ON THE INFLUENCE OF OXYGEN GAS UPON THE OPTICAL ABSORPTION BANDS OF EVAPORATED BARIUM OXIDE FILMS IN THE ULTRAVIOLET REGION

BY

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ABSTRACT

By measuring the optical absorption of BaO films evaporated in vacuum, it is observed at room temperature that the threshold for absorption occurs at 320 mμ and the second rapid rise in absorption begins at 250 mμ approximately. Two absorption bands are observed between 320 mμ and 250 mμ: one has a maximum at about 303 mμ, while the other has a maximum at about 285 mμ. Tyler assumed that the absorption bands in the region of 320 mμ~250 mμ are exciton bands, and various *experimental results concerning these absorption bands have also been reported by* other investigators.

In our laboratory, the effect of oxygen gas upon the absorption bands under various heat treatments has been investigated. By measuring the change of oxygen gas pressure in a definite volume as well as the amount of BaO, it has been observed that the absorption bands in the region of 320 mμ~250 mμ vanished out and at the same time the reduction of oxygen gas pressure in the definite volume occurred corresponding to the stoichiometric amount of oxygen in BaO.

Thus, the result of the present experiment seems to suggest that the 320 mμ~ 250 mμ absorption bands are due to the production of excitons.

1. Introduction

Since Tyler (1) found that the edge of optical absorption of evaporated BaO films lies at 3.8 ev ($\approx$320 mμ) and a second increase in the absorption constant occurs at 4.8 ev ($\approx$260 mμ) approximately, several experimenters have investigated the energy bands in BaO by optical methods. The location of the absorption edge at about 3.8 ev as reported by Tyler was confirmed by Taft and Dickey (2) on the basis of studies on photoelectric emission from thin metallic film deposited on the surface of BaO layers. In the case of BaO single crystals, the optical absorption and photo-conductivity were measured by Tyler and Sproull (3), thus obtaining the results that the threshold photon energy for both the optical absorption and photoconductivity is 3.8 ev ($\approx$320 mμ) and that a first absorption band is accompanied by photoconductivity, but not a second absorption band. Judging from the fact that the absorption constant is of the order of 10^5 cm^{-1} at the peak of the first absorption band, Tyler has assumed that this absorption band may be attributed to the production of excitons in BaO

lattice, and that this band is accompanied by photoconductivity due to the thermal dissociation of excitons or excitation ionization of impurity centres.

Also, by measuring the spectral distributions of photoelectric yield for BaO surfaces prepared in different ways, Apker *et al.* (4) observed that the abrupt rise at 5.0 ev is characteristic of all samples, but the behaviour for $h\nu < 5.0$ ev depends on the procedure in which the sample was prepared. They attributed the rise in the yield at $h\nu \approx 3.8$ ev to exciton-induced photoelectric emission from some kinds of impurity centres.

Later, measurements of the optical absorption of BaO films at temperatures between 15°K and 370°C were carried out by Zollweg (5), who reported that the two strongest absorption peaks in the region between 3.8 ev and 5.0 ev are to be caused by exciton absorption. Recently, Jahoda (6) has measured the reflectivity spectrum of BaO single crystals in the ultraviolet region and making use of the Kramers-Kronig relation, he has obtained the spectral distribution of optical absorption constant which is similar to Zollweg's. Thus, he has concluded that the absorption bands between 3.8 ev and 5.0 ev are exciton bands. These experimental results have also been explained theoretically by Overhauser (7).

Independent investigation on the optical absorption of BaO films has been carried on in these several years in our laboratory. Takazawa and the present writer (8) observed that the absorption bands in the region of $320\,m\mu \sim 250\,m\mu$ vanished out suddenly when BaO film was exposed to oxygen gas, but no alteration occurred in the case of the absorption band beginning at about $250\,m\mu$, and these results led us to the conclusion, contrary to the results by Tyler and others, that the absorption bands in the region of $320\,m\mu \sim 250\,m\mu$ are due to some kinds of lattice imperfection.

In order to decide whether the above-mentioned absorption bands are due to exciton production or to some kinds of lattice imperfection, the present writer has attempted to measure quantitatively the ratio of the amount of oxygen gas necessary for vanishing out absorption bands to the amount of BaO, under various heat treatments, and to the description of the results of our measurements the present paper is mainly directed.

2. Experimental apparatus and techniques

The evaporation vacuum-cell used in the present experiment is shown schematically in Fig. 1. The cell whose total volume is about 20 cc consists of two parts: one is made of glass and has vacuum cocks, electrodes and thermistor bead, while the other is a fused quartz tube on whose inside surface BaO film was evaporated. These two parts were connected to each other by a joint using silicon grease. By cooling the jointed part by water, it was possible to heat the quartz tube up to about

