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Oxygen Vacancies in Barium Oxide*

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It has been shown by Dash that an optical absorption band at 2.0 ev occurs in BaO crystals when these are treated in barium or other metal vapors, giving the crystals a blue color. In order to determine the way the stoichiometric excess of metal is present in the lattice, the diffusion of the blue coloration into BaO has been measured over the range 800°C to 1300°C. The diffusion constant has been found to obey the empirical relation, $D=2500\exp(-32\,500/T)$. Comparison of this with Redington's results for the diffusion of Ba^{140} into BaO indicates that the diffusion process giving the coloration does not transport barium. It is concluded that the principal lattice defects in BaO with excess metal are oxygen vacancies, and the absorption band is like the F' band in alkali halides. Chemical determinations of the barium excess are compared with optical determinations.

I. INTRODUCTION

THIS work was undertaken as part of a study of semiconduction phenomena in BaO. Clear BaO crystals have been grown by a vapor deposition technique[1] and red crystals of BaO have been grown by solution in barium.[2] Pell[3] has measured the Hall effect in both kinds of crystals and found that semiconduction is always n type. Redington[4] has measured the diffusion of Ba^{140} in the clear crystals.

Since conductivity is n type, one should expect that the electron donors in a chemically pure BaO crystal would be either interstitial barium, oxygen vacancies, or some aggregations of such defects. If, in addition, the crystal contains appreciable chemical impurities, substitutional defects might constitute the donors. In order to decide which among these possibilities is the principal type of donor, we have first studied the defects responsible for a stoichiometric excess of barium. The results presented below seem to indicate that the principal effect of tempering BaO crystals in an atmosphere of barium (or other reducing agents) is the creation of oxygen vacancies.

Suggestions have occasionally been made in the oxide-coated cathode literature that a stoichiometric excess of barium in BaO was probably in the lattice primarily through the presence of oxygen vacancies.[5] These suggestions have been based on an analogy with the alkali halides and on the existence of considerable lattice strain around an interstitial Ba atom because of its large size.

Dash[6] has heated BaO crystals in atmospheres of Ba, Ca, Mg, and Al.[7] He measured the optical absorption and found that in each case the absorption band was the same (the absorption gives a blue color to the crystals). Hence the type of lattice defect responsible for the optical absorption is the same in each case, and must be either interstitial barium, oxygen vacancies or aggregates of such defects.

In order to determine which of these defects predominates in additively colored BaO crystals, the diffusion of the blue coloration was studied. The results are presented in Part II and show that this diffusion is quite different from the diffusion of Ba^{140} measured by Redington.[4] Hence the coloration is not produced by diffusing barium and can only be caused by oxygen vacancies or aggregates thereof. Part III gives a rough comparison of optical and chemical determinations of the stoichiometric deficiency of oxygen, from which it is concluded that the barium excess is probably dispersed in the lattice in atomic units rather than in colloidal aggregates.

II. DIFFUSION OF COLORATION

Single crystals[1] of BaO were cleaved to provide samples about 3×3×3 mm. A crystal was placed on an MgO crystal in one (closed) end of a cylindrical enclosure machined from "Puron" (high purity iron). A few cubic millimeters of King Laboratories' barium metal (99+ percent pure) was placed near the other (open) end of the Puron tube and the tube was closed with a well-fitting Puron plug. The inside dimensions of the enclosure were 15/64 in. diameter×5 in. long. Thermocouples were attached to the tube at the position of the crystal and near the other end. This assembly was placed in a nichrome tube which was sealed at one end and which was connected to a water-cooled brass vacuum system at the other end. The system was evacuated with a forepump and liquid nitrogen trap. The nichrome tube was inserted through a hole in the door of a "Globar" furnace, with the water-cooled brass parts remaining outside the furnace.

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* This work has received support from the U. S. Office of Naval Research.

[1] Sproull, Dash, Tyler, and Moore, Rev. Sci. Instr. **22**, 410 (1951).

[2] G. Libowitz, J. Am. Chem. Soc. **75**, 1501 (1953).

[3] E. M. Pell, Phys. Rev. **87**, 457 (1952).

[4] R. W. Redington, Phys. Rev. **87**, 1066 (1952).

