optical spectra) for the existence of trapped electron centers, at this higher temperature, which could supply electrons in sufficient numbers. F centers are ruled out as a source of electrons since they are stable[2] up to 100°C and in any case their population relative to NH_3X is exceedingly small. It appears likely that annihilation occurs by some dissociation of the NH_3X molecule, illustrated by the latter three possibilities.

In each of the last three cases, one of the direct dissociation products is a paramagnetic species (H°, NH_2, X°) which is then required to combine with another to produce a stable nonparamagnetic molecule. The intermediate paramagnetic product must be able to diffuse swiftly through the lattice. For this reason, the second process appears most likely as the actual means of annihilation of NH_3X centers.

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Additive Coloration of Alkaline-Earth Chalcogenides*

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Procedures for the additive coloration of single crystals of the alkaline-earth chalcogenides are described. Both the coloring bombs and the two-section vacuum furnace are made of tantalum. Coloring temperatures used range from 1500 to 1900°C, with the pressure of the metallic vapor ranging up to several atmospheres.

I. INTRODUCTION

IN the additive coloring process, color centers are introduced into a solid by heating the crystals in a vapor of their metallic constituent. The literature pertaining to the color centers thus produced in the alkali halides is vast.[1] However, very few studies have been reported for similar studies in the alkaline-earth chalcogenides. Such studies are of great interest because the alkaline-earth chalcogenides may be regarded as divalent counterparts to the alkali halides. Sproull *et al.*[2–4] have identified and studied the F' centers (anion vacancies containing two electrons) in additively colored barium oxide crystals. Weber[5] reported color centers induced in magnesium oxide crystals by heating them in oxygen and in calcium and magnesium vapors. However, Soshea *et al.*[6] showed that the oxygen-induced color centers in Weber's work were due to impurities and cast doubt on Weber's interpretation of his metal-induced absorption bands. Studies of the optical absorption induced in several of the alkaline-earth oxides by various forms of irradiation have also been reported[6,7]; however, the complexity of the absorption spectra produced makes it difficult to identify the color centers responsible for the various observed bands.

In the present investigation, techniques have been developed for carrying out the additive coloring process at much higher temperatures than have hitherto been achieved. Using coloring temperatures as high as 1900°C, both F and F' centers, that is, anion vacancies containing one and two electrons, respectively, have been produced in calcium oxide[8] and strontium oxide[9] and F' centers have been produced in magnesium oxide.[10] These color centers have been studied both as a function of the coloring temperature and the pressure of the vapor of the metallic constituent.

The experimental technique used is an adaptation of the familiar double-furnace principles commonly employed in the additive coloration of the alkali halides.

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[1] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Co., New York, 1962).

[2] R. L. Sproull, R. S. Bever, and G. Libowitz, Phys. Rev. **92**, 77 (1953).

[3] W. C. Dash, Phys. Rev. **92**, 68 (1953).

[4] C. Timmer, J. Appl. Phys. **28**, 495 (1957).

[5] H. Weber, Physik **130**, 392 (1951).

[6] R. W. Soshea, A. J. Dekker, and J. P. Sturtz, J. Phys. Chem. Solids **5**, 23 (1958).

[7] Y. Chen and W. A. Sibley, Phys. Rev. **154**, 842 (1967).

[8] W. C. Ward and E. B. Hensley, following paper, Phys. Rev. **175**, 1230 (1968).

[9] B. P. Johnson and E. B. Hensley (to be published); see also Bull. Am. Phys. Soc. **12**, 411 (1967).

[10] K. L. Kroes and E. B. Hensley (to be published); see also Bull. Am. Phys. Soc. **13**, 420 (1968).

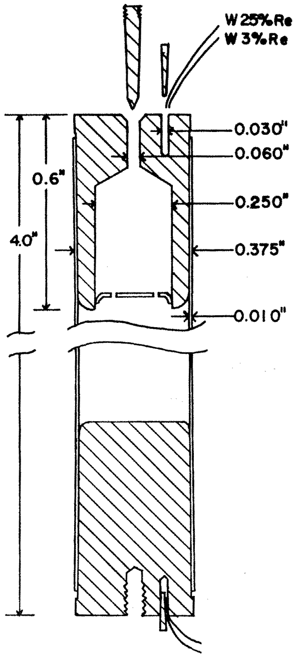

FIG. 1. Cross-sectional view of coloring bomb. The construction was entirely of tantalum except for the thermocouples.

