CHARACTERISTICS OF THERMORADIATIVE DESTRUCTION OF BaS₂O₆·2H₂O

S. E. Bogushevich, V. N. Makatun, A. K. Potapovich, and I. I. Ugolev

Earlier it was shown that the ion-radical products of thermal decomposition of barium dithionate have extraordinarily high stability up to 850 K [1]. Such unique stabilizing properties of the matrix relative to radical particles allow us to propose the possibility of using the given system for chemical dosimetry.

The purpose of this work was a study of the nature, characteristics of accumulation and thermal stability of radical particles formed on gamma irradiation of barium dithionate, and also the effect of radiative defects on the process of thermal decomposition of dithionate.

The crystalline barium dithionate used in the experiment $BaS_2O_6 \cdot 2H_2O$ was synthesized by the procedure of [2]. The degree of purity of the given compound was controlled by the methods of x-ray phase analysis (XPA), Raman spectroscopy, and EPR. The amount of water of crystallization in the samples was determined by thermogravimetrical methods. Barium sulfite was obtained by pouring a solution of sodium sulfite into a solution of barium nitrate with further filtering of the precipitate and drying in a vacuum. The degree of purity of the salt obtained was determined by the method of IR spectroscopy (UR-20 instrument, KBr tablet) and EPR.

The initial barium dithionate samples were preliminarily stirred in an agate mortar. The average particle size was $\sim 10^{-6}$ m. Gamma irradiation of the samples was performed in air at atmospheric pressure and room temperature in an RKhM- γ 20 setup (⁶⁰Co). BaSO₃ powder was irradiated by the dose $2 \cdot 10^4$ Gy. EPR spectra were recorded on an ERS-230 instrument (East Germany), $\lambda = 3$ cm. For measurements of the values of the g factors a standard of Mn²⁺ in MgO was used.

Thermal annealing of paramagnetic centers (PMC) obtained in $BaS_2O_6 \cdot 2H_2O$ on gamma irradiation by the dose $4 \cdot 10^4$ Gy was performed directly in the resonator of the spectrometer in air on an increase in the temperature from 323 to 473 K every $10^{\circ}C$ (time interval 20-25 min) with simultaneous recording of the spectra. The kinetics of thermal decomposition at 463 K of gamma irradiated barium dithionate and the initial unirradiated compound and also dehydrated dithionate irradiated by the dose $3.5 \cdot 10^4$ Gy were compared.

Gamma irradiation of $BaS_2O_6 \cdot 2H_2O$ at room temperature leads to formation of radicals characterized by an intense isotropic EPR signal with a g factor of 2.0036. An analysis of the literature data obtained for gamma irradiated dithionates, sulfates and hydrosulfates of alkali metals, and also for potassium methyldisulfonate $K_2CH_2(SO_3)_2$ [3-5] gives a basis to rather surely attribute this signal to the SO_3^- ion radical. Besides, additional information of inclusion of sulfur in the radical is given by isotropic satellites with a constant hyperfine interaction from ³³S (I = 3/2), equal to ~ 115 Oe.

It can be expected that gamma irradiation of $BaS_2O_6 \cdot 2H_2O$ at 77 K must lead to formation of radicals - products of radiolysis of the water of crystallization (H·, OH·, O⁻, HO₂), as occurs on radiolysis of some inorganic crystalline hydrates [6-8]. However, in irradiated $BaS_2O_6 \cdot 2H_2O$ at 77 K we did not succeed in detecting any other radicals but SO_3^- . It is possible that on radiolysis of barium dithionate a rather complex chain of processes with participation of OH·, O⁻, O⁻₂, radicals occurs and final stabilization of the ion-radical SO_3^- . The considerable content of the given radicals in the structure of dehydrated barium dithionate relative to other FMCs, formed in the course of its gamma irradiation indicates participation of water of crystallization in formation and stabilization of SO_3^- radicals (their nature was not made more precise).

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Fig. 1. Temperature dependence of content (%) of SO_3^- radicals (1) and of water of crystallization (2) in $BaS_2O_6 \cdot 2H_2O$.



Fig. 2. Accumulation of paramagnetic centers $(SO_2^- \text{ ion radicals})$ in the process of thermal decomposition (T = 463 K) of barium dithionate, irradiated by the doses: $0 (1), 0.2 \times 10^4 (2), 1 \times 10^4 (3), 2 \times 10^4 (4), 5 \times 10^4 (5), 10 \times 10^4 (6), \text{ and } 20 \times 10^4 \text{ Gy}(7); 8)$ dehydrated sample, $D = 3.5 \times 10^4 \text{ Gy}.$

Storage of irradiated samples of barium dithionate in air at room temperature for several months showed that the concentration of SO_3^- radicals practically does not change. An increase in temperature leads to their gradual annealing. Figure 1 shows the dependence of the relative concentration of SO_3^- ion radicals on temperature (curve 1). From Fig. 1 it is seen that with a temperature increase (approximately to 363 K) insignificant annealing of radicals occurs and only in the region of removal of water of crystallization (curve 2) does their intense recombination begin.

