

*Cathodo-luminescence of Samarium as Applied to the Structural Studies of Alumina. III. On Alumina derived from Boehmite and Bayerite through Thermal Decomposition*

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**Introduction**

Both hydrargillite and bayerite are synthetic alumina-trihydrates, the latter being considered to be a metastable form, while boehmite is a synthetic alumina-monohydrate. Starting from a solution of sodium aluminate, hydrargillite is obtained by slow hydrolysis owing to seeding as in the case of Bayer process, the bayerite is yielded by rapid precipitation through introduction of

carbon dioxide gas at 40°C, and the boehmite is produced by precipitation with sodium bicarbonate. The boehmite and the bayerite can also be prepared by steam digestion of the hydrargillite and by the action of water on an amalgamated aluminium respectively.

The bayerite is, on being heated, transformed into a poorly crystallised boehmite, followed by an extremely poorly crystalline and then a more completely ordered  $\gamma$ -modification of alumina, the latter being said to

be changed to  $\alpha$ -modification at temperatures higher than about 1200°C.

The present authors have applied cathodo-luminescence spectrum of samarium to elucidate the thermal decomposition process of the bayerite and the boehmite.

In the present paper are shown some results of investigations on cathodo-luminescence spectra of samarium imbedded in samples of alumina, which have been produced from bayerite and boehmite.

### Experimental Results and Discussion

Results of cathodo-luminescence spectra for samarium-bearing samples of alumina, which were derived from boehmite and bayerite prepared in various ways, are described separately and some discussions concerning them are also given.

**1) On Aluminas derived from Boehmite, which is produced in a Solution of Sodium Aluminate.**—Boehmite was precipitated from a solution of sodium aluminate by sodium bicarbonate<sup>1)</sup>. This precipitate was washed with water as usual, dried at 110°C, soaked in a solution of samarium nitrate and then converted to anhydrous alumina by calcination, either over a blast flame of coal gas mixed with air or in a direct flame of coal gas mixed with oxygen. These samples of samarium-bearing alumina were submitted to spectrographic investigations of their cathodo-luminescences. Fig. 1, (a), (b) and (c) represent the results schematically.

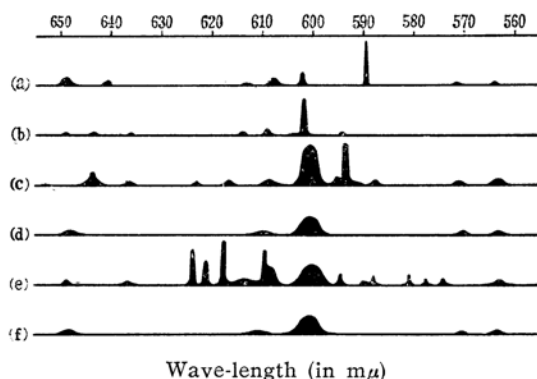


Fig. 1. Schematic representation of cathodo-luminescence spectrum of samarium-bearing alumina derived from boehmite, which was precipitated from sodium aluminate solution by sodium bicarbonate.

There appeared, as can be seen from Fig. 1 (a), D-line of sodium (589 mμ) and three luminescence bands at 602, 608 and 613 mμ,

in addition to four bands of the luminescence prototype I<sup>2)</sup>, namely two bands in a spectral region of 640–650 mμ and two bands in 560–570 mμ, after the sample had been calcined over a blast flame of coal gas mixed with air. A band situated at 602 mμ may be ascribed to the luminescence prototype III<sup>2)</sup>, while bands at 608 and 613 mμ may be ascribed to either the luminescence prototype II<sup>2)</sup> or III. The appearance of D-line of sodium in the cathodo-luminescence spectrum indicates that alkali was not removed by an ordinary washing with water from the precipitate of the boehmite prepared in a solution of sodium aluminate.

Several bands of the luminescence prototype II were perceptible and the D-line faded away in the cathodo-luminescence, as shown in Fig. 1 (b), when this sample of alumina had been heated more intensely, namely in a direct flame of coal gas and oxygen for a short time. A band was seen at 609 mμ, and another band at 602 mμ which was of a moderate intensity in Fig. 1 (a) became most intense.