1,000°C and to exhaust gases from the tube thoroughly. The filament made of plati-
num wire of 0.3 mm diameter was used and was coated with $BaCO_3$ (Merck Ultra
Pure) which was pasted in distilled water. The cell was connected by another joint
to the vacuum system. After having exhausted, $BaCO_3$ was converted to BaO by
heating the $BaCO_3$ coated platinum filament slowly up to about 1,000°C, the heating
having been continued until gas evolution has substantially ceased. Then the quartz
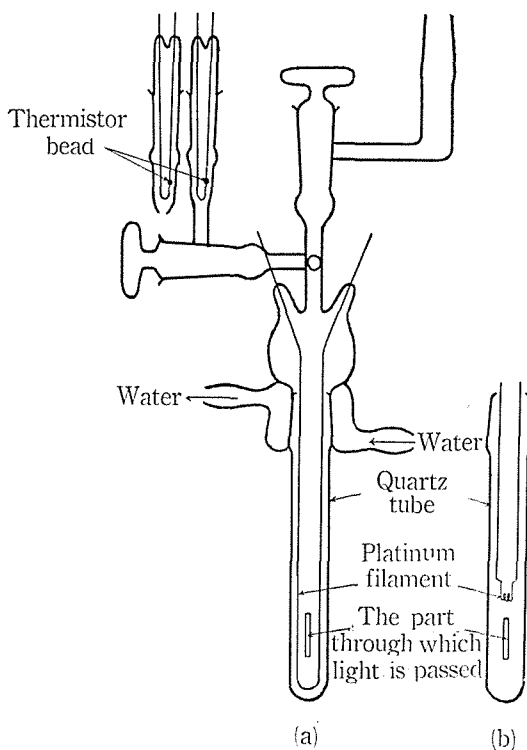tube was heated in a furnace up to about 1,000°C.

Fig. 1. Evaporation vacuum cell.

After these procedures, by heating the filament at temperatures of 1,200°C～
1,300°C the BaO film was evaporated on the inside surface of the quartz tube whose
temperature was slightly higher than room temperature. The temperature of the coated
filament was measured by an optical pyrometer. In all cases the optical absorption
of BaO film was measured at room temperature by the use of a Beckman DU
spectrophotometer. Oxygen gas prepared by heating $KMnO_4$ in a vacuum chamber
was dehydrated by P_2O_5 for a few days, and after having finished the measurement
of the optical absorption of the BaO film in vacuum, the dehydrated oxygen gas was
led to the evaporation cell through a cold trap of dry ice-alcohol or liquid oxygen.

Then, the relationship between the change of optical densities at the peaks of

the absorption bands and the change of oxygen gas pressure was observed by means of a thermistor vacuum gauge. Fig. 2 shows the thermistor gauge as used under such a condition that another thermistor bead exposed to atmosphere was used as a temperature compensator.
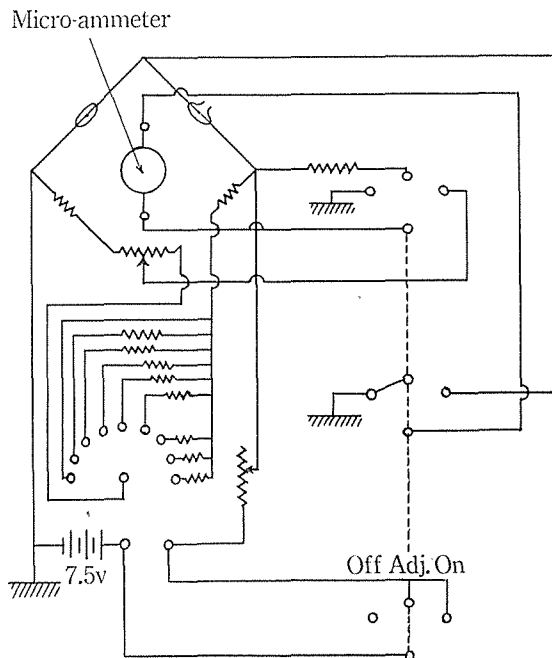
Micro-ammeter

Fig. 2. Schematic diagram of the thermistor vacuum gauge.

The thermistor gauge was calibrated in such a manner that a micro-ammeter with full scale of $10\,\mu$A indicates the zero point at one atmospheric pressure. The characteristic curve for oxygen gas is shown on semilogarithmic scale in Fig. 3, taking the logarithm of oxygen gas pressure as ordinate and the electric current as abscissa. It will readily be seen that this characteristic curve is linear in a range from 5×10^{-1} mmHg to 5×10^{-2} mmHg. It was able to observe pressure differences of 5×10^{-2} mmHg at 1 mmHg, 2×10^{-2} mmHg at 0.5 mmHg, 2×10^{-3} mmHg at 1×10^{-1} mmHg and 2×10^{-3} mmHg at 5×10^{-2} mmHg, respectively. The limiting pressures capable of being observed were about 5 mmHg and 5×10^{-3} mmHg respectively.