Prolonged isothermal heating of irradiated crystalline hydrate BaS_2O_6 (338-343 K, heating time approximately up to 34 h) leads to complete removal of water from the substance (from the data of differential thermal analysis). In this case the dependence of the content of SO_3^- ion radicals on time is in correspondence with the content of hydration water, analogous to that described above. Thus, processes of recombination of radicals and removal of water of crystallization are mutually connected. It is possible that on disruption of the structure of the crystals, besides direct recombination, interaction of SO_3^- radicals with water of crystallization according to the scheme:

$$2SO_3^- + H_2O \rightarrow [HSO_3]^- + [HSO_4]^-$$

becomes probable.



Fig. 3. EPR spectra of gamma irradiated at T_{room} samples: $BaS_2O_6 \cdot 2H_2O$ (1); BaS_2O_6 , dehydrated (2); $BaSO_4$ (3) and $BaSO_3$ (ethanol for determination of the principal values of the g factors DFPG (g = 2.0035)) (4).

Thermal decomposition of $BaS_2O_6 \cdot 2H_2O$ leads to formation and stabilization of SO_2^- ion radicals [1]. In this case we detected a difference in the rates of decomposition on preliminary irradiation of barium dithionate samples by different doses. Since the process of accumulation of SO₇ radicals in the final product is adequate to the process of thermal decomposition of the initial substance [1], the dependence of the rate of its thermal decomposition on the dose of preliminary gamma irradiation was studied using the kinetics of accumulation of stabilized SO₂ (see Fig. 2). From Fig. 2 it is seen that all the kinetic curves independent of the degree of irradiation of the investigated samples have the same S-form shape, as also the curves belonging to unirradiated $BaS_2O_6 \cdot 2H_2O_6$. This fact indicates that the process of thermolysis, occurring in unirradiated barium dithionate is identical to the process occurring in the gamma irradiated substance, and is autocatalytic. However, the rate of decomposition of the irradiated compound is higher than that of the unirradiated, and increases proportional to its dose of gamma irradiation (Fig. 2, curves 1-5). Simultaneously with the increase in rate a shortening of the duration of the induction period of the given process occurs. An analysis of the literature data [9-11] on the effect of preliminary irradiation on thermal decomposition of the substance indicates an increase in the rate of the given process for irradiated compounds in connection with the arising of radiative defects, which are centers of nucleus formation in concrete realizations. In the case of thermal decomposition of irradiated $BaS_2O_6 \cdot 2H_2O$ as the causes of acceleration of the reaction, besides formation in the structure of the substance of centers of nucleus formation, there may be first radiolysis of water, leading to its removal from the substance and an increase in the defectiveness of its structure; second, interaction of SO_3^- radicals between each other with formation of sulfate anions as the final product without expenditure of additional energy on breaking the S-S bond in the dithionate anion; third, an increase in the rate of formation of the $[HSO_3]^-$ anion on interaction of the water of crystallization with SO_3^- in comparison with its interaction with $[S_2O_6]^{2-}$ anion.

In [1] it was explained that for stabilization of the SO_2^- ion radicals in the final product of thermolysis of $BaS_2O_6\cdot 2H_2O$ barium sulfite is responsible. The process of formation of $BaSO_3$ in the course of postradiative thermal decomposition of barium dithionate probably occurs, already after the arising in the system of $[HSO_3]^-$ anions and possibly occurs according to the scheme:

$$2 [HSO_3]^- \rightarrow [SO_3]^{2-} + H_2O + SO_2.$$

Correspondingly with an increase in the rate of formation of $[HSO_3]^-$ on account of an increase (on an increase in the dose of gamma irradiation) in the concentration of SO_3^- ion radicals an increase in the rate of the examined reaction occurs. The final product of the reaction of thermolysis of dithionate-barium sulfate must form due to interaction of sulfur with SO_2 [1, 12]. Thus the increase in the rate of decomposition of irradiated barium dithionate with an increase in the dose of preliminary irradiation is connected with an increase in the final product of sulfite anions.

The following experimental result is in favor of the given conclusion. In the $(5-6)\cdot10^4$ Gy region saturation of $BaS_2O_6\cdot 2H_2O$ by SO_3^- radicals occurs; their concentration ceases to change. Correspondingly the rate of formation of barium sulfite also must not change. Actually, radiolysis of the substance by a more considerable dose - $(10; 20)\cdot10^4$ Gy already does not lead to a further increase in the rate of accumulation of SO_2^- radicals, and consequently, to acceleration of its thermal decomposition (Fig. 2, curves 6, 7). Besides, from Fig. 2 (curve 8) it is seen that the rate of thermolysis of preliminarily irradiated dehydrated barium dithionate is the least. This fact additionally indicates that the water of crystallization actually takes part in formation of $[SO_3]^{2-}$ anions.