After being roasted further in a flame of coal gas mixed with oxygen, this sample exhibited cathodo-luminescence bands of the prototype II at 587.5, 609, 616.5 and 623 mμ (Fig. 1, c). The facts that two bands situated at 594 and 600 mμ were very intense and only one relatively strong band at 644 mμ was seen in a spectral region of 640–650 mμ, would be characteristic of the sample of alumina under consideration, and would show that this sample was not composed of the pure  $\alpha$ -modification. It is to be mentioned that the peak of a band near 600 mμ shifted, as the duration of heat treatment was lengthened, slightly toward a short wave-length side, namely from 602 to 600 mμ. The conclusion may thus be drawn from the above experiment that small amounts of alkali remaining in the precipitate of the boehmite washed with water as usual, exerted conspicuous influences upon the luminescence spectrum of the impregnated samarium.

Hydrochloric acid was added for the purpose of removing the tenaciously sticking alkali from the sample of the boehmite and thus the alkali was converted to sodium chloride. This sodium compound was then found to be easily eliminated by an ordinary washing with water.

The sample of the boehmite thus purified has been dried at 110°C, moistened with the solution of samarium nitrate and calcined in flames of coal gas-air and of coal gas-

1) A.S. Russell and C.N. Cochran, *Ind. Eng. Chem.*, **42**, 1337 (1950).

2) E. Iwase, *This Bulletin*, **28**, 596 (1955).

oxygen respectively. The cathodo-luminescence spectrum consists, in the former case, of prototype I (Fig. 1, d), while in the latter case almost entirely of prototype II, except that a broad luminescence band of prototype I with its intensity-maximum at 601 m $\mu$  remains still fairly intense (Fig. 1, e). Here the normal  $\gamma$ - $\alpha$  transformation of alumina is assumed to have been taking place.

It is well known that the so-called  $\beta$ -<sup>3)</sup>, or  $\zeta$ -modification<sup>4,5,6,7)</sup> happens to be produced, when appreciable amounts of alkali are present in the alumina. The considerable variations observed in the feature of luminescence spectrum of samarium when the alkali is present, may presumably be attributed to the formation of alumina resembling the  $\beta$ -, or  $\zeta$ -modification.

Two intermediate anhydrous aluminas were reported in the transformation sequence from the boehmite to  $\alpha$ -alumina, according to X-ray studies by Thibon<sup>8)</sup>, Brown<sup>9)</sup>, and Prettre<sup>10)</sup>, while three were reported according to those by Stumpf<sup>11)</sup>, Funaki<sup>12)</sup>, Day<sup>13)</sup>, Brown<sup>9)</sup>, and Prettre<sup>10)</sup>. For instances, Stumpf et al<sup>7)</sup> stated that a transformation from the boehmite to anhydrous alumina proceeds in the following sequence, Boehmite  $\rightarrow$   $\gamma$ -alumina  $\rightarrow$   $\delta$ -alumina  $\rightarrow$   $\theta$ -alumina  $\rightarrow$   $\alpha$ -alumina, and the boehmite begins to be dehydrated at 360°C and is converted to nearly anhydrous alumina at 450°C. The  $\gamma$ -,  $\delta$ - and  $\theta$ -aluminas are considered to be essentially intermediate forms having oxygen network of cubic close-packing. The plain hexagonal close-packed oxygen network of  $\alpha$ -alumina seems not yet attained at temperatures much higher than 1200°C, as was given in Fig. 7, (c) of Stumpf's paper<sup>7)</sup>, this observation coinciding with a result of the present authors that the alumina obtained by an intense roasting in a direct flame of a mixture of coal gas and oxygen, showed a mixed cathodo-luminescence spectrum of the prototypes I and II (Fig. 1, e).

