Cathodo-luminescence of Samarium as Applied to the Structural Studies of Alumina. V. On Alumina Derived from Hydrargillite by Thermal Treatments

By Eiichi IWASE and Seijiro NISHIYAMA

(Received June 13, 1955)

Introduction

As is well known, hydrargillite is a stable form of alumina-trihydrate and is obtained as an industrial product of Bayer process through slow hydrolysis of sodium aluminate solution. Its thermal dehydration and transformation have been studied by numbers of investigators, since these are important problems from a practical point of view.

Mechanisms regarding thermal dehydration and transformation of the hydrargillite to α-alumina are very complicated. It has, until quite recently, been presumed that the thermal decomposition of the hydrargillite occurs through a singular consecutive sequence(1). A dual series of thermal transformation of the hydrargillite has, however, been postulated by Brown(2) and Day(3).

The present authors have applied a technique of the cathodo-luminescence spectrum of samarium to the investigations on the feature of the thermal decompositions of the hydrargillite. The results obtained and some interpretations relating to them are given in this paper.

Experimental

For the purpose of removing as much as possible of the remaining alkali, the sample of hydrargillite obtained by Bayer process was treated as follows; it was at first immersed in hydrochloric acid, washed with water, and then dried at 110°C. Experimental results are described separately in two parts, according to the degree of thermal decomposition of the purified hydrargillite prior to, and the calcination temperature after the addition of samarium, which acts as an activator for causing cathodo-luminescences.

1) On the Samarium-bearing Alumina derived from Calcination of Pydrargillite, at its dried State Samarium Being added Initially.—One ml. of 1% samarium nitrate solution was added directly to each 1 g. of the purified hydrargillite mentioned above, which was then calcined either at a temperature between 750 and 940°C or in a direct flame of coal gas mixed with oxygen. These samarium-bearing aluminas were exposed to the action of cathode-rays and the luminescence brought about was spectrographically investigated by employing a glass-prism spectrograph of Feuss.

Luminescence bands of the prototype II(4) become much more distinct, being accompanied with bands of the prototype I(4), as calcination has been made at a more elevated temperature. Variations in the feature of the cathodo-luminescence spectrum are related with the temperature of one hour's heat treatment as follows; bands of the prototype II commence to appear with a sample, which has been subjected to a heat treatment at about 750°C. and these bands become considerably more intense with that at 850°C. Luminescence bands of the prototype I remain unaltered, so far as the calcination temperature of the sample has not exceeded 940°C. The sample gives cathodo-luminescence bands of the genuine prototype II, without being accompanied by any band of the prototype I, after being heated at a greatly elevated temperature,

---

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

(2) J.F. Brown, D. Clark and W.W. Elliott, *J. Chem. Soc.*, **1953**, 84.

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

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

namely in a direct flame of coal gas mixed with oxygen. The structural change from an alumina giving rise to the cathodo-luminescence bands of the prototype I into that of the prototype II, corresponds to a transformation between the so-called γ- and α- modifications of alumina. A ready and gradual γ-α transformation is supposed to take place with the increasing temperature, when the dried original sample of the hydrargillite has been subjected to a calcination in the presence of samarium.

2) On the Samarium-bearing Alumina prepared from Hydrargillite by Calcination of its thermally Decomposed Products, to which Samarium was added.—The hydrargillite purified as already mentioned was previously treated at certain temperatures between 150 and 1200°C. The heating duration was one hour for the temperature range between 150 and 850°C, and fifteen minutes for that between 900 and 1200°C, unless otherwise stated. Samarium was added to each of these thermally treated samples, which was afterward ignited over a blast flame of coalgas-air for one hour to ensure the expellation of volatile constituents. Such constituents, if present, would hinderthe appearance of luminescence under the excitation by cathode rays. Cathodo-luminescence spectra given by these samples of samarium-bearing alumina are summarised schematically in Fig. 1 and reproduced in Fig. 2, in order to facilitate mutual comparisons.

