some lines. Detailed analysis revealed, that the sharp simultaneous leap of integral width parameter is observed for lines ((004), (103), (114)) corresponding to reflections from the planes containing oxygen atoms. For example, the variation of integral width parameter for (004) line exceeds the experimental standard deviation by the factor of four (Fig. 2). It is necessary to point out that the peak broadening was not detected for reflections containing a contribution from only the atoms of barium ((002), (101), (110)). A typical dependence for (002) line is shown in Fig. 2.

It is well known that the lattice of mechanically activated powders contain structural imperfections, which can be annealed at higher temperatures. To clarify the relationship between thermal and structural properties of

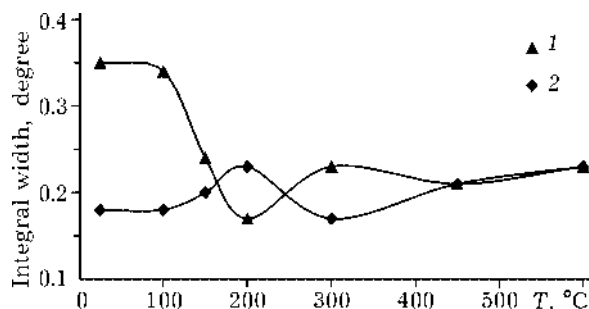


Fig. 4. Dependence  $\text{BaO}_2$  integral width on annealing temperature: 1 and 2 - (004) and (002) lines, respectively.

sample No. 4, its thermal annealing at different temperatures has been carried out. The dependence of the lattice parameters of these annealed samples as a function of annealing temperatures is exhibited in Fig. 3. It can be seen, that a discontinuous changes of the unit cell parameters are revealed for the samples annealed at temperatures higher than 150 °C. For these samples the sharp increase of the unit cell parameters to the previous values is observed. Moreover, the monotone decrease of parameter  $c$  has been seen, when the annealing temperature is increased above 200 °C. Similar dependence is observed also for untreated samples. But in this case, the decrease of parameter  $c$  starts at the temperatures higher than 450 °C. Authors of [6] connected the same dependence for untreated sample with the process of oxygen give off. Thus, the data given in Fig. 3 indicate that the process of oxygen give off for activated sample starts at significantly lower temperatures.

The sharp change of the unit cell parameters for the samples being annealed, shown in Fig. 3, is accompanied by the corresponding contraction of those very lines, which were broadened at the mechanical treatment stage. At the same time, the integral widths of other lines do not change so significantly. As an example the integral width parameters of (004) and (002) lines as a function of annealing temperature are exhibited in Fig. 4.

The thermal data of mechanically activated  $\text{BaO}_2$  samples [3, 4] were used in order to calculate their decomposition temperature. For each sample the parameter  $T^*$  was calculated, which was determined in the following manner. The temperature corresponding to 50 %

loss of active oxygen was chosen on the curves of weight loss. Values of  $T^*$  and unit cell volume as functions of treatment duration are exhibited in Fig. 5. As can be seen, there is strong correlation between decomposition temperature and unit cell volume.

The solubility of mechanically treated solid substances was studied in details mainly in connection with the problems of raw material processing. It is well known that the solubility of mechanically activated solid substances increases significantly due to grinding and formation of structural imperfections [1, 2]. All mechanically activated  $\text{BaO}_2$  samples were tested by their dissolving in the distilled water. The dependence of  $\text{BaO}_2$  solubility in relative units *vs.* treatment duration is shown in Fig. 6 (curve 1). The solubility of untreated sample, which is equal to 0.27 g per 100 ml of water, was taken as 100 %. As can be seen from this figure, the maximum value of solubility is observed for sample No. 4. It is for this sample that the structural anomaly shown in Fig. 1 was found.

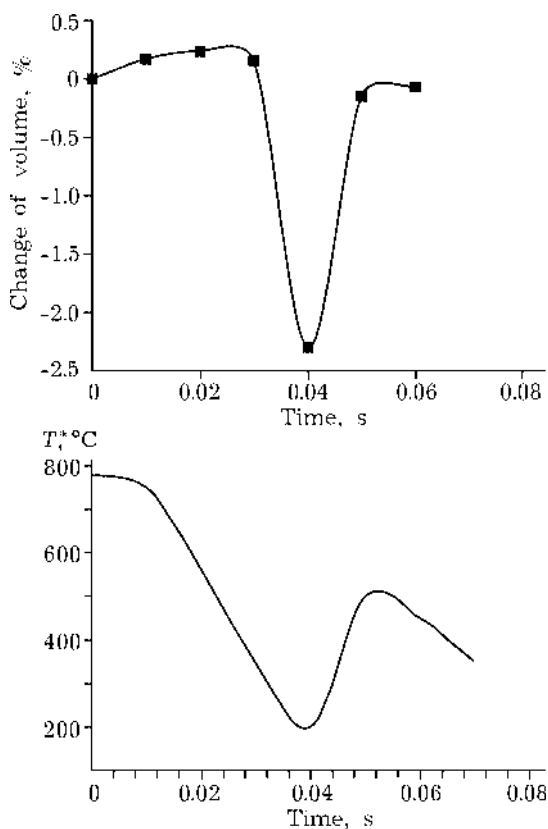


Fig. 5. Dependence of unit cell volume and  $T^*$  on mechanical treatment duration of  $\text{BaO}_2$  samples.