The thermistor gauge was also used as a qualitative indicator of gas pressure in the evaporation cell. When the cell was exhausted sufficiently, only a small amount of increase of gas pressure in the cell was observed even when the quartz tube was heated at ~500°C for about thirty minutes. In such a case the alteration of the optical densities of the evaporated film in the ultraviolet region scarcely occurred at room temperature for several hours.
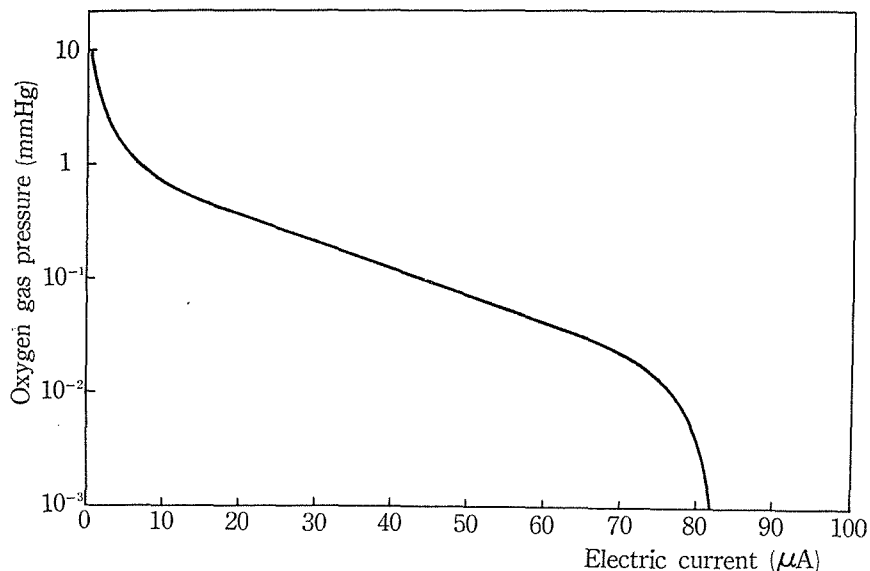
Fig. 3. The characteristic curve for oxygen gas at room temperature.

3. Experimental results

Fig. 4 shows a typical absorption spectrum of BaO films in the ultraviolet region, as observed at room temperature. The spectrum observed under no heat treatment is shown by curve A, while curve B shows the spectrum as observed after having heated the BaO films at about 400°C in vacuum and then quenched. It is easily seen that there are two absorption bands in the region between 320 mμ and 250 mμ, a large band in the region of wavelengths shorter than 250 mμ and presumably a broad band in the region of wavelengths longer than 320 mμ, though the last one has not yet been recognized definitely. Also it is found that the positions of absorption peaks were shifted to longer wavelength side under heat treatment in vacuum and at the same time the sharpening of the band shape took place.

In order to obtain the concentration of the absorption centres responsible for the absorption bands in the region of 320 mμ~250 mμ, an order estimation of the absorption constants at the absorption peaks was attempted in the following way. Regarding the BaCO$_3$ coated platinum filament in the form of coil, as shown in Fig. 1 (b), as a point and thus assuming that BaO was evaporated spherical-symmetrically from the platinum coil, the distribution of the BaO film thickness on the inside surface of the quartz tube was calculated approximately by making use of the total amount of BaO film which was measured by a steelyard.

Then, the optical densities at the absorption peaks were calculated by taking the absorption constants there to be of the order of 10^5 cm^{-1}, and it was found that the

calculated values were in good agreement with observed ones. Judging from this result it is certain that the absorption centres have high concentration as obtained by Tyler and others.

In other cases of the present experiment, a platinum filament with the shape of a straight line as shown in Fig. 1 (a) was generally used in order to make the thickness of BaO film as uniform as possible. In such a case the total amount of BaO had to be of the order of 0.5 mg in order to obtain appropriate optical densities.
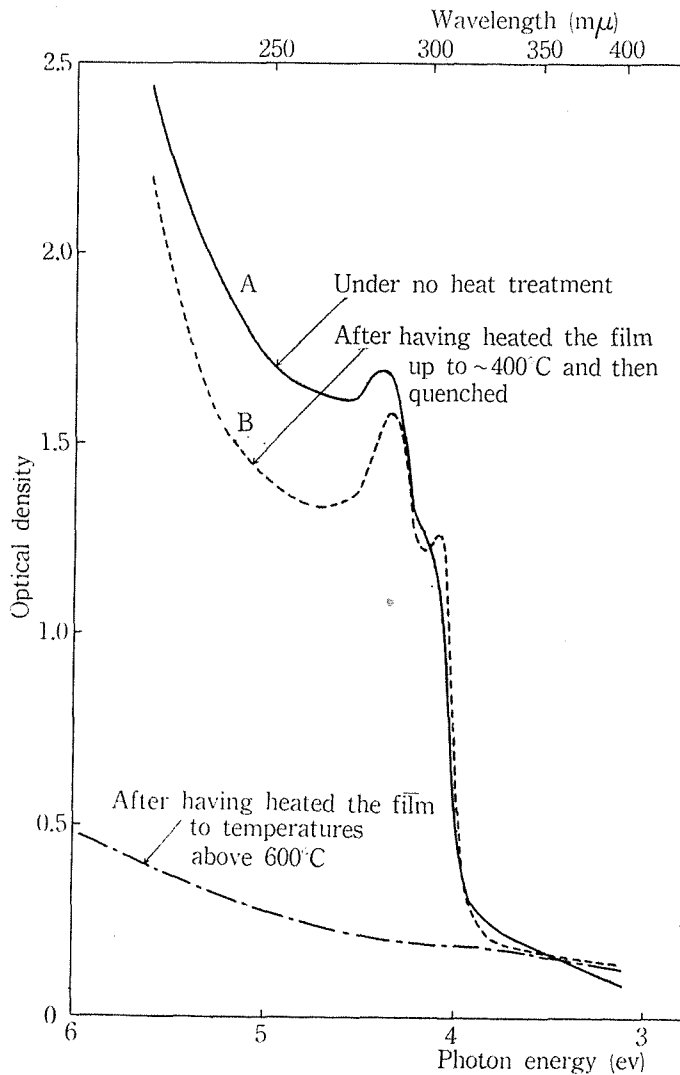

Fig. 4. Optical absorption curves for BaO film in vacuum observed at room temperature.