It is seen from Figs. 1 and 2 that previous heat treatments of the hydrargillite bring about extremely marked effects on the cathodo-luminescence spectrum of samarium. Bands of the prototype II can be seen accompanied by bands of the prototype I in the case of the samples previously heated at certain temperatures between 150 and 230°C (Fig. 1, a). This luminescence spectrum is identical with that given by the hydrargillite treated as follows; the purified original hydrargillite was soaked with the solution of samarium nitrate and ignited over a blast flame of a mixture of coal gas and air. Luminescence bands belonging to the prototype II are, on the whole, reduced in intensity with a result of the complete lack of some bands, for example a band at 574 mμ, and a broad diffuse band of the prototype I with its peak at 600 mμ is also much weakened. when a previous heat treatment has been made at 250°C for one hour (Fig. 1, b). It is worth mentioning that an intense band at 597 mμ characteristic of the prototype III[4] becomes now extremely intense. A new band is observed at 644 mμ, very near a band at 648 mμ, and there also begin to appear two bands at 561 and 562.5 mμ in place of a diffuse band at 563 mμ.

When the duration of heat treatment at 250°C has been increased from one to five hour, the cathodo-luminescence spectrum changes markedly (Fig. 1, c): Bands situating at 561, 562.5, 612 and 644 mμ becomes much more distinct, several new bands are perceptible at 566, 568, 601.5 and 615.5 mμ, and the intensity maximum of a band lying between two bands at 618 and 624 mμ seems to be slightly shifted, namely from 621 to 620 mμ. As to a set of three bands around a spectral region of 610 mμ, a sudden reversal is brought about in the order of intensity, when the duration of heating at 250°C has been lengthened (Fig. 1, c); the weakest band at 612 mμ grows now considerably intense, and a feeble band at 610 mμ is detectable instead of a band at 609 mμ, namely the most intense band among the above three given by the sample, which was previously treated at a lower temperature. The feature of the luminescence spectrum thus obtained seeems characteristic of intermediate products of the thermal decomposition of the hydrargillite. This luminescence spectrum was already designated as the prototype III by one of the present authors[4] and was distinguished from the well-defined prototypes I and II. The luminescence prototype III is always seen with the samples of the hydrargillite, which have been subjected to a previous heat treatment at any temperature above 250 and below 900°C (Fig. 1, c). The structure of the alumina giving rise to this particular cathodo-luminescence spectrum, when once formed, is extremely persistent in the case of an intense heat treatment and remains unaltered after being heated at a temperature as high as 1200°C for fifteen minutes. However, when this samarium-bearing sample of alumina has been roasted intensely in a direct flame of coal gas mixed with oxygen, it gives distinctly the cathodo-luminescence spectrum of the prototype II owing to the corundum structure of the alumina, but a band situated at 597 mμ, namely the strongest and the most characteristic band of the prototype III, still remains intense in this spectrum.

Some changes occur in the cathodo-luminescence spectrum, if the sample of the hydrargillite has been submitted to an initial heat treatment exceeding 950°C. These changes might be ascribed to the fact that the temperature of the initial heat treatment has been higher than that of the final heating over a blast flame of coal gas mixed with air. Through heat treatments at 950 and 1000°C for fifteen minutes (Fig. 1, d), four bands at 605.5, 608, 610 and 612 mμ become almost equal in intensity, and this is also the case with two bands situated at 561 and 563 mμ.

In the case of a sample previously heated at 1050°C (Fig. 1, e), two bands at 566 and 568 mμ disappear, three bands at 618, 621 and 624 mμ may be arranged in a sequence of intensity just like in the cathodo-luminescence spectrum of the prototype II, and the same relation holds with the three bands at 607–8, 609 and 612 mμ. All the bands lying in a spectral region between 560 and 597 mμ become fairly weakened.

No remarkable differences are found in luminescence spectra given by the samples, which have been previously heated at 1050 and 1100°C respectively, except that two bands at 561 and 562.5 mμ appear jointly in the luminescence spectrum of the latter sample (Fig. 1, f).

A band situated at 597 mμ is greatly reduced in its intensity and overlaps with a diffuse band at 600 mμ in the case of a sample heated previously at 1150°C (Fig. 1, g). A band at 594 mμ begins