Anhydrous aluminas immediately pro-

duced, namely  $\gamma$ - and  $\delta$ -modifications were prepared from this purified boehmite by previous heat treatments at 550 and 1150°C respectively. These modifications of alumina were, after samarium had been added, heated at a moderately elevated temperature, namely over a blast flame of coal gas mixed with air. Their luminescence spectra caused by cathode-ray excitation were investigated, and all these were found to be of the simple prototype I, as is given in Fig. 1 (f). However, the cathodo-luminescence spectrum of the pure prototype II was obtained after these modifications of alumina had been subjected to an intense heat treatment in a coal gas-oxygen flame. Consequently, it was confirmed that confused intermediate configurations of virtually anhydrous aluminas yielded by thermal decomposition of the boehmite, have almost no effect on luminescence spectra of the resulting aluminas.

**2) On Alumina derived from Boehmite, which is produced by Autoclaving of Hydrargillite.**—The boehmite can also be prepared by a steam digestion of hydrargillite<sup>14)</sup>, since the hydrargillite is said to be metastable as compared with the boehmite under water at 200°C<sup>15)</sup>. Fine crystals of the hydrargillite, namely the product of Bayer process were heated in the presence of steam at 200, 300 and 340°C for one hour under pressure of steam in an autoclave. These were washed with hydrochloric acid and then with water, and dried at 110°C. It was concluded from measurements of loss on ignition that compositions apparent were  $\text{Al}_2\text{O}_3 \cdot 1.7 \text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot 1.2 \text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 1.1 \text{H}_2\text{O}$  for the samples subjected to steam treatments at 200, 300 and 340°C respectively. The dried samples thus obtained were, after samarium had been added, calcined over a blast flame of coal gas mixed with air, and their luminescence spectra caused by cathode-ray bombardments were investigated. The results are shown in Fig. 2.

A sample with its composition very near to that of the boehmite gave mainly a luminescence spectrum of prototype I (Fig. 2, c), while those prepared by steam digestion at 200 and 300°C gave mixed luminescence spectra of the prototypes I and II (Fig. 2, a and b). Bands of the prototype II were thus seen in the cathodo-luminescence spectrum, when the hydrargillite remaining undecomposed were present mixed with the newly produced boehmite, as in the cases of the

3) A. F. Wells, "Structural Inorganic Chemistry," Oxford, Clarendon Press, (1945) p. 335.

4) H. B. Barlett, *J. Amer. Ceram. Soc.*, **15**, 361 (1932).

5) E. J. W. Verwey, *Z. Krist.*, **91**, 66 (1935).

6) C. A. Beevers and S. Brohult, *Z. Krist.*, **95**, 472 (1936).

7) H. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1401 (1950).

8) H. Thibon, J. Charrier et R. Tertian, *Bull. soc. chim. France*, [5] **18**, 386 (1951).

9) J. F. Brown, D. Clark and W. W. Elliott, *J. Chem. Soc.*, 1953, 85.

10) M. Prettre, B. Imelik, L. Blanchin und M. Petitjean, *Angew. Chem.*, **65**, 549 (1953).

11) H. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1398 (1950).

12) K. Funaki and Y. Shimizu, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **56**, 53 (1953).

13) M. K. B. Day and V. J. Hill, *Nature*, **170**, 539 (1952); *J. Phys. Chem.*, **57**, 946 (1953).

14) H. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1399 (1950).

15) "Gmelins Handbuch anorg. Chem.", **35**, Aluminium Teil B, 8 Aufl., Verlag Chemie, Berlin (1934), S. 108.

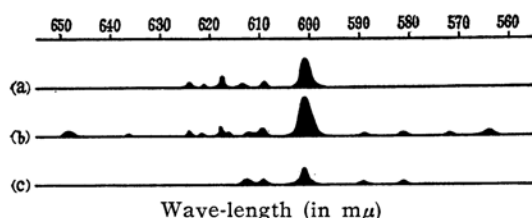


Fig. 2. Schematic representation of cathodo-luminescence spectrum of samarium-bearing alumina derived from steam-digested hydrargillite.

above two samples having apparent compositions of  $\text{Al}_2\text{O}_3 \cdot 1.7 \text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 1.2 \text{H}_2\text{O}$ . These samples as well as that converted to the boehmite gave all the luminescence spectrum of the pure prototype II, after an intense heat treatment had been made in a direct flame of coal gas-oxygen. On the other hand, the products derived from the hydrargillite by calcination at relatively low temperatures, have shown similar results on which we will report fully in a later paper.