The crystals to be colored were sealed in one end of a long metal cylinder. The metal to be used in producing the metallic vapor was sealed in the opposite end. The temperature of the crystal-end of the coloring bomb was then raised to the desired coloring temperature and the opposite end of the coloring bomb was heated to a temperature that would produce the desired pressure of the metallic vapor.

II. APPARATUS

The construction of the coloring bomb is illustrated in Fig. 1. Because of the high temperatures to be employed, the composition was essentially restricted to the refractory metals. Although attempts were made to use molybdenum tubing, this was found to be unsatisfactory as the fibrous structure of this metal led to the development of small longitudinal cracks. Seamless tantalum tubing was finally chosen and found to be quite satisfactory. No deleterious effects from the metallic vapors at the high temperatures used have been observed. The end plugs were machined from solid rods of tantalum and were given a 2° taper so that they could be press fitted into the ends of the tantalum tubing.

A serious problem encountered in the early stages of this work was the seizing of these plugs to the tantalum tube, tearing a channel through which the metallic vapor could escape from the bomb. This problem was eventually solved by polishing both surfaces and applying a thin coating of an antiseizing compound[11] prior to pressing the plugs into the tube.

As is illustrated in Fig. 1, the upper plug was bored out to contain the crystal which was then held in place by a small disk of tantalum metal pressed into the opening. This disk was perforated with small holes to permit the passage of the metallic vapor. The massiveness of the plug wall insured the uniformity of the coloring temperature. The bombs were evacuated through a small hole in the top plug which was later sealed with a tapered pin.

The temperatures of the two ends of the bomb were measured using tungsten–3%-rhenium versus tungsten–25%-rhenium thermocouple wires 0.005 in. in diameter. No attempt was made to weld a junction between the wires because of the extreme brittleness resulting from the welding process. Instead, the wires were pinned into a 0.030-in.-diam hole in the plug by means of a tapered tantalum pin. The fact that the two thermocouple wires were not in direct contact did not matter since their temperatures and that of the tantalum pin were equal. An iron support rod was threaded into the bottom plug of the bomb to provide support in the furnace.

Although these bombs were completely satisfactory for both strontium oxide and calcium oxide, some difficulties were encountered at the higher pressures and temperatures required for coloring magnesium oxide. At temperatures above 1800°C and pressures higher than one atmosphere, the strength of the walls of the coloring bomb proved to be inadequate, resulting in a ballooning of the walls with the eventual rupture of the bombs. The substitution of 0.020-in.-wall tubing improved this situation. However, for the highest temperatures and pressures it was found necessary to tightly wrap the bombs with 0.005-in.-diam tungsten wire. This technique proved completely satisfactory for the highest temperatures and pressures encountered to date.

Details of the construction of the coloring furnace are shown in Fig. 2. The heating element consists of a vertical tantalum cylinder which is divided into two sections in order to separately control the temperatures of the two ends of the coloring bomb. The horizontal tantalum strips (F, I, and K) not only support the heater and provide electrical connections for passing current longitudinally through the heater, but also act as thermal insulators, greatly improving the temperature distribution along the heater. Many hours of usable life can be obtained from these heaters with a vacuum of about 10^{-6} Torr.

III. DISCUSSION

Prior to coloring a crystal it was found desirable to anneal the crystal at a temperature near that to be used in the coloring process. This removed changes in the absorption spectra due to temperature alone, making comparisons of the uncolored crystal with the colored crystal more meaningful. For this purpose, a

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[11] Such as Molykote G, supplied by the Alpha-Molykote Corp.

bomb with the upper tantalum plug open at the top was used.

SrO, CaO, and MgO crystals were usually annealed at temperatures around 1500°C. Because of the higher coloring temperatures involved with MgO, a higher annealing temperature would have been desirable. However, it was found that in the absence of Mg vapor at temperatures of about 1600°C or higher, MgO reacted with the Ta to give a compound identified by x-ray diffraction as $MgTa_2O_6$. This compound was molten at the reaction temperature which accelerated the rate of the reaction. In the presence of Mg vapor, this reaction was not observed to occur.