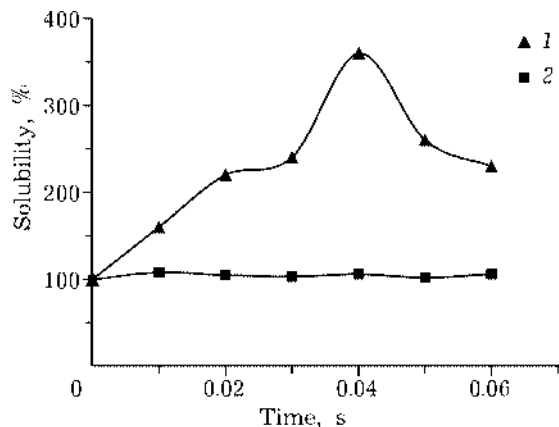


Fig. 6. BaO<sub>2</sub> solubility vs. mechanical treatment duration: 1 – activated samples, 2 – activated and annealed samples.

Thus, the data showed in Fig. 6 demonstrate the significant increase of solubility for mechanically activated BaO<sub>2</sub> samples. In order to investigate the influence of thermal annealing on the solubility of BaO<sub>2</sub> samples, they were annealed at 200 °C and their solubility was measured. The corresponding dependence of BaO<sub>2</sub> solubility is shown in Fig. 6 (curve 2). Inspection of curves in Fig. 6 revealed, that the significant increase of solubility for mechanically activated BaO<sub>2</sub> samples is connected with the internal strains of powder particles. The thermal annealing removed these strains and led to the decrease of BaO<sub>2</sub> solubility.

## CONCLUSIONS

The present analysis established the existence of the modified metastable tetragonal BaO<sub>2</sub> lattice, which is observed at the definite stage of intensive mechanical treatment. The formation of the latter one is accompanied by the contraction of the interatomic distances and by increase of the integral width of some reflections containing contribution of oxygen atoms into scattering amplitude. What this means, is some part of oxygen atoms in such modified crystal lattice is disordered. The observed “compressed” BaO<sub>2</sub> lattice is stable at room temperature and in the absence of mechanical treatment. The thermal annealing of this sample at 150 °C and higher temperatures or further mechanical blows restored the previous values of unit cell parameters and widths of above-mentioned reflections. What this

means, is structurally disordered oxygen atoms return to former site in the lattice. The dependence of the unit cell parameters on the annealing temperature, which shows itself as the emission of active oxygen at lower temperatures in comparison to untreated BaO<sub>2</sub> sample has been established. The distinct correlation between the distinct structural anomaly, decomposition temperature and solubility of BaO<sub>2</sub> was found. Thus, the present analysis established the possibility of the essential change of BaO<sub>2</sub> properties through the intensive mechanical treatment, which will permit to extend the range of BaO<sub>2</sub> applications.

Finally it should be noted that the grinding can lead to high-pressure polymorphism, numerous examples of which are adduced in [2]. The first time such transition of PbO<sub>2</sub> (lead dioxide) to its high pressure phase by simple grinding has been discovered in [7]. Later it that Grinding for several hours in the mortar assembly as was found later in [8], produced varying amounts of high-pressure phases for PbO, PbO<sub>2</sub>, CaCO<sub>3</sub>, MnF<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub>. All these high-pressure polymorphic transitions are realized through crystal symmetry change. The metastable crystal state found for the sample No. 4 is akin to the above-mentioned high-pressure phases, since the formation of the structure of sample No. 4 is accompanied by contraction of the crystal lattice. The corresponding value of pressure  $DP$  can be evaluated using the relation [9]:  $DP = -CDV/V$ . Here,  $C$  is compressibility of crystal lattice,  $DV/V$  is relative change of volume. Taking into account the value of compressibility  $C \sim 10^{11}$  N/m<sup>2</sup> and  $DV/V \sim 0.03$  for sample No. 4, one can deduce that  $DP \sim 3$  GPa (30 kbar). This value of  $DP$  is close to the relevant ones observed for the high-pressure phases in [2, 8]. At the same time, rearrangement of BaO<sub>2</sub> crystal lattice occurs without symmetry change, moreover, even the relation  $c/a$  is invariable. Thus at room temperature and atmospheric pressure the metastable tetragonal phase of BaO<sub>2</sub> with the “compressed” lattice is observable, which can be obtained without grinding in disintegrator and only through applying the hydrostatic pressure of about 30 kbar. The sharp simultaneous leap of unit cell parameters in relation to the duration of treatment and tem-

perature of annealing, is akin to their behaviour in the phase transition of the first kind.

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