[5] See, for example, G. Herrmann and S. Wagener, *Die Oxydkathode* (J. A. Barth, Leipzig, 1948), second edition, Vol. I, pp. 96–97; A. S. Eisenstein, in *Advances in Electronics* (Academic Press, Inc., New York, 1948), Vol. I, pp. 8–9.

[6] W. C. Dash, thesis, Cornell, 1952 (unpublished), and Phys. Rev. **91**, 68 (1953).

[7] Crystals were also heated in contact with finely divided carbon; the same kind of effect was thereby produced as in the metal treatments, but it was considerably smaller in magnitude.

The arrangement described provided an inert enclosure with a temperature gradient along the axis of the tube. The crystal was at the hot end and the plug at the cool end. After an initial outgassing period the temperature of the enclosure was raised to the desired value. Condensation of barium then sealed the plugged end of the tube. No liquid barium could come in contact with the crystal,[8] which was about 1 cm or more from the source of barium vapor.

After heating the crystal at a constant temperature for a measured time, the crystal was cooled quickly, removed, and cleaved to provide a slab approximately 3×3 mm and from 0.35 to 0.65 mm thick. This slab was taken from the center of the original cube. It was encased in "Bioplastic" in the drybox.[9]

Figure 1 consists of photographs of sections of such crystals. The crystal of Fig. 1(a) was colored uniformly by heating for 3 hours at 1120°C in an atmosphere of barium. It was then heated to 1090°C for 7 minutes in a vacuum, and bleaching started at the surface (bottom in the figure) and moved inward. However, the distribution of coloration density did not at all obey a diffusion equation; the crystal is completely clear (except for scattered light at the edge) up to a certain distance and abruptly changes to a coloration unchanged by the second heating. This situation is similar to that found by Stasiw[10] in KCl at low temperatures (<500°C) and thought by him to be caused by the formation of colloidal K. Since this phenomenon occurs near the *upper* end of the accessible temperature range in BaO, bleaching experiments could not be used to obtain diffusion constants. Another bleaching run was made at 840°C and this gave results like Fig. 1(a); from these two runs one can estimate the temperature dependence of the bleaching process to correspond to an activation energy of ~1.2 ev (assuming it is an exponential function of temperature).

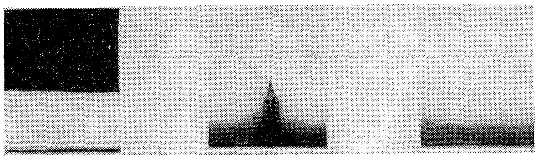

FIG. 1. Photographs by transmitted light of BaO crystals with excess barium. (a) shows the bleaching of an originally uniformly colored crystal; (b) and (c) show the diffusion of coloration into clear crystals.

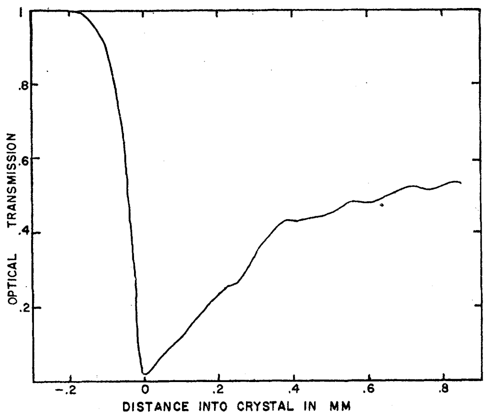

FIG. 2. Microdensitometer record of optical transmission *vs* distance into a BaO crystal. The crystal was treated for 260 hours at 815°C in an atmosphere of barium. The densitometer slit width was 0.02 mm. The crystal was 0.4 mm thick.

Because bleaching did not appear to be a simple diffusion process, the chief experiments consisted of measuring the rate of diffusion of coloration *into* clear crystals. Figures 1(b) and 1(c) show sections of such crystals. In Fig. 1(b) diffusion has proceeded rapidly along a flaw (which had not been apparent before heating the crystal in barium), and therefore such a section is of no value for quantitative measurements. The section shown in 1(c) is typical of those measured.

The optical density as a function of the distance from the surface which had been exposed to barium vapor was measured with a projection microdensitometer.[11] A glass filter (Corning No. 3484) and $CuCl_2$ filter (1 percent solution, 1 cm thick) was used to transmit a narrow band of wavelengths near 2.0 electron volts, which is the peak of the absorption band.