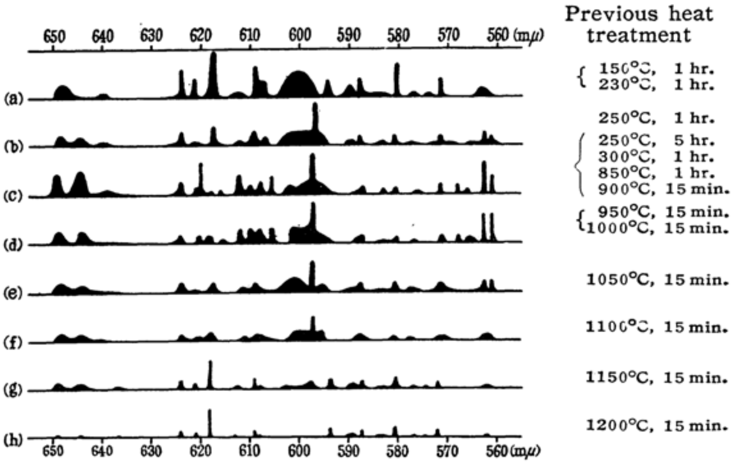


Fig. 1. Schematic representation of cathodo-luminescence spectra given by samarium bearing aluminas, which were derived from hydrargillite through previous heat treatments at various temperatures, followed by soaking with samarium nitrate solution and then roasting over blast flame of coal gas-air.

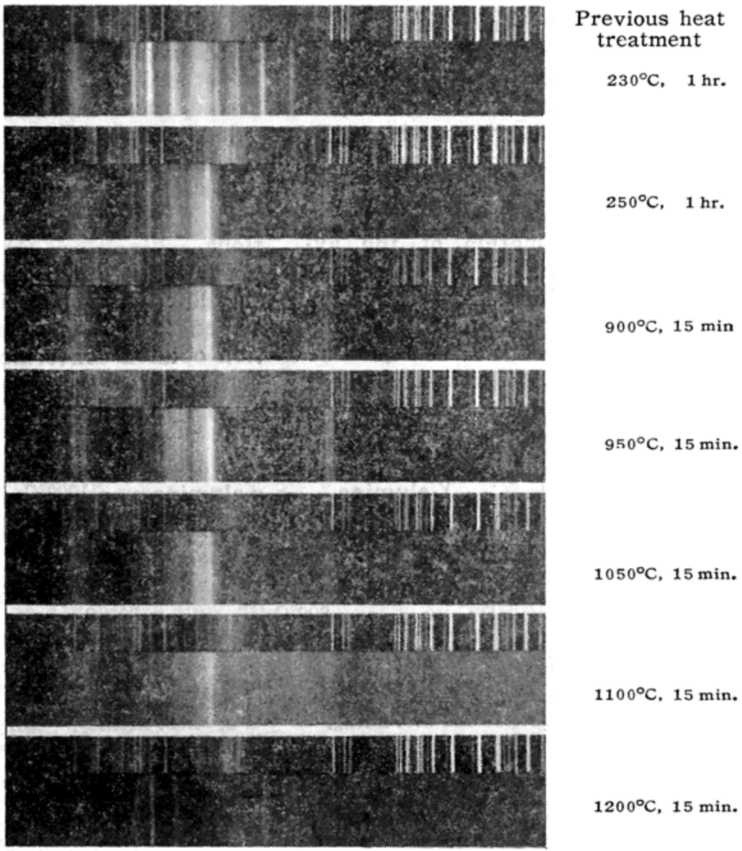


Fig. 2. Cathodo-luminescence spectrograms of samarium-bearing aluminas derived from hydrargillite by subjecting previously to various heat treatments prior to the addition of samarium, final heat treatment being made over a blast flame of coal gas-air. Spectral lines of iron-arc are taken for reference.

to appear distinctly and another band at 618 mμ becomes now the most intense one in this luminescence spectrum. Thus the luminescence spectrum is transformed entirely to the prototype II.

Finally, the circumstances are quite the same in a sample previously roasted at 1200°C (Fig. 1, h) as in that at 1150°C.

An alumina is completely transformed to α-modification through an intense initial heating at temperatures higher than 1150°C prior to the addition of samarium. This may be comfirmed by the fact that a luminescence spectrum of samarium imbedded in the above-mentioned alumina is the pure prototype II.

Discussion

First of all, the chief views hitherto set forth are briefly surveyed on thermal transformations from the hydrated to the anhydrous alumina. The view has, until quite recently, been accepted that the hydrargillite is thermally decomposed through a singular sequence of consecutive transformations. The hydrargillite dehydrates, on being heated, to boehmite, which passes on further calcination to stable α-alumina through numbers of intermediate modifications termed collectively as γ-alumina[5]. This γ-alumina was separated into two or more phases as the results of close examinations on X-ray diffraction patterns; two phases were differentiated by Tertian[6], Thibon[7], and Prettre[8], three phases by Rooksby[9], Thibon[7], and Funaki[10], and four phases by Frary[11], and Stumpf[12].

