

## VISIBLE RADIATION FROM COLUMBIUM OXIDE

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## ABSTRACT

**Radiation from columbium oxide, heated in the hydrogen flame** to various temperatures below 1000°C, was studied with the spectrophotometer. Two distinct and strikingly different types of visible radiation were found. *Phase O* (in the oxidizing region of the flame) is selective with luminescence bands superimposed upon the radiation due to temperature. *Phase R* (in the reducing region) resembles that of a black body both as to spectral distribution and intensity. This phase was traced to the formation of a lower oxide  $\text{Cb}_2\text{O}_4$  which is jet black at temperatures of incandescence and radiates as a black body. The change from one phase to the other was instantaneous when the oxide was shifted in the flame.

**Formation of black suboxides in the hydrogen flame.**—Similar black suboxides were observed in the case of *titanium oxide* and *tantalum oxide*, and to the formation of these in the reducing flame, phase R is doubtless to be ascribed whenever radiation of that type occurs.

THIS white and highly refractory oxide ( $\text{Cb}_2\text{O}_5$ ) exhibits certain remarkable peculiarities as to the character of its visible radiation at the lower temperatures of incandescence. When a fragment a few millimeters in diameter is gradually inserted from the side into the outer layers of a hydrogen flame, instead of becoming "red hot" it glows with a pale greenish blue color. Pushed further into the flame the color of the incandescent fragment changes abruptly to a deep red.

The contrast is a most striking one and the transition may readily be shown to depend on the position of the oxide within the flame rather than upon any change of temperature. These two types of radiation, which in conformity with the previous study of somewhat similar conditions in the incandescence of titanium oxide<sup>1</sup> we shall call respectively *phase O* and *phase R*, are mutually and instantly interchangeable. So sharp is the boundary between the portions of the flame where they occur that it is easy to move the bit of oxide into a position where the inner part, lying nearer to the axis of the flame, is red, and the outer, in the oxidizing layer, is green-blue. If now the piece of oxide be made to oscillate at right angles to the axis of the flame this boundary will be seen to be fixed with reference to the flame. There is no perceptible lag, such as would be easily observable if the change depended upon alternate heating or cooling of the oxide.

<sup>1</sup> Nichols, Phys. Rev. (2) **22**, 420 (1923).

## APPROXIMATE ANALYSIS OF THE VISIBLE RADIATION

Through a spectroscope of low dispersion the spectra of both phases are seen to be continuous but the appearance of that of phase O suggests a group of very broad nearly submerged bands covering the entire range of the visible region. For the comparison of these spectra the following scheme was adopted.

Across the outer surface of the base of an alundum crucible a shallow depression was cut about .05 cm deep and 1.0 cm in width. This served as a holder for a thin layer of the oxide which could be pressed into the channel in powdered form, completely filling it, with the smooth face of the layer flush with the alundum surface on either side. Thus mounted it could be raised into a vertical plane and heated by means of the hydrogen flame without breaking down. With a camel's hair brush half of the surface of the oxide was moistened with a solution of uranyl chloride leaving a sharp dividing line *LL* (Fig. 1). After heating, the moistened region remained impregnated with uranium oxide, which imparted to it the radiating properties of a very nearly perfect black body.

When a flame of hydrogen *HH* from a small vertical jet *J* was brought up until its outer layers were in contact with the layer of oxide, the region *B* to the left of the median line, became red hot, while the corresponding region *W* to the right assumed the radiating condition known as *phase O*. An image of the contiguous fields of glowing material was then sharply focussed in the vertical transverse plane, passing through one collimator slit of a large Hilger spectrophotometer with the line *LL* parallel to the slit. By turning a sheet of plate glass *G* (Fig. 2) in the path of the beam of light, the image of *BW* could be shifted to the right or left so that the portion corresponding to *B* alone or to *W* alone would fall upon the slit *S*. Thus any desired wave-length of the spectrum of the light from *B* or *W* could be compared with the corresponding wave-length of the comparison lamp which was mounted, in the manner described in various earlier papers, on a photometer bar before the other slit of the spectrophotometer. The comparison source was a tungsten filament of low voltage maintained by a storage battery at approximately 2000°K. By turning *G* through a pre-determined angle the spectrum under observation could be shifted back

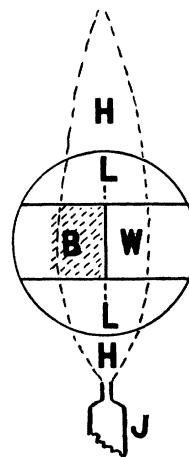


Fig. 1.

and forth between  $B$  and  $W$  at will and thus, by the method of substitution, the relation of these spectra to one another was readily determined.