Figure 2 shows a densitometer record of optical transmission *vs* distance into the crystal. These data are plotted again (solid line) in Fig. 3 on a logarithmic scale, so the ordinate is proportional to the absorption constant A. Since the same spectral dependence of optical absorption was found under a variety of temperature and time conditions, it is apparent that the absorption in Fig. 3 is produced by a single type of absorbing center and that the concentration of this center decreases toward the center of the crystal. Furthermore, the concentration should be[12] a constant times A.

The diffusion constant for the motion of the coloration was obtained from curves such as Fig. 3 by comparing them with the one-dimensional diffusion equation,

$$A = A_0 + A_1\{1 - \mathrm{erf}(x^2/4Dt)^{\frac{1}{2}}\}, \qquad (1)$$

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[8] This precaution was taken since observations by Redington, Dash, and the authors indicated that whenever BaO crystals were heated in contact with liquid barium, the crystals exhibited the red coloration characteristic of crystals grown from solution in barium (reference 2). The coloration density in such cases was always constant to a definite depth (a function of temperature and time) and zero beyond that depth. The cause of this coloration is not yet known, but the circumstances under which it arises suggest colloidal barium or aggregations of oxygen vacancies.

[9] This protects the crystal from the atmosphere; after a few days the crystal so encased begins to show decomposition, but the densitometer data was taken within a day after cleaving the crystal.

[10] O. Stasiw, Z. tech. Phys. **16**, 343 (1935). See especially Fig. 4.

[11] The authors are indebted to Dr. C. W. Gartlein for help in using this instrument, which he developed.

[12] A. Smakula, Z. Physik **59**, 603 (1930); F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

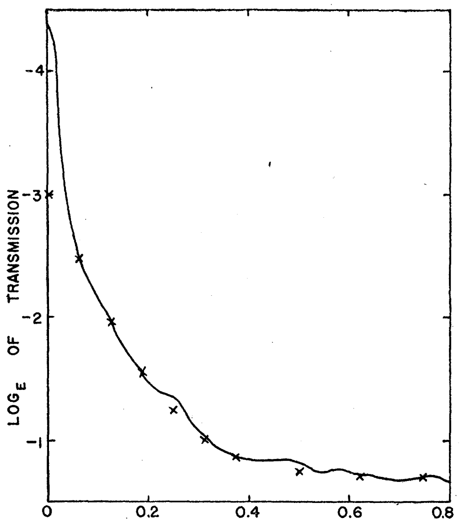

FIG. 3. The solid line is a replot on a logarithmic scale of the data of Fig. 2. The crosses are a fit of Eq. (1) to the data, giving $D=2.30\times10^{-10}$ cm²/sec.

where x is distance into the crystal in cm, D is the diffusion constant in cm²/sec, A_0 and A_1 are constants and t is the time (in sec) of tempering in barium vapor. This equation is valid[13] for a semi-infinite crystal with either of the following boundary conditions:

1. A constant stoichiometric excess of barium at the surface, and initially a constant (or zero) excess of barium throughout the crystal. 2. Zero oxygen concentration at the surface, and initially a constant (or zero, in which case $A_0=A_1$) excess of barium throughout the crystal. The crystals used were not "semi-infinite," but the distribution for the solid bounded by two parallel planes[14] is nearly identical with (1) when the width of the crystal (in the direction of x) is of the order of 10 diffusion lengths $[(Dt)^{\frac{1}{2}}]$ or more. In practice, crystal widths satisfied this condition. Since the crystals were also finite in the y and z directions, there is diffusion in these directions as well. The experimental conditions were that y and z were constants, and therefore[15] the only effect of y and z diffusion was to increase A_0 in Eq. (1). The densitometer record of the edge of a transparent (uncolored) crystal showed strong absorption for a distance of 0.05 mm either side of the edge, caused by scattering and an imperfect edge. Therefore the part of the curve of Fig. 3 that was within 0.05 mm of $x=0$ was ignored in fitting Eq. (1) to it.

A typical fit of (1) to data is indicated by the crosses of Fig. 3. Although 3 parameters were used in fitting, two of these (A_0 and A_1) do not affect the shape of the curve. The agreement is therefore satisfactory and D can be computed with precision of ±30 percent or better.