**3) On Alumina derived from Bayerite, which is produced in a Solution of Sodium Aluminate.**—Bayerite was prepared by rapid carbonation of a sodium aluminate solution at  $40^\circ\text{C}$ <sup>14,15</sup>. It was washed with water as usual, dried at  $110^\circ\text{C}$  and wetted by the solution of samarium nitrate. The samarium-bearing alumina derived from calcination of this bayerite at  $1000^\circ\text{C}$  for one hour gave, under excitation by cathode-rays, a luminescence spectrum of prototype I accompanied by the intense D-line of sodium, as is given in Fig. 3, (a).

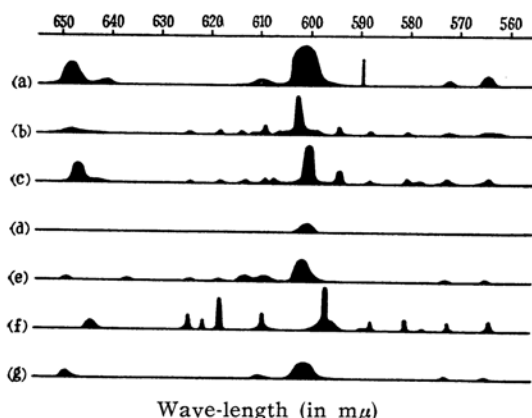


Fig. 3. Schematic representation of cathodo-luminescence spectrum of samarium-bearing alumina derived from bayerite, which was produced by carbonation of sodium aluminate solution.

A heat treatment of short duration in a coal gas-oxygen flame changed the cathodo-luminescence spectrum (Fig. 3, b); the D-line disappeared, and some bands of prototype II could then be seen, being overlapped with still remaining bands of prototype I. The most intense and sharp band situated at  $602 \text{ m}\mu$  was worthy of note, which was perceptible also in the already-mentioned case of the boehmite simply washed.

The cathodo-luminescence spectrum remained, on the whole, almost unaltered even after the repeated calcination in a direct flame of a mixture of coal gas and oxygen (Fig. 3, c). Differences were, however, found in the wave-length of the peak of the most intense band near  $600 \text{ m}\mu$  and in that of an intense band at  $640\text{--}650 \text{ m}\mu$ . These two bands shifted toward a somewhat shorter wave-length side; the former from  $602$  to  $600 \text{ m}\mu$ , and the latter from  $648$  to  $646 \text{ m}\mu$ . These observations resembled those in the case of the boehmite similarly treated, which the authors already referred to.

The bayerite was made thoroughly free from alkali by immersing it at first in hydrochloric acid and then washing with water, because traces of the alkali, which could not have been removed from the bayerite by an ordinary washing with water, might be expected to cause alterations in the luminescence spectrum of the impregnated samarium. Some experiments similar to those described above were carried out with this purified bayerite. Samarium was added to this sample, which was subsequently calcined at  $1000$ ,  $1100$  and  $1200^\circ\text{C}$  respectively. Only a broad band with its intensity-maximum at  $601 \text{ m}\mu$ , the most intense luminescence band of prototype I was seen in the case of the sample calcined at  $1000^\circ\text{C}$  (Fig. 3, d). A number of weak luminescence bands appeared, in addition to the intense band near  $600 \text{ m}\mu$ , when the temperature of heat treatment had been raised, namely bands at  $608$ ,  $614$  and  $619 \text{ m}\mu$  were seen with the sample treated at  $1100^\circ\text{C}$ , and bands at  $608$ ,  $614$ ,  $619$ ,  $624$ ,  $637$  and  $648 \text{ m}\mu$  with that at  $1200^\circ\text{C}$  (Fig. 3, e). The sample roasted in a direct flame of coal gas mixed with oxygen gave a peculiar luminescence spectrum under cathode-ray bombardment (Fig. 3, f). This luminescence spectrum implied, besides several bands characteristic to the prototype II, three bands situated at  $596.5$ ,  $643.5$  and  $564 \text{ m}\mu$ . The first of these was the most intense band of prototype III, but the latter two were proved to be smaller in the wave-length as compared with the corresponding bands of prototype I.