By moving the hydrogen flame a trifle nearer to the base of the crucible and thus converting phase O of the radiation of the  $\text{Cb}_2\text{O}_3$  into phase R, a similar set of observations gave the relations between the spectrum of this phase and the spectrum of the comparison lamp or of the uranium oxide. These measurements give directly the composition of the visible radiation from the glowing oxides in terms of the composition of the light from the comparison lamp.

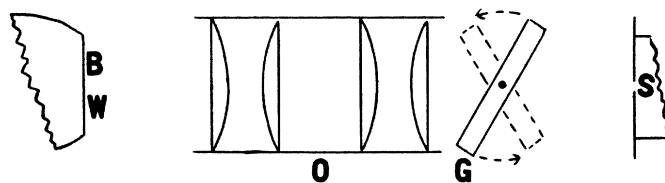


Fig. 2.

In Table I, as already stated,  $I_0$  is the brightness of the glowing columbium oxide (phase O) in terms of that of the corresponding region in the spectrum of the comparison lamp. The conditions of the measurements were such that the two spectra were very nearly of equal brightness in the yellow (at  $.5890\mu$ ). Similarly  $I_B$  is the brightness, under the same conditions of comparison, of the glowing uranium oxide. To make the values of  $I_0$  and  $I_B$  as nearly as possible strictly comparable, measurements of the two were made alternately throughout the spectrum.

TABLE I  
*Distribution of intensities in the spectrum  $\text{Cb}_2\text{O}_3$ .*

$\lambda$	$I_0$	$I_B$	$I_0/I_B$	$\lambda$	$I_0$	$I_B$	$I_0/I_B$
$.4590\mu$	.0930	.0240	3.88	$.5771\mu$	1.320	2834	4.76
$.4675$	.1551	.0266	5.83	$.6018$	.9766	4852	2.01
$.4793$	.2488	.0310	8.02	$.6298$	1.008	.5333	1.89
$.4918$	.2825	.0363	7.79	$.6620$	.8503	.8547	0.996
$.5052$	.2644	.0472	5.99	$.6765$	1.468	1.294	1.134
$.5175$	.2644	.0643	4.13	$.6924$	1.276	1.693	0.754
$.5372$	.6645	.1480	4.49	$.7007$	1.562	1.762	0.886
$.5557$	.1457	.2635	5.53				

In Fig. 3,  $I_0$  is plotted as function of the wave-length and the corresponding intensity of the spectrum of the comparison lamp is represented by the horizontal line  $TT$  having the ordinate unity. Clearly the spectrum of  $\text{Cb}_2\text{O}_3$  under conditions which give radiation of phase O, consists of several rather broad overlapping bands. Uranium oxide, on the contrary, at the same temperature ( $820^\circ\text{C}$  as determined by the optical

pyrometer), shows no indications of a banded spectrum. The curve  $I_B$  (also given in Fig. 3) is of the character which one would expect to obtain for a non-selective radiator at the temperature in question.