Fig. 5 shows the change in the absorption bands occurred when the film was exposed to dry oxygen gas with pressure of about 1 mmHg at room temperature. It was observed that a broad absorption band in the region of wavelengths longer than 320 mμ vanished out suddenly, notwithstanding that the magnitude of the band varied, as shown in Fig. 6, with the film thickness as far as its optical densities were concerned. It was found, however, that the absorption bands in the region of wavelengths shorter than 320 mμ was not remarkably affected even when the film had been exposed for a day to oxygen gas whose pressure was about 80 mmHg.

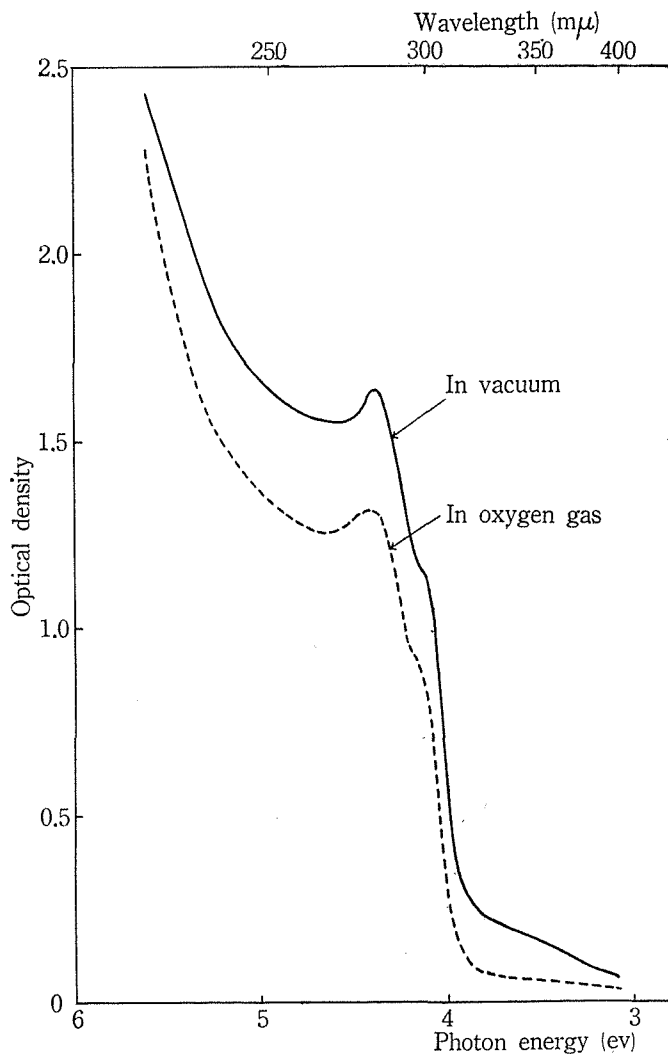Fig. 5. Absorption curves for BaO film observed at room temperature.
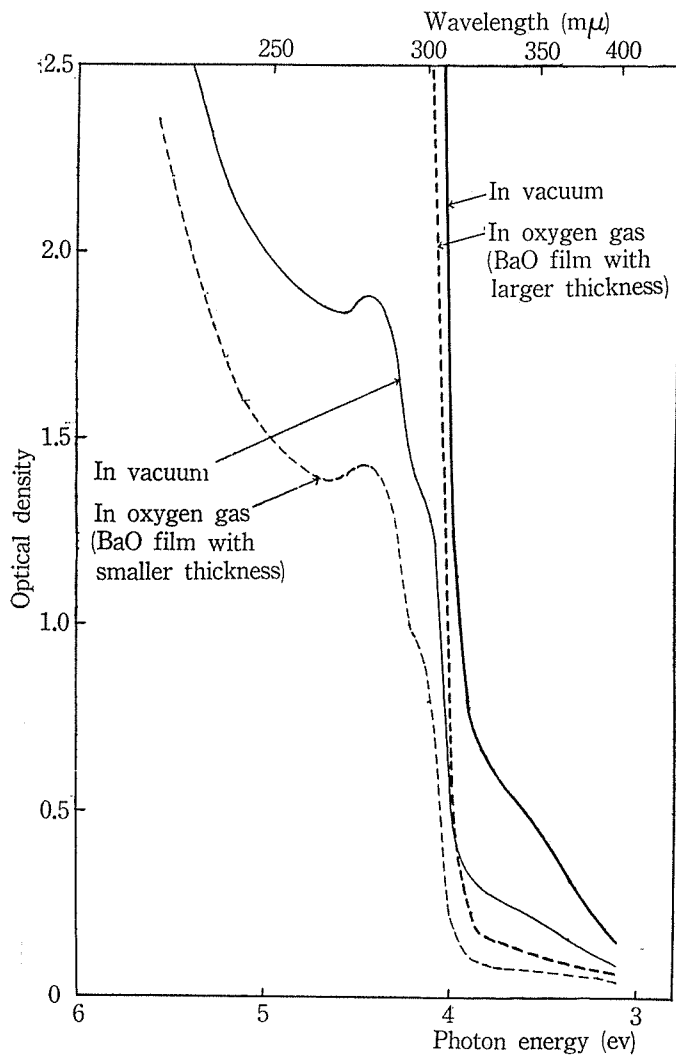
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Fig. 6. Absorption curves for BaO films with different thicknesses,
          observed at room temperature.