According to Stumpf et al.<sup>7)</sup> the sequence

16) R. Fricke and H. Severins, *Z. anorg. Chem.*, **175**, 249 (1928); *ibid.*, **179**, 287 (1929).

of thermal transformation from the bayerite to  $\alpha$ -alumina is as follows: Bayerite  $\rightarrow$  boehmite  $\rightarrow$   $\eta$ -alumina  $\rightarrow$   $\theta$ -alumina  $\rightarrow$   $\alpha$ -alumina. The  $\theta$ - $\alpha$  transformation, namely a transition from a well-crystallised anhydrous alumina of cubic close-packed oxygen network to that of hexagonal one, is said to take place at 1210–1260°C, but the transition curve between  $\theta$ - and  $\alpha$ -alumina was indicated by these investigators as a dotted line in their Fig. 6 (a), which means probably a complicity of this transition, corresponding exactly to the present authors' observation on the complicated feature of the cathodo-luminescence spectrum of samarium as mentioned above.

Stumpf and others<sup>7,17)</sup> stated that the bayerite commences to be dehydrated at 160–200°C, is converted to the boehmite at 250–270°C and becomes nearly anhydrous alumina at 470–500°C.

Stumpf<sup>7)</sup> as well as Thibon<sup>8)</sup> postulated an intermediate formation of the boehmite in the way of transition from the bayerite to anhydrous alumina, while Tertian<sup>18)</sup> concluded that the boehmite was sometimes not formed. Sato<sup>19)</sup> arrived at the same conclusion as that of Tertian from a differential thermal analysis. According to Day<sup>13)</sup> the formation of the boehmite is of a secondary nature in this case. Anhydrous aluminas intermediately yielded during thermal decomposition of the bayerite to the  $\alpha$ -alumina were formerly considered exclusively as  $\gamma$ -modification, but they have afterwards been subdivided into two<sup>7)</sup> ( $\eta$  and  $\theta$ ) or three phases<sup>13)</sup> ( $\gamma$ ,  $\delta$  and  $\theta$ ) from the results of X-ray investigations.

The present authors have prepared the boehmite and the  $\eta$ -alumina by thermal decomposition of the bayerite at 230–270 and 900°C respectively. The former is a poorly crystallised form of alumina-monohydrate, and the latter is an extremely poorly crystalline  $\gamma$ -modification of alumina. Samarium ions imbedded in the intermediately produced boehmite and anhydrous alumina having such a low degree of crystallinity are always found to give a cathodo-luminescence spectrum of prototype I, so far as these samarium-bearing samples of boehmite and anhydrous alumina have been treated over a blast flame of coal gas mixed with air (Fig. 3, g), but the cathodo-luminescence spectrum changes clearly to prototype II, after these samples have been calcined intensely in a direct flame of

coal gas-oxygen.

4) **On Alumina derived from Bayerite, which is produced on Amalgamated Aluminium.**—The bayerite can also be prepared in another way, namely by the action of water on an amalgamated aluminium<sup>1)</sup>. This sample was dried at 110°C, and samarium was added to it. The samarium-bearing bayerite thus yielded was subjected to heat treatments.