Knowing the distribution of intensities in the spectrum of the comparison lamp, the values of  $I_0$  might readily be expressed in terms of relative energy, but it is more interesting for our present purpose to compare the radiation of the glowing columbian oxide with that of a black body at the same temperature. This comparison is afforded by the ratio  $I_0/I_B$  for the various regions of the spectrum and is given graphically in Fig. 4 where

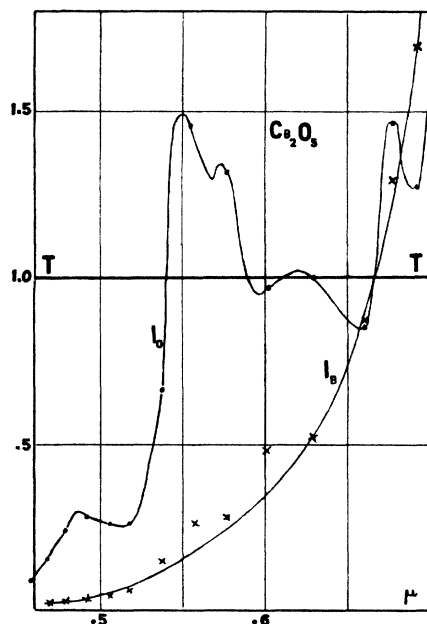


Fig. 3. Intensity distribution  $I_0$  of spectrum of  $\text{Cb}_2\text{O}_5$ , taking the comparison spectrum as unity,  $TT$ .

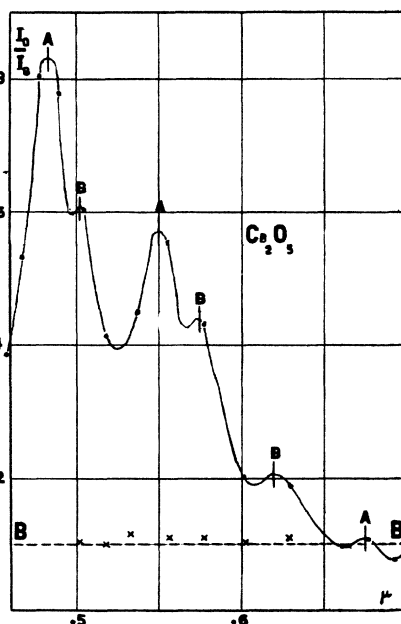


Fig. 4. Intensity distribution of spectrum of  $\text{Cb}_2\text{O}_5$  referred to that of a black body taken as unity,  $BB$ .

$I_B$  is represented by the horizontal line  $BB$  of ordinate unity. The curve for  $I_0/I_B$  in this diagram brings out the crests of the overlapping bands more definitely than does the corresponding curve in Fig. 3. The resolution is not sufficient to bring out the finer structure of the spectrum but six crests may be quite closely located.

H. L. Howes<sup>2</sup> in a study of calcium oxide and of certain sulphides when excited to luminescence by the hydrogen flame, has found their spectra to be made up of overlapping bands equidistant as to frequency and coinci-

<sup>2</sup> H. L. Howes, Phys. Rev. (2) **17**, 469 (1921).

dent with the bands of the same substances when excited by cathode rays.<sup>3</sup> More recently, Tanaka<sup>4</sup> in an exhaustive investigation of the cathodo-luminescent substances, made under the present writer's direction, has established a definite relation between the frequency interval between bands and the atomic weight of the activating element. A consideration of the frequency relations of the crests in Fig. 4 is therefore not without interest. Tanaka's interval for columbium would be very close to 21 and an inspection of the location of the bands in the spectrum now under consideration shows that they may in fact be arranged in two sets such that the distance, measured in frequency units, between neighboring members of a set is an even multiple of Tanaka's interval. Calling these sets *A* and *B* we find the following relations.

TABLE II  
*Frequency relations of the bands of phase O.*

Set A			Set B		
$\lambda$	$1/\lambda \times 10^3$	Differences	$\lambda$	$1/\lambda \times 10^3$	Differences
.4831 $\mu$	2070	252 = 21 $\times$ 12	.5020 $\mu$	1992	252 = 21 $\times$ 12
.5500	1818		.5747	1740	
.6748	1482	336 = 21 $\times$ 16	.6196	1614	126 = 21 $\times$ 6

It is believed that the crests recorded in Table II represent groups of bands rather than single bands, and experiments are in progress to determine by a photographic method the finer structure of this spectrum and of the spectra of other glowing oxides.