Next, by heating the BaO film in oxygen gas with pressure of about 1 mmHg, it was observed that the two absorption bands between 320 mμ and 250 mμ began to decrease at about 200°C as the oxygen gas pressure in the cell decreased and that after both the magnitude of the absorption bands and the oxygen gas pressure had reached their respective minimum values, the magnitude of the bands began to increase at about 400°C as the oxygen gas pressure increased, as shown in Fig. 7. Such a reaction is similar to the well-known chemical reaction $BaO \underset{800°C}{\overset{500°C}{\rightleftarrows}} BaO_2$, which occurs when BaO is heated in the air, the only difference being that the

temperature at which the reaction in the present experiment occurred is much lower than that at which the above-mentioned chemical reaction occurs.

It can be seen from Fig. 7, however, that the absorption band beginning at about 250 mμ in BaO is not affected under the present heat treatment. Thus, in order to decide whether this reaction might be the chemical reaction $BaO \rightleftarrows BaO_2$ or not, a quantitative measurement was carried out more precisely in the following way.
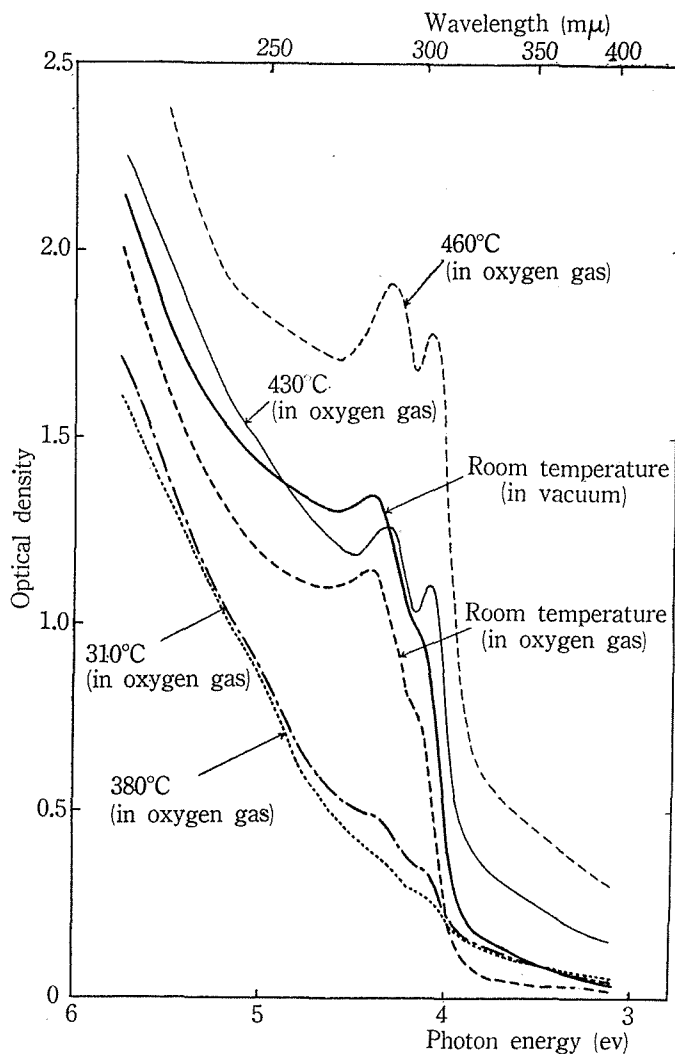

Fig. 7.   Changes occurred in the absorption bands of BaO film observed
at room temperature, after having heated the film in oxygen gas
at various temperatures indicated.

First, under such a condition that BaO on the platinum filament had all evaporated, the amount of BaO film was calculated from the amount of $BaCO_3$ pasted on the filament which was measured by a steelyard, and dry oxygen gas whose pressure had been measured by an oil manometer was stored beforehand in a small region of about 2 cc to which a thermistor bead was attached. Then, after having measured the optical absorption of BaO film in vacuum, the stored oxygen gas was diffused into the cell and the relation between the magnitudes of the bands and oxygen gas pressure was observed under various heat treatments. It was thus found that the magnitudes of the bands in the region from 320 mμ to 250 mμ generally decreased linearly with the decrease of the oxygen gas pressure and that the amount of decrease of oxygen which was calculated from the decrease of oxygen gas pressure in the cell was of the same order of magnitude as the stoichiometric amount of oxygen in the BaO film.

Similar experiments were also carried out for the BaO film heated up to 400°C ~500°C in vacuum beforehand and then quenched, and the results as shown in Fig. 8 were obtained. In this case, the influence of oxygen gas upon the absorption bands in the ultraviolet region was not observed at room temperature. By heating the film in oxygen gas, however, it was observed that the magnitudes of the two absorption bands in the region of 320 mμ~250 mμ began to decrease at about 300°C and after the magnitudes of these bands had reached their respective minimum values, they began to increase at about 500°C. As shown in Fig. 9, an exactly linear relationship was observed between the optical density at one of the peaks of the bands and the oxygen gas pressure in the cell.