The resulting alumina gave, after being heated over a blast flame of coal gas mixed with air, luminescence bands of prototype I accompanied by those of prototype II of low intensity under cathode-ray bombardment (Fig. 4, a), while that roasted much more

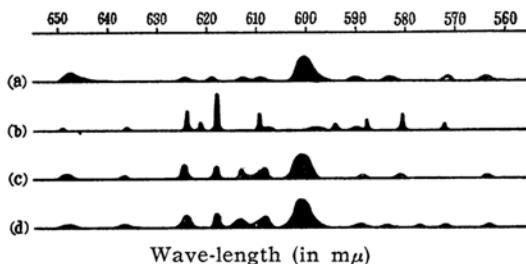


Fig. 4. Schematic representation of cathodo-luminescence spectrum of samarium-bearing alumina derived from bayerite, which was produced by action of water on amalgamated aluminium.

intensely in a direct flame of coal gas mixed with oxygen, exhibited those of the genuine prototype II (Fig. 4, b). Thermal transitions may reasonably be expected to have proceeded more simply and more readily in this case than in the before-mentioned cases of the bayerite and the boehmite, which were prepared in a solution of sodium aluminate, since the present preparation of the bayerite has been carried out free from alkali.

Partial decomposition was previously caused by submitting this sample of the bayerite to heat treatment at various temperatures; 200, 400 and 600°C. These intermediately decomposed products were soaked in the solution of samarium nitrate and then heated moderately over a blast flame of coal gas-air for 1 hour. In Fig. 4, (c) and (d) show cathodo-luminescence spectra for two of these samarium-bearing alumina, namely when heated previously at 200 and 400°C respectively. These luminescence spectra were found to be always of the prototype I overlapped by luminescence bands of the prototype II, no matter at what stages of decomposition samarium had been added.

It is to be noted that two bands are perceptible side by side at 608 and 613 mμ in an immediate vicinity of the spectral region of 610 mμ in the luminescence spectra given

17) A.S. Russell and C.N. Cochran, *Ind. Eng. Chem.*, **42**, 1339 (1950).

18) R. Tertian et D. Papee, *Compt. rend.*, **236**, 1565 (1953).

19) T. Sato, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **55**, 66 (1952); **56**, 478 (1953).

by the samarium-bearing  $\gamma$ -alumina, as shown in Fig. 4, (c) and (d), prior to the appearance of an intense luminescence band at  $609\text{ m}\mu$  belonging to the  $\alpha$ -alumina. So far as a final heat treatment was carried out over a blast flame of coal gas mixed with air, luminescence bands of prototype II are seen much more distinctly in the cases of samples of alumina, to which samarium was added at the intermediate stages of thermal decomposition, than in the cases of those, to which samarium was added directly to the dried original bayerite. It is thus confirmed that the heating over a blast flame of coal gas-air does not convert these samples of the bayerite completely to the genuine  $\alpha$ -alumina. A much higher temperature is needed for this transition, namely  $1260$  or  $1300^\circ\text{C}$ , as already reported by Stumpf<sup>7)</sup> and Day<sup>20)</sup> respectively. A cathodoluminescence spectrum of the pure prototype II was in fact given by partially decomposed products resulting from the calcination of the bayerite at  $400$  and  $600^\circ\text{C}$ , when these products had been treated in a coal gas-oxygen flame after the impregnation of samarium.

### Summary

Investigations were carried out on cathodoluminescence spectra of samarium ions im-

bedded in alumina, which had been derived from bayerite and boehmite. The mode of thermal transformation of these alumina was concluded from the spectrographic results mentioned above.

A conversion to anhydrous alumina different from  $\alpha$ -modification, presumably to  $\beta$ - or  $\zeta$ -modification, occurred owing to the effect of the contaminating alkali minutely present, when this alumina was derived from calcination of either boehmite or bayerite, each of which had been produced in a solution of sodium aluminate.

The boehmite and the bayerite, purified thoroughly from the alkali, as well as those prepared in the absence of the alkali are readily converted to  $\alpha$ - through  $\gamma$ -modification of alumina by thermal treatments.

The heating of the bayerite obtained through rapid carbonation of a solution of sodium aluminate is not, however, likely to result in a simple  $\gamma$ - $\alpha$  transformation of alumina even when the alkali has been removed by careful washing.

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<sup>20)</sup> M.K.B. Day and V.J. Hill, *J. Phys. Chem.*, **57**, 948 (1953).