In the present investigation, as in some earlier studies of incandescent oxides, the visible radiation from uranium oxide has been taken as representing with sufficient closeness that of a black body of the same temperature. In support of this assumption the following observation may be cited. Into one end of a cylindrical copper block about 5 cm long and 2.5 cm in diameter, a hole about .5 cm in diameter and 4 cm in depth, was bored parallel to the axis. When the block was suspended over a large Bunsen burner and heated to uniform incandescence, the appearance of the end with the hole was as follows.

(1) With the flame adjusted so as to maintain the surface of the copper in a reduced metallic state, the aperture, because of the radiation under black body conditions from within, appeared as a cherry red disk on a very dark background.

<sup>3</sup> Nichols, Howes and Wilber, *Phys. Rev.* (2) **12**, 351 (1918).

<sup>4</sup> Tanaka, *Jour. Opt. Soc. Amer.* **7**, 287 (1924).

(2) With the flame shifted so as to oxidize the surface of the copper, the radiation from the end of the rod was so nearly equal to that from the hole that the latter was *just barely perceptible*.

(3) The flame having been extinguished and a small portion of the oxidized surface contiguous to the hole having been moistened with a solution of uranium chloride, the block was again heated to incandescence. It was now observed that in the oxidizing flame the patch to which the uranium chloride had been applied and which was now covered with a very thin layer of uranium oxide was scarcely to be distinguished from the surrounding surface *or from the hole*. In the reducing flame, however, this patch, which was not reduced by the flame, stood out against the much weaker radiation from the metallic copper and, so far as could be judged by the eye, was almost of the same brightness and color as the hole from which it could be distinguished only by its shape. Settings with the optical pyrometer when the block was at 870°C confirmed the judgment of the eye, the relative brightness being as follows; hole, 1.00; CuO, .954; uranium oxide, .954; metallic copper, .14. The value for copper is what one would expect, being intermediate between that given for the green .17 and for the extreme red .09.<sup>5</sup>

Quite aside from the above measurement, there can be no doubt in the mind of one who has seen them side by side upon the incandescent surface, of the essential equality of the two oxides, nor of their approximately complete blackness to one who has viewed them by reflected light at a temperature of 500° or more. This last observation was checked by measuring the melting point of minute crystals of KCl placed upon the incandescent oxide. The pyrometer, using the calibration given by the Bureau of Standards, yielded the accepted melting point within 3° when the settings were made upon the uranium oxide. It will be understood that these very high values of relative emissivity apply only to oxides formed by the hydrogen flame in the manner described and used practically in the nascent state, and not necessarily to these two substances in general.

#### PHASE O: A LUMINESCENT EFFECT

That the visible radiation indicated graphically in Fig. 4, is partly at least to be ascribed to luminescence is obvious when we consider that all intensities above the horizontal line *BB* or a line very near to that, are in excess of the black body intensities for the various wave-lengths and at the given temperature. That the portion of the area under the curve

<sup>5</sup> LeChatelier, Measurement of High Temperatures, Trans. by Burgess, p. 497.

which is due to temperature radiation must be much smaller than that which would correspond to a black body becomes obvious when we flood the radiating surface with white light strong enough to quench the incandescence. It is then seen that we have to do with an oxide which is *nearly white*, and therefore capable of relatively feeble radiation in accordance with the Kirchhoff relation.

In addition to the above criterion there are the following characteristics which suggest luminescence.

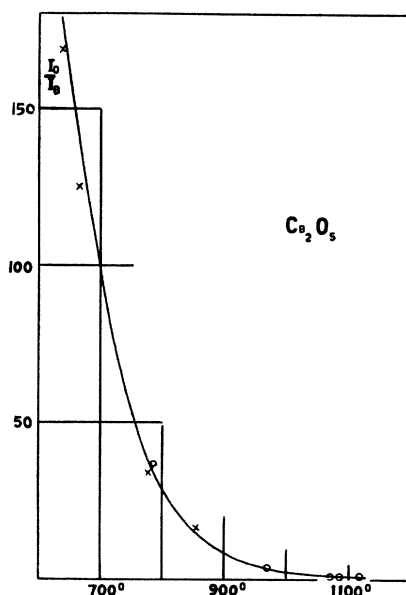


Fig. 5. Ratio of brightness to that of a black body, as a function of temperature.