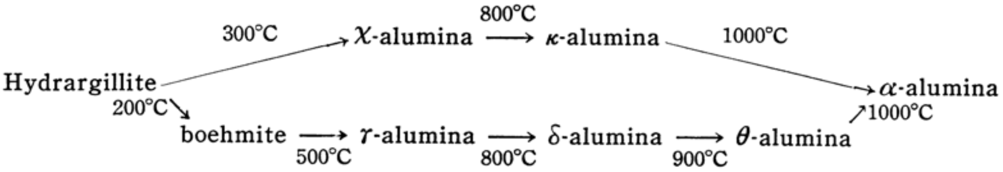
The thermal transformation of the hydrargillite to the α-alumina proceeds, according to Stumpf's studies[13] on Debye diffraction patterns, through the following singular consecutive sequence.

Hydrargillite$\rightarrow$boehmite$\rightarrow\chi$-alumina$\rightarrow\gamma$-alumina$\rightarrow\kappa$-alumina$\rightarrow\theta$-alumina$\rightarrow\alpha$-alumina (χ-, γ-, κ-, and θ-alumina were formerly termed as γ-alumina).

However, Day and Hill[3] have recently suggested that the boehmite is produced from the hydrargillite by means of a secondary reaction; the hydrargillite is at first decomposed directly into a virtually anhydrous alumina and water vapour during its thermal decomposition, and afterwards there results the boehmite by a subsequent reaction between these two primary products.

When a fluid phase is absent, transformations from the much hydrated to the anhydrous alumina are supposed to take place, during the heat treatment, locally in inner structures of the hydrated crystals with a limited opportunity for an atomic rearrangement. Definite transformation temperatures can consequently be assigned with difficulty, and the temperatures at the start and at the finish of the transformations extend usually over somewhat wide ranges, depending on the grain-size of the hydrated crystals and the manner of the heat treatment. Mixtures of products may thus result from the thermal dehydration and the thermal transformation of the hydrargillite, joining one product with the other in this transition sequence. Roosby[9] stated that κ-modification of alumina postulated by Stumpf and others[13] was really a mixture of κ- and θ-modifications, and Day and others[14] also explained that χ-modification was in fact composed of γ- and χ-modifications.

Contrary to the above-mentioned view of singular transformation series, Brown[2] assumed for the first time a dual transformation opinion concerning the thermal decomposition of the hydrargillite as represented by the following detailed scheme:



---

5) F. Haber, *Naturwissenschaften*, **13**, 1007 (1925); J.D. Edwards, F.C. Frary and Z. Jeffries, "Aluminum Industry, Aluminum and Its Production", New York, McGraw-Hill (1930), p. 166; R. Fricke und G.F. Huttig, "Handbuch der allgemeinen Chemie IX, Hydroxide und Oxyhydrate", Akademische Verlag, Leipzig, (1937); W. A. Lalande, W.S.W. McCarter and J. B. Sanborn, *Ind. Eng. Chem.*, **36**, 99 (1944); G. Feachem and H.T.S. Swallow, *J. Chem. Soc.*, **1948**, 267; R.J. Taylor, *J. Soc. Chem. Ind.*, **68**, 23 (1949); H. Remy, "Lehrbuch der Anorganischen Chemie", Bd. I, Akademische Verlag, Leipzig (1952), S. 308, 309; S.J. Gregg and K.S.W. Sing, *J. Phys. Chem.*, **56**, 388 (1952).

6) R. Tertian, *Compt. rend.*, **230**, 1677 (1950).

7) H. Thibon, J. Charrier et R. Tertian, *Bull. soc. chim. France*, [5], **18**, 385 (1951).

8) F. Blanchin, B. Imelik et M. Prettre, *Compt. rend.*. **236**, 1025 (1953); M. Prettre, B. Imelik, L. Blanchin und M. Petitjean, *Angew. Chem.*, **65**, 549 (1953).

9) H.D. Rooksby, "X-ray Identification and Crystal Structures of Clay Minerals", Mineralogical Society (1951), p. 244.