It should be noted that gamma irradiation of barium sulfite both at room temperature and at 77 K also leads to stabilization in it of SO_2^- radicals. Radiolysis of $BaSO_4$, $BaS_2O_6 \cdot 2H_2O$, and dehydrated dithionate (77 K, room temperature) does not lead to formation of the SO_2^- radical (Fig. 3). This fact gives additional information on the role of $BaSO_3$ in stabilization of the given paramagnetic particles, and its formation is an intermediate stage in the process both of thermal transformation of $BaS_2O_6 \cdot 2H_2O$ and of its thermoradiative destruction.

The rather expressed dependence of the final concentration of SO_2^- radicals on the irradiation dose attracts attention. However, an analysis of the causes of this dependence requires a careful examination of the measurement errors and performing further investigations.

Thus, on the basis of the above given material the conclusion can be drawn that the basic participants in thermal decomposition of barium dithionate after gamma irradiation are SO_3^- ion radicals and water of crystallization. Their interaction (through the intermediate stage of formation of the $[HSO_3]^-$ anion) leads to formation of BaSO₃, first, which is responsible for stabilization of SO_2^- ion radicals and second, takes part in autocatalytic acceleration of the investigated reaction. The general scheme of the mechanism of thermal decomposition of gamma irradiated $BaS_2O_6 \cdot 2H_2O$ can be represented in the following way:*

 $[S_{2}O_{6}]^{2-} \xrightarrow{\gamma} 2SO_{3}^{-},$ $2SO_{3}^{-} + H_{2}O \rightarrow [HSO_{3}]^{-} + [HSO_{4}]^{-},$ $2[HSO_{3}]^{-} \rightarrow [SO_{3}]^{2-} + H_{2}O + SO_{2},$ $2[SO_{3}]^{2-} + SO_{2} \rightarrow [SO_{4}]^{2-} + 2SO_{2}^{-},$ $[S_{2}O_{6}]^{2-} + 2SO_{2}^{-} \rightarrow 2[SO_{3}]^{2-} + 2SO_{2}.$

Barium sulfite forming in the final stage and SO_2 gas again enter into the reaction, which also leads to its autocatalytic acceleration. Thus, the given scheme allows us to explain the effect of sharp acceleration of the reaction of thermal decomposition of barium dithionate in an SO_2 atmosphere.

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*See also [1].

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PHOTO- AND RADIATION-INDUCED CHANGE IN THE OPTICAL PROPERTIES OF As2S3

Ya. A. Teteris and G. Ya. Skuin'

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The effect of photo- and radiation-induced change (PIC and RIC) in chalcogenide semiconductors (CGS), which is primarily characterized by a change in optical properties, has been widely studied. It has been shown in many studies [1, 2] that exposure of As_2S_3 films to light results in a shift in the optical absorption edge toward lower energy, i.e., photodarkening of the films is observed. According to [3], irradiation by a high energy ⁶⁰Co γ source is also accompanied by As_2S_3 darkening. It should follow that PIC and RIC are characterized by the same general features. Instead, there is experimental data that shows the difference in the PIC and RIC processes in As_2S_3 . For example, exposure to light gives rise to an increase [2], while to γ radiation a decrease [4], in the geometric dimensions of As_2S_3 samples. According to [5, 6], the microhardness of glassy As_2S_3 increases under the effect of γ radiation, but decreases during optical irradiation.

This study draws a comparison of the change in optical properties of As_2S_3 films under the effect of argon laser light ($h\nu = 2.41 \text{ eV}$, I = 0.66 W/cm²), and ⁶⁰Co γ source radiation ($h\nu = 1.17$ and 1.33 MeV, I = 4 Gy/sec).

Films with thicknesses of 0.06 to 150 μ m were prepared using a hot sputtering method in a vacuum of 5 × 10⁻⁴ Pa. The samples were first annealed at 185°C in an argon atmosphere in a vacuum chamber irradiated by laser light until PIC saturation or γ particles to a dose of 4 MGy.

The dependence of the optical absorption coefficient (α) of the freshly sputtered, annealed, and irradiated As₂S₃ films on photon energy hv is shown in Fig. 1. Thermal annealing of the new films leads to a change in α over a broad spectral range (curves 1, 2). For hv < 4.4 eV, α grows and for hv > 4.4 eV it decreases. Irradiation of the thermally annealed films by γ particles (curves 2, 3) without exposure to light (curves 2, 4) causes an increase in α only in the region of hv < 2.35 eV, and in the hv > 2.35 eV spectral region for even weak optical irradiation of the films.

When $\alpha < 10^3$ cm⁻¹, optical absorption of CGS is determined by the Urbach tail, which is characterized by an exponential functional dependence of the absorption coefficient on the eenergy of an absorbed photon of light [1]

$$\alpha(h\nu) = \alpha_0 \exp\left[-\beta(E_0 - h\nu)\right]. \tag{1}$$

The Urbach absorption tail, which arises in association with structural disordering as a result of the deformation of valence angles and chemical bond lengths, is common in amorphous semiconductors. It follows from theoretical arguments [7], that the deformation of valence angles has an effect on the density of states in the upper part of the valence band, and according to [8], a direct correlation between the slope of the exponential part of the absorption curve β and distortion of the valence band is observed. A decrease in β is due

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