(a) *The spectral structure.* The band structure, which has already been described, is characteristic of all known luminescence spectra.

(b) *The ratio of brightness to that of a black body of the same temperature diminishes rapidly with rising temperature and approaches unity at temperatures above 1000°.* The change of the ratio of  $I_0/I_B$  with the temperature is shown in Fig. 5 in which the observations grouped along the logarithmic curve indicate the ratios obtained in two overlapping runs, one for the lower, designated by crosses, and one for the higher ranges, designated by circles.

The curve in Fig. 5 is similar to those found for the *blue glow*<sup>6</sup> of such oxides as CaO, MgO, BeO, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>; but the luminescent bands

<sup>6</sup> Nichols and Howes, Jour. Opt. Soc. Am. **6**, 42 (1922); also Phys. Rev. (2) **19**, 300 (1922).

in the case of  $\text{Cb}_2\text{O}_5$  extend through the entire spectrum and the color of the glow is a very pale blue-green.

The point of lowest temperature in Fig. 5 represents very nearly the threshold for this type of luminescence for  $\text{Cb}_2\text{O}_5$ ; that is, at lower temperatures nothing is visible while when  $640^\circ$  is reached the effect appears quite suddenly.

(c) *Fatigue*. When a coating of the oxide not previously heated to incandescence is suddenly brought to a given temperature its initial brightness exceeds any subsequent value and it falls at first rapidly and then more and more slowly to a nearly constant state. This effect of fatigue, which is another of the characteristics of luminescence as distinguished from temperature radiation, is shown in the curve in Fig. 6, in which the abscissas are the times in minutes from the application of the flame, and the ordinates are intensities as expressed by the ratio  $I_0/I_B$ . It will be noted by comparison with Fig. 5 that the brightness falls to the value for the temperature in question,  $860^\circ\text{C}$ , after about 25 minutes.

Among the substances tested by the present writer in collaboration with Professor H. L. Howes in the preliminary study of incandescent oxides<sup>7</sup> was a mixture supposed to consist chiefly of the oxides of columbium and tantalum. This was designated tentatively as niobium oxide (and wrongly as  $\text{Nb}_2\text{O}_4$ ). The behavior of this substance corresponded in some respects to that of  $\text{Cb}_2\text{O}_5$ . It was, for example, luminescent throughout the visible spectrum with the greatest excess of radiation in the blue violet. It also ceased to luminesce at about  $1100^\circ\text{C}$ . It differed from our present oxide in showing signs of fusion just above  $1100^\circ$  instead of melting at  $1300^\circ$ , and it was strongly luminescent below the threshold value of  $640^\circ$ . Phase R, if it existed, was not observed.

#### OBSERVATIONS ON RADIATION OF PHASE R

As has been stated in the opening paragraph of this paper, a sudden transition in the type of radiation occurs when the columbium oxide is moved from the outer oxidizing zone of the hydrogen flame into the inner reducing regions. Upon comparing the appearance of the glowing oxide with that of uranium oxide at the same temperature, it is seen at once that the two glowing surfaces are scarcely to be distinguished either as to color or brightness.

Spectrophotometric measurements by the method used in the study of Phase O, readings being made alternately of the brightness of the radiation from the columbium oxide (Phase R) and from the contiguous surface

<sup>7</sup> Nichols and Howes, *Phys. Rev.* (2) **19**, p. 369



of uranium oxide, confirm the impression as to the approximate identity of the two, both as to the composition of the light and as to the equality of temperature.