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

11) F.C. Frary, *Ind. Eng. Chem.*, **38**, 129 (1946).

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

13) H.C. Stumpf, A.S. Russell, J.W. Newsome and C.M. Tucker, ibid, 1401, Fig. 5 (a).

14) M.K.B. Day and V.J. Hill, *J. Phys. Chem.*, **57**, 949 (1953).

15) G. Ervin, *Acta Cryst.*, **5**, 106 (1952).

The thermal dehydration and transformation of the hydrargillite occur through two series of routes before the α-alumina is produced, the one initially through the boehmite and then anhydrous aluminas, and the other directly through other anhydrous aluminas. His opinion is based mainly on the following significant facts. Firstly, the studies on X-ray diffraction patterns indicated that the disappearance of the hydrargillite agreed with the formation of the χ-alumina, and the amount of this χ-alumina remained unchanged for a while in the course of heating. Secondly, a differential thermal analysis gave a curve possessing three peaks; the first peak was due to the change from the hydrargillite to the boehmite, the second from the hydrargillite to the χ-alumina, and the third from the boehmite to γ-alumina respectively. Thirdly, the water content-ignition temperature curve for the hydrargillite showed an arrest in a range of temperature between 300 and 400°C, corresponding to the approximate composition of alumina-hemihydrate. The products in these states of decomposition consisted consequently of the monohydrated boehmite and the virtually anhydrous χ-alumina mixing in almost equal amounts.

There are some doubtful points as to whether or not each of these intermediate modifications of the alumina itself is really presumable to be a single phase[15]. According to Jellinek[16], the thermal transformation of the aulmina derived from calcination of the hydrargillite is a gradual process. This conception was expressed by Ervin[17] as a continuous transition from the disordered to ordered structure of alumina, and by Brown[2] as that from poorly crystallised to well crystallised alumina through a slow diffusion of aluminium ions into the lattice of oxygen ions.

The present authors have taken each 1 g. of the sample of the hydrargillite and heated it for five hours at certain definite temperatures respectively. The dehydration isobar thus obtained is illustrated in Fig. 3. This dehydration-isobar curve goes smoothly until a distinct arrest is observed at the composition of approximately $Al_2O_3 \cdot 0.7H_2O$. The composition corresponding to this arrest was, however, $Al_2O_3 \cdot 0.5H_2O$ according to Brown[18] and Milligan[19], and $Al_2O_3 \cdot 0.35H_2O$ according to Weiser and Milligan[20]. The above-mentioned observation that there is no inflection showing the existence of monohydrated alumina in the water content-calcination temperature curve of the hydrargillite, was also confirmed by Day[21]. Bentley and Feachem[22] observed, on the other hand, that the anhydrous alumina is rehydrated to the boehmite in the presence of steam. The boehmite, as is well known, is obtained when the hydrargillite has been dehydrated in a closed system. All these facts might elucidate the fact that some parts of the χ-alumina primarily yielded through a direct dehydration of the hydrargillite, are surely converted into the boehmite by reaction with the adsorbed water, which has been released from the hydrargillite during the heat treatment. Thus the practical calcination of the hydrargillite proceeds as indicated in the accompanying diagram[3].

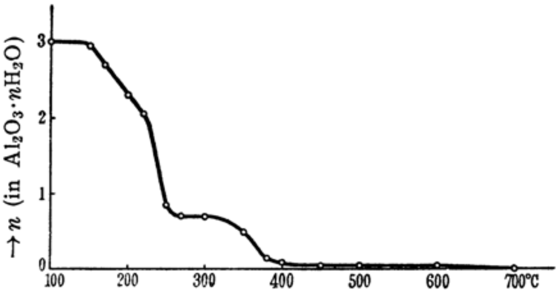


Fig. 3. Dehydration-isobar curve of hydrargillite.

$$\begin{tikzcd}
 & \chi\text{-alumina} \arrow[r] \arrow[d] & \kappa\text{-alumina} \arrow[rrrd] & & & \\
\text{Hydrargillite} \arrow[ur] & & & & & \alpha\text{-alumina} \\
 & \text{boehmite} \arrow[r] & \gamma\text{-alumina} \arrow[r] & \delta\text{-alumina} \arrow[r] & \theta\text{-alumina} \arrow[ur] &
\end{tikzcd}$$

The primarily yielded χ-alumina gives rise, on subsequent calcination at higher temperatures, to mixtures of two series of anhydrous aluminas, namely $\chi \rightarrow \kappa \rightarrow \alpha$ associated with the original dehydration product, the χ-alumina, and $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ associated with the boehmite component, this component being derived from a secondary reaction between the χ-alumina and its adsorbed water.