Figure 4 is a plot of $\log_{10}D$ *versus* $1000/T$ on which the estimates of possible errors in D are shown. The points follow a straight line, which probably indicates that there is a single activation energy of 2.8 electron volts for diffusion of the coloration in this temperature range. The D_0 value is 2500 cm²/sec.[16]

Figure 4 bears no resemblance to Redington's[4] results for the diffusion of barium into barium oxide crystals. The most important difference is that he found activation energies of about 11 ev and about 0.4 ev, but no intermediate values. We therefore conclude that the coloration process does not transport barium; if it does, it should have been the dominant process in Redington's experiments and would have been easily observed.

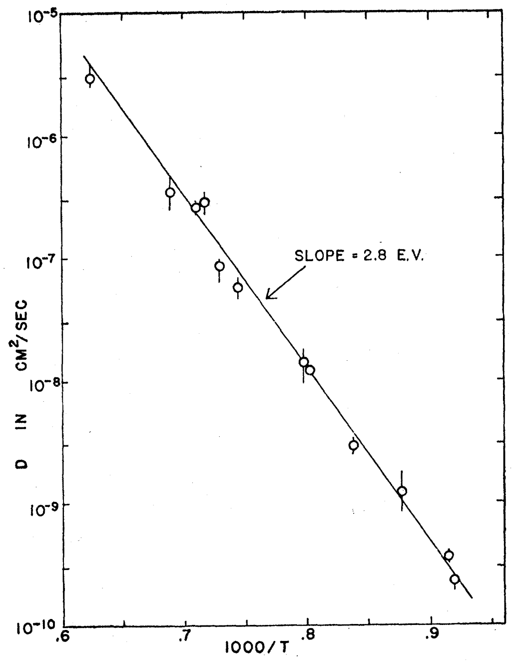

FIG. 4. Diffusion constant D as a function of absolute temperature T. The vertical lines are estimates of errors in D values based on the extent to which Eq. (1) fits the data. For all points except the top point the errors in temperature and time were negligible compared to the possible error in fitting the curves. The temperature uncertainty in the top point was about ±25° and the time uncertainty ±10 percent.

It might be thought that the rate-limiting process in the diffusion of the coloration would be the excitation of the electrons bound to the defects, the defect moving more readily when it has lost its electron. This would require that the binding energy of an electron to a defect be 2.8 ev. It is unlikely that this can be the case in BaO since 2.8 ev is much higher than the probable

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[13] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford, University Press, London, 1947).

[14] Reference 13, pp. 82–83.

[15] Reference 13, p. 162.

[16] The vapor pressure of barium is, of course, different at the different temperatures at which the crystals were tempered. This can change the total amount of excess barium in the crystal, but it seems impossible that the distribution (relative concentration as a function of distance) of barium could be seriously affected by this change. The vapor pressure of barium rises with an activation energy of 1.9 ev. [See J. P. Blewett, J. Appl. Phys. **10**, 670 (1939).]

electronic activation energies.[17] Furthermore it seems unlikely that the coloration is caused by electrons diffusing into the crystal and being trapped at the impurities, interstitials, or vacancies already existing in the crystal, since: 1. The attainable absorption constants reach 200 cm^{-1}; and 2. to preserve electrical neutrality barium would have to move into the crystal.

We conclude from these considerations that the only possibility consistent with these experiments is that the coloration is caused by the diffusion of neutral oxygen to the surface to combine there with barium (or other reducing agent[6]). The optical absorption band is then caused by the electrons trapped at the oxygen vacancies. In order to preserve electrical neutrality and in the absence of any other diffusion process, two electrons must be trapped at each oxygen vacancy. This situation is analogous to the F' centers in the alkali halides. Since this absorption band is produced with a variety of reducing-agent treatments, we conclude that the principal lattice defects in BaO with a stoichiometric excess of metal are oxygen vacancies.

III. CHEMICAL AND OPTICAL DETERMINATIONS OF EXCESS BARIUM

Crystals of BaO can be colored uniformly to depths of the order of 1 mm by heating at about 1100°C for several hours in an atmosphere of barium and then quenching to room temperature. Two such crystals were studied to compare the amount of excess barium in the lattice determined chemically with that determined by the optical absorption, using the Smakula formula.[12] (Kleinschrod[18] performed such experiments on KCl and Mott and Gurney[19] have computed the oscillator strength f for absorption by F-center electrons from this data.)