In case when the amount of oxygen in the cell was less than the stoichiometric amount of oxygen in the BaO film, the decrease of the magnitude of the bands was stopped at intermediate values as shown in Fig. 10.

Judging from these results it may be concluded that the change of the magnitudes of the absorption bands between 320 mμ and 250 mμ due to oxygen gas should be attributed to the chemical reaction $BaO \rightleftarrows BaO_2$ and that a large absorption band which was still observed after the bands in BaO in the region of 320 mμ and 250 mμ vanished out should be due to BaO_2.

Whenever BaO film was heated to temperatures above 600°C in vacuum as well as in oxygen gas for about twenty minutes and then quenched, the film became transparent in the ultraviolet region as shown in Figs. 4 and 8; in other words, all the bands in the ultraviolet region vanished out. In such a film, the optical absorption bands could not appear again by any heat treatment.

Next, we have investigated the effect of H_2O vapour upon the absorption bands in BaO. Pure H_2O vapour was prepared in such a way that after having exhausted the vacuum chamber, H_2O frozen beforehand in the cold trap was evaporated in the chamber. After the optical absorption of BaO in vacuum had been measured, an appropriate amount of H_2O vapour was introduced into the cell.
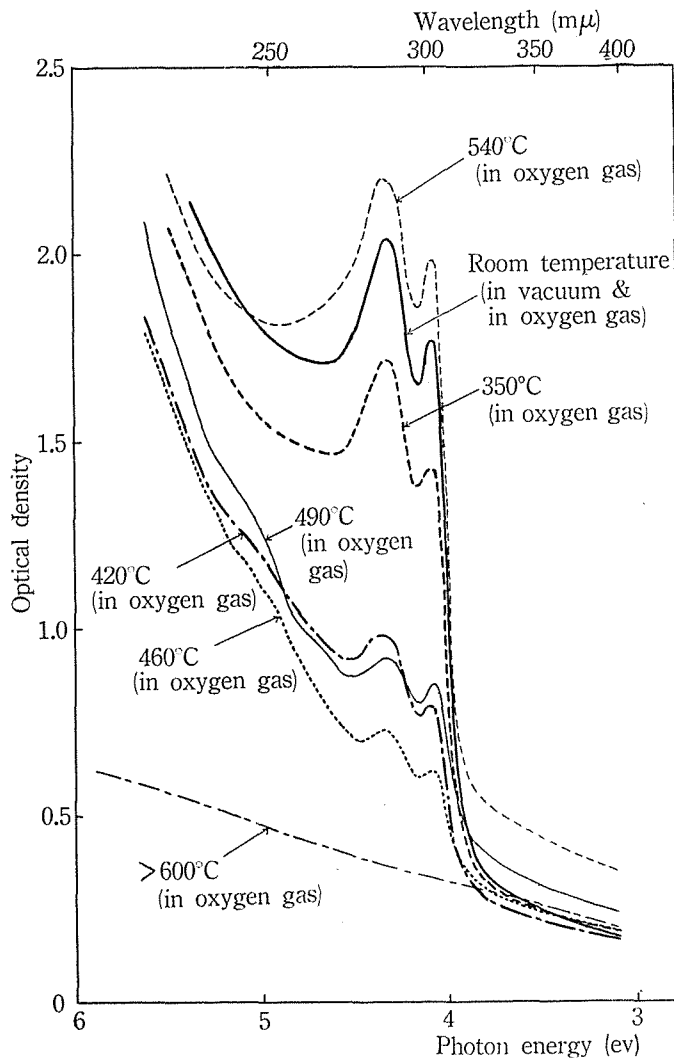

Fig. 8. Changes occurred in the absorption bands of BaO film which was heated in vacuum up to 400°C~500°C beforehand and then quenched. The obvervations were done at room temperature, after having heated the film in oxygen gas at various temperatures indicated.
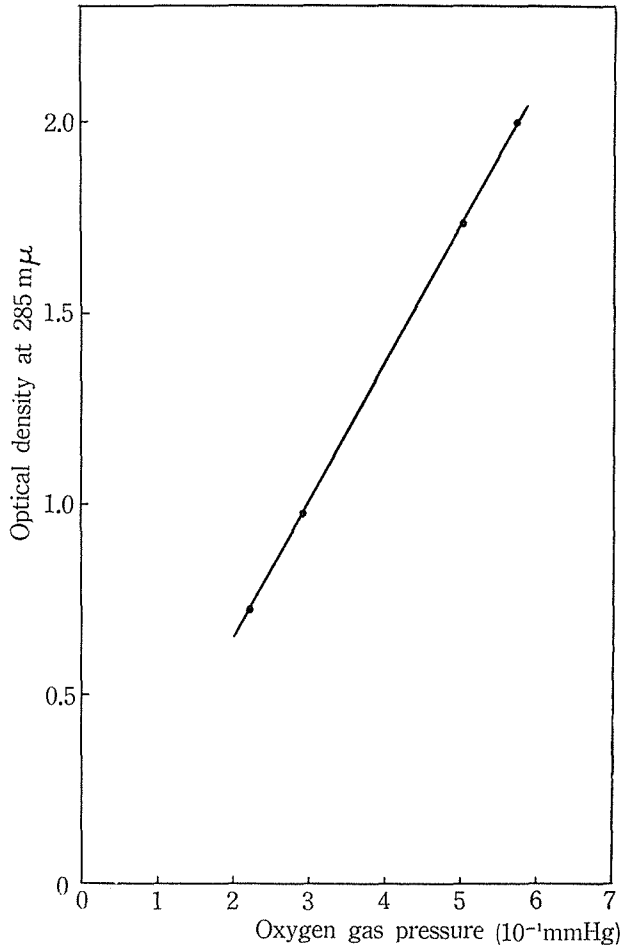
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Fig. 9. Relationship between the optical density at one of
the absorption peaks (285 mμ) and oxygen gas
pressure in the experiment shown in Fig. 8.