In Fig. 7 are plotted the results of such a run. The curve portrays the radiation from the uranium oxide at various wave-lengths, the points marked by crosses showing the departure of the brightness of the radiation of the columbium oxide from that of the uranium oxide. These departures, while all in the same direction, are insignificant as compared with the departure of the luminescent Phase O as is more strikingly

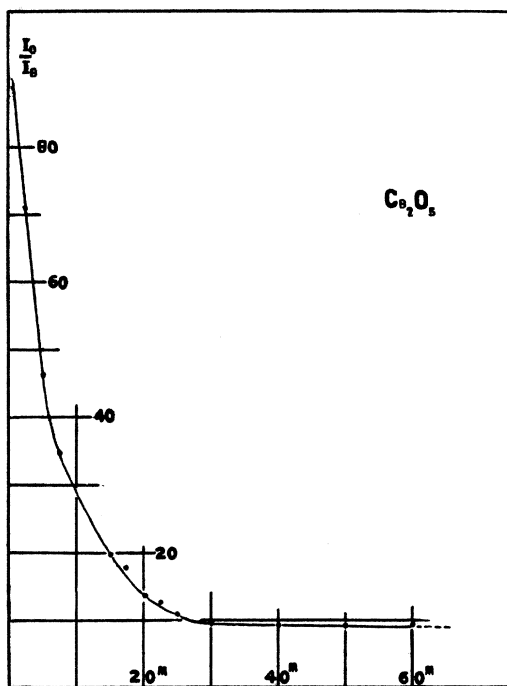


Fig. 6.

Brightness of oxide coating heated to 860°,  
as a function of time in minutes.

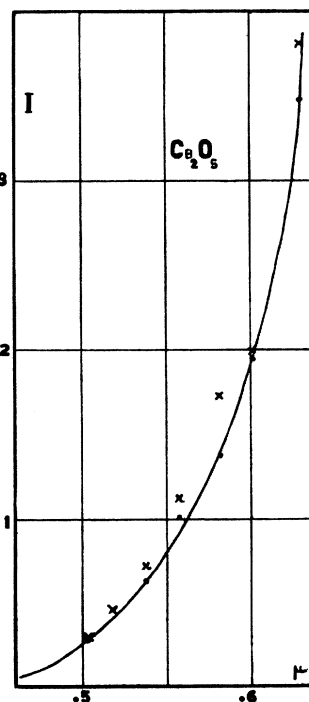


Fig. 7.

Comparison of Phase Radiation with  
that of uranium oxide (full line).

shown by means of the points marked by crosses along the horizontal line in Fig. 4, where the radiation from the uranium oxide is taken as unity throughout the spectrum. The variation is perhaps most reasonably to be accounted for by supposing that the luminescence was almost but not entirely suppressed.

If now the effect of moving the coating across the boundary between the oxidizing and the reducing zones of the flame were merely to deprive

it of the exciting action which produces luminescence, we should have a white oxide of relatively very feeble radiating power instead of a surface which, as appears to the eye and also as determined by the optical measurements just given, radiates *like a black body*.

The very simple explanation of this apparent anomaly is at once afforded by illuminating the glowing oxide strongly with white light, for then the regions from which radiation of Phase R come *are seen to be jet black* while the surrounding and luminescent regions in the oxidizing portions are a yellowish white. The boundary between black and white shifts instantly with every movement of the flame, like a shadow. Evidently the surface of the oxide within the reducing regions of the flame is converted into a black and consequently into a non-luminescent substance, probably into the black tetra-oxide  $\text{Cb}_2\text{O}_4$  known to the chemists.

#### ANALOGOUS CHANGES IN $\text{TiO}_2$ AND $\text{Ta}_2\text{O}_5$

After the completion of the above observation, titanium oxide, the substance first known to have two phases of radiation, and tantalum pentoxide were similarly tested. The titanium oxide darkened within the regions giving radiation of Phase R but the color as viewed by reflected light was a blue-gray rather than black, possibly due to the formation of  $\text{Ti}_2\text{O}_3$ . Tantalum oxide under similar conditions blackens, reducing probably to the well known black tetraoxide  $\text{Ta}_2\text{O}_4$ .

It is probable, in view of these observations, that whenever an incandescent oxide shows two distinct types of radiation in the hydrogen flame, the effect is due to the formation of a superficial layer of a black oxide within the reducing regions of the flame whereby the luminescence of the substance is partly or entirely destroyed, while its temperature radiation proper is raised from the lower intensity characteristic of a white substance to that pertaining to a black body.

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September, 1924.