The chemical determination of the stoichiometric excess of barium was made by the hydrogen liberation method.[2,20] The crystal was permitted to react with water vapor in a vacuum system and then the excess water was removed by a liquid nitrogen trap. The gas remaining in the vacuum system was hydrogen from the reaction $\text{Ba}+2\text{H}_2\text{O}=\text{Ba(OH)}_2+\text{H}_2\text{(gas)}$. By measuring the hydrogen pressure with a thermocouple gauge the amount of excess Ba in the BaO was measured.[21] The results of these determinations on two crystals are shown in Table I. The volume of each crystal was about 5 cubic mm.

TABLE I. Comparison of amounts of excess metal in two crystal samples. The optical measurements are probably correct to within a factor of 2. The chemical measurements are ±20 per cent.

Crystal No.	Barium vapor treatment	Excess barium (chemical) (%)	Excess barium (optical) (%)
1	1120°C for 5 hours	0.04	0.03
2	1050°C for 3 hours	0.03	0.02

The optical absorption constant of a section of crystal No. 2 as a function of photon energy was measured and gave results similar to those found by Dash.[6] The shape of the absorption curve permits only a very rough estimate of the number N_0 of absorbing centers per cc. The peak height of this absorption band is about 160 cm^{-1}, and the full width at half-maximum is estimated to be about 2 ev. One can estimate N_0 from the Smakula formula[12,22]

$$N_0=1.29\times10^{17}\frac{n}{f(n^2+2)^2}W\alpha\left\{\frac{4E_0+W}{4E_0+2W}\right\}.$$

Here W is the full width at half-maximum in electron volts, α is the maximum absorption constant (at the center of the band) in cm^{-1}, n is the index of refraction (2.0 for BaO), f is the oscillator strength, and E_0 is the photon energy at the band center in electron volts. An oscillator strength $f=\frac{1}{2}$ will be assumed, but all that one knows about f until better measurements are available is that it is probably less than unity. N_0 for crystal No. 2 is thus about 4×10^{18} cm^{-3}. If each such center is an oxygen vacancy, there would be about 0.02 percent excess barium (by weight). A similar figure was also computed for crystal No. 1, and these appear as the last column in Table I.

The principal difficulty with applying this approach to the above data is that the spectral dependence[6] of the optical absorption does not indicate a simple band, particularly in crystals colored densely enough to make good chemical determinations possible. It is therefore not yet possible to compute an oscillator strength with an interesting precision. The comparison of Table I does enable us to conclude, however, that the excess barium is probably atomically dispersed in the lattice, rather than as colloidal metal; if much of the barium were present in aggregations of many atoms, the chemical determination would show far more barium than that computed from the Smakula formula.[23]

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[17] Hannay, McNair, and White, J. Appl. Phys. **20**, 669 (1949); W. W. Tyler and R. L. Sproull, Phys. Rev. **83**, 548 (1951).

[18] F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).

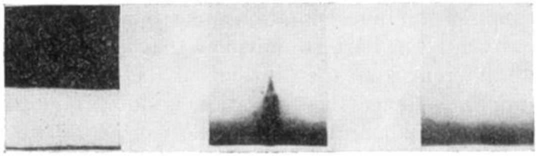
[19] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 115.

[20] T. P. Berdennikowa, Physik. Z. Sowjetunion **2**, 77 (1932).

[21] If the crystal were stoichiometric BaO, hydration would of course occur but no hydrogen would be liberated.

[22] R. Hilsch and R. W. Pohl, Z. Physik **68**, 721 (1931), Eq. (1), p. 733. This formula has been widely quoted and misquoted, since there is a typographical error in Smakula's final equation [reference 12, Eq. (4), p. 607]: the "n_0" in the denominator should be "n_0^2." (n_0 is the index of refraction). This error makes a difference of only a factor of 1.6 in KCl but causes more trouble in materials like BaO with larger indices of refraction. This situation is alleviated, but complicated, by the fact that the Hilsch and Pohl article contains correct simplifications that are valid in most cases. Many authors appear to have *quoted* the incorrect equation (from Smakula's paper or from review articles or books) but *used* the correct expression from Hilsch and Pohl.

[23] If the absorbing center were a combination of two oxygen vacancies and one barium vacancy, there would be one excess barium atom per center and hence we could not distinguish this combination from a single oxygen vacancy by measurements like those described. See Seitz's model (reference 12, p. 405) for the "M center."



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