It was thus observed at room temperature that the magnitudes of all the absorp-
tion bands in the ultraviolet region were decreased in approximately proportion to
the amount of H_2O vapour as shown in Fig. 11. When an amount of H_2O vapour
which is enough to cause such a reaction that all BaO's $\rightarrow$ Ba(OH)$_2$ was introduced
into the cell, it was observed that the two bands in the region between 320 mμ and
250 mμ vanished out at room temperature, while the band in the region of wave-
lengths shorter than 250 mμ still remained, as shown also in Fig. 11. This pheno-
menon is fairly similar to a phenomenon occurred when BaO film was exposed to
oxygen gas, which was observed by Takazawa and the present writer some years
ago (8). The above-described results of our present experiment seem to suggest

that oxygen gas used in our previous experiment had contained H_2O vapour to some extent.

Further additional experiments were carried out in case when BaO film was irradiated by AH–6 mercury lamp for ten hours, and it was observed that no change occurred in the absorption bands.
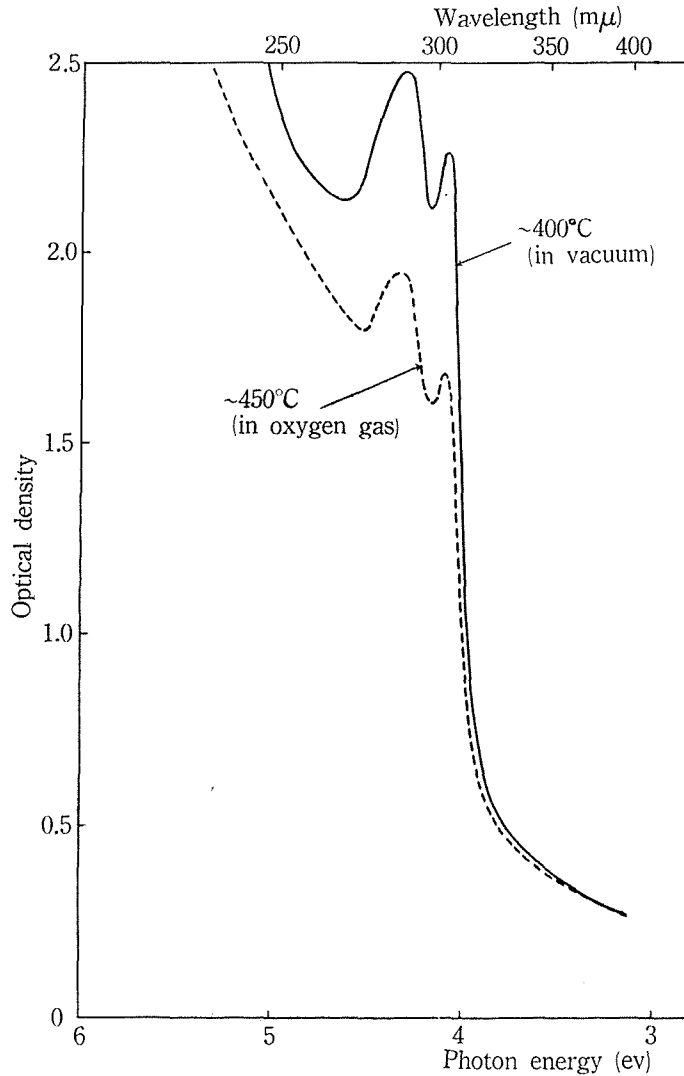