When the objective of a coloring run was to make quantitative measurements of the absorption induced by the coloring process, the annealed crystals were polished and absorption measurements of the uncolored crystals were recorded. One or more of of these crystals was then placed in the upper plug of the coloring bomb. Turnings of the desired metal were loaded into the bottom of the bomb, typically to a depth of about 1 in. With the top plug lubricated with the antiseizing compound, it was pressed into the tube with a small arbor press. The thermocouples were then pinned into the upper and lower plugs and the bomb firmly positioned in the furnace.

After evacuating the furnace chamber, the bomb was outgassed for about 30 min at a temperature of about 500°C. The tapered pin, which was threaded into the end of the movable rod (A), was then inserted into the hole in the top plug and tapped into place. The movable rod was then unscrewed from the pin and retracted. The temperature of the upper heater was slowly raised to the desired level for the coloring process. After this temperature was obtained, the temperature of the lower heater was raised to the level that would produce the desired pressure of the metallic vapor as determined from published vapor pressure data.

The minimum temperatures and coloring times, necessary to insure that the coloration process had reached equilibrium and that the density of color centers was uniform throughout the crystal, were not determined. However the lowest values used that resulted in equilibrium for crystals about 1 mm thick can be stated. For SrO, these were 1530°C for 2.5 h; for CaO, 1650°C for 5 h; and for MgO, 1600°C for $\frac{1}{2}$ h. It is believed that these can all be reduced, especially for CaO.

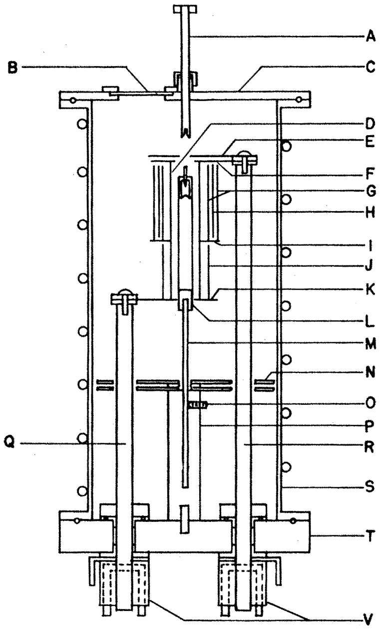

FIG. 2. Details of coloring furnace. The components are: (A) movable brass rod for inserting pin in top of bomb; (B) glass viewing window; (C) brass top, sealed with O ring; (D) heating element made of 0.003-in.-thick tantalum foil, 0.75 in. in diameter, 5 in. long, with spot-welded seam; (E) tantalum heat shield; (F) top heater support and current conductor of 0.010-in.-thick tantalum; (G) concentric heat shields of 0.003-in. tantalum foil, 1.0 in. and 1.25 in. in diameter, respectively; (H) two or three layers of 0.001-in. tantalum foil, loosely wrapped; (I) middle heater support which extends back to a vertical copper rod (not visible) connected to base; (J) concentric heat shield; (K) lower heater support and current conductor (heaters and concentric shields are attached to horizontal supports by small, spot-welded tabs of tantalum); (L) coloring bomb; (M) iron support rod; (N) stainless steel heat shield disks; (O) one of three set screws for positioning bomb; (P) lava support; (Q,R) copper conductors insulated from base by canvas based phenolic washers and sealed with O rings; (S) water-cooled brass chamber, 6 in. in diameter and 13 in. high, sealed to base by O ring; (T) steel base plate; (V) water-cooled nuts. The upper and lower sections of the heater were supplied by 5-V, 200-A and 5-V, 60-A transformers, respectively, each controlled by a variable autotransformer. The chamber was evacuated by CVC-type VMF20 diffusion pump.

After the coloring process was completed, the bombs were sawed open and the crystals removed. The end plugs could usually be salvaged and used for several bombs.

Results obtained for the additive coloring of CaO [8] are presented in the following paper, and results for SrO [9] and MgO [10] are now being prepared for publication.