Fig. 10. Changes in the absorption bands of BaO film, after having heated the film in a small amount of oxygen gas, observed at room temperature.
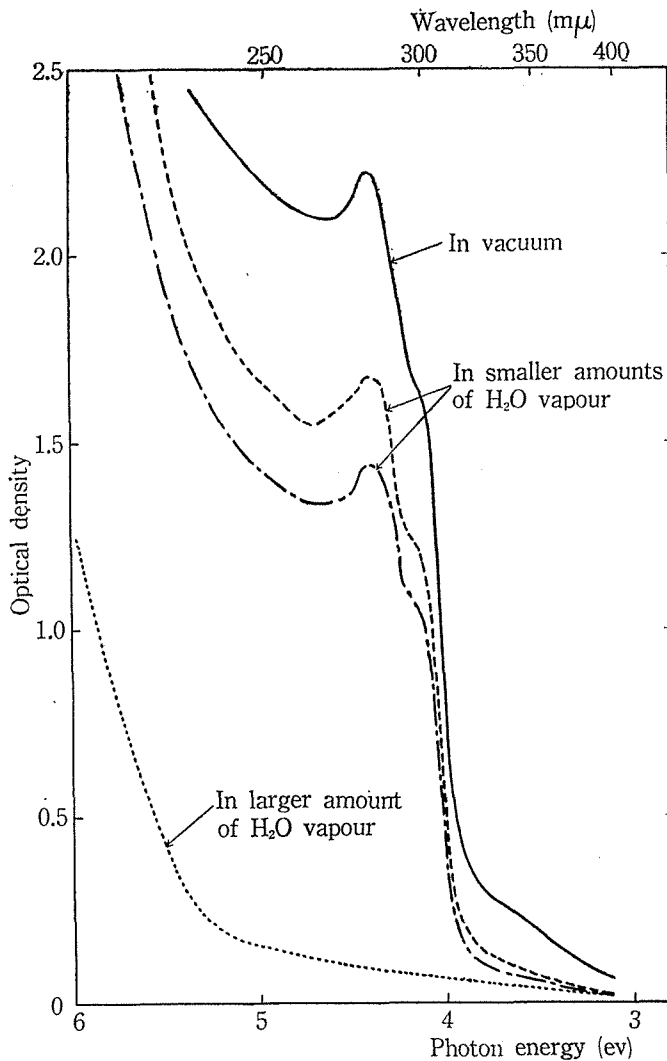
Fig. 11. Curves of optical density *versus* photon energy for BaO film when
various amounts of H_2O vapour were introduced into the cell.

4. Summary and conclusion

In the present experiment, the optical absorption of BaO film evaporated in
vacuum has been measured and it has been first observed at room temperature that
there are two absorption bands in the region of wavelengths between 320 mμ and
250 mμ, a large band in the region of wavelengths shorter than 250 mμ and presum-
ably a broad band in the region of wavelengths longer than 320 mμ. Secondly, it
has been found that the positions of the absorption peaks are shifted to longer

wavelength side under heat treatments in vacuum and at the same time the sharpening of the band shape takes place.

The absorption bands in the region of 320 mμ~250 mμ have been assumed by Tyler to be exciton bands and the exciton characteristics of these bands have been investigated by other experimenters.

In our laboratory, the influence of oxygen gas upon the absorption bands in the region of wavelengths between 320 mμ and 250 mμ has been previously investigated. In the first place, the high concentration of the absorption centres responsible for these bands was confirmed by the order estimation of absorption constant at the absorption peak. On the other hand, it has been observed by Takazawa and the present writer that when BaO film was exposed to oxygen gas at room temperature, the absorption bands in the region between 320 mμ and 250 mμ vanished out.

In the present experiment, the influence of oxygen gas upon the absorption bands of BaO film has been quantitatively investigated by the use of a thermistor vacuum gauge in order to decide whether the bands in the region of 320 mμ~250 mμ are exciton bands, as assumed by Tyler, or not.

It has thus been found that a broad band in the region of wavelengths longer than 320 mμ vanished out suddenly when the BaO film has been exposed to oxygen gas at room temperature, while the absorption bands in the region of wavelengths shorter than 320 mμ is not remarkably affected even when the film has been exposed for a day to oxygen gas with pressure fairly higher than 1 mmHg.

By heating the BaO film in a definite amount of oxygen gas, it has been observed that the magnitudes of the absorption bands in the region of wavelengths between 320 mμ and 250 mμ decrease almost linearly till about 400°C with the decrease of oxygen gas pressure in the cell, and it has been shown by a quantitative measurement that this phenomenon should be attributed to the chemical reaction BaO→BaO$_2$. If defects or impurities in BaO lattice were the cause of the absorption bands between 320 mμ and 250 mμ, it would perhaps be most likely that these bands are due to the presence of oxygen vacancies. If so, it would be expected that the magnitudes of these bands are changed by heating the film in oxygen gas without being accompanied by the chemical reaction BaO→BaO$_2$. The above-mentioned fact that the vanishing out of these bands associated with the heating of the BaO film in oxygen gas is accompanied by the chemical reaction BaO→BaO$_2$ seems to show, however, that these bands are inherent in BaO lattice itself, but not due to defects in BaO lattice.

Further, we have observed that whenever the BaO film was heated to temperatures above 600°C in vacuum as well as in oxygen gas and then quenched, all the bands in the ultraviolet region vanished out, and it is presumable that this phenomenon is associated with a large change in crystal perfection in the BaO film.

Next, the influence of H_2O vapour upon the absorption bands has been investigated and it has been observed that the change occurred in the bands when the BaO film had been exposed to H_2O vapour at room temperature is fairly similar to the results obtained by us some years ago (8).

Lastly, it has been found that no change in the absorption bands in the region of $320\,m\mu \sim 250\,m\mu$ occurs by irradiation of light with wavelengths covering their absorption peaks.

Thus, we are finally led to the conclusion that, in conformity with the results by Tyler and others, the absorption bands of the BaO film in the region of wavelengths between $320\,m\mu$ and $250\,m\mu$ are due to the production of excitons.

Acknowledgments

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