---

[16] M.H. Jellinek and I. Frankuchen, *Ind. Eng. Chem.*, **37**, 163 (1945).

[17] G. Ervin, ibid, 108.

[18] J.F. Brown, D. Clark and W.W. Elliott, ibid, 87.

[19] L.H. Milligan, *J. Phys. Chem.*, 26, 247 (1929).

[20] H.B. Weiser and W.O. Milligan, ibid., **36**, 3010 (1932); **38**, 1175 (1934).

[21] M.K.B. Day and V.J. Hill, *J. Phys. Chem.*, **57**, 947 (1953).

[22] F.J.L. Bentley and C.G.P. Feachem, *J. Soc. Chem. Ind.*, **46**, 148 (1945).

It was also observed by the present authors, as shown in Fig. 4, that the powders of the hydrargillite is, in the course of slow heating, effluent twice over two different ranges of temperatures; namely, violent dehydration occurs apparently at two steps. This observation is likely to support the view of Day rather than that of Brown.

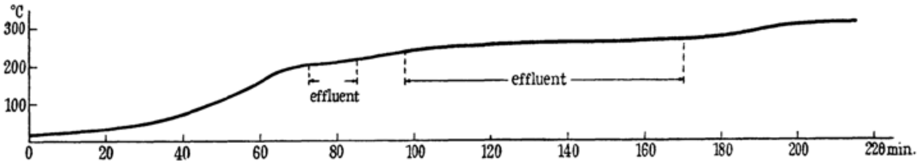


Fig. 4. Effluent phenomena observed in the course of slow heating of hydrargillite-powders.

TABLE I

RELATIVE INTENSITY OF REFLECTIONS FROM (400) PLANES

Intermediate phase of alumina	I	II	III	IV
χ	ww(2.00 Å)	w(1.99 Å)	——	mw(2.11 Å)
κ	mw(2.00 Å)	w(2.055 Å)	mw(2.06 Å)	mw(2.06 Å)
γ	s(2.00 Å)	s(1.985 Å)	msb(1.98 Å)	s(1.982 Å)
δ	ms(2.005 Å)	s(1.985 Å)	s(1.99 Å)	s(1.985 Å)
θ	ms(2.03 Å)	s(2.01 Å)	ms(2.02 Å)	s(2.016 Å)

I) H.C. Stumpf, A.S. Russell, J.W. Newsome, and C.M. Tucker, *Ind. Eng. Chem.*, **42**, 1402 (1960).
II) H. Thibon, J. Charrier, et R. Tertian, *Bull. soc. chim. France*, 18, 387 (1951).
III) J.F. Brown, D. Clark, and W.W. Elliott, *J. Chem. Soc.*, **1953**, 86.
IV) M.K.B. Day and V.J. Hill, *J. Phys Chem.*, **57**, 948 (1953).

Code:
s —— strong
ms —— medium strong
mw —— medium weak
w —— weak
ww —— very weak
b —— broad

The reason why the thermal decomposition of the hydrargillite proceeds through two different routes is indeed not easily accounted for, but some structural interpretations are given here. The χ-alumina is initially yielded from the thermal decomposition of the hydrargillite, and the γ-alumina is then derived from the boehmite, which has been produced by a subsequent reaction between the abovementioned χ-alumina and its adsorbed water. Both of these aluminas might probably be assumed to possess structures very near to a spinel type[23]. A line situated at about 2.0 Å in the X-ray powder diffraction pattern is indexed as the (400) line for the spinel unit cell, and its intensity is supposed to be affected by the relative distribution of aluminium ions between two kinds of interstices of a cubic close-packed oxygen network; namely octahedral and tetrahedral interstices, since this line is caused by the reflection from the (400) planes passing through all the oxygen positions and the octahedral aluminium positions, but not the tetrahedral aluminium positions[15]. If its intensity is weak, the aluminium ions in the alumina under consideration would take seats in the tetrahedral interstices in preference to the octahedral interstices of the cubic close-packed oxygen network. The χ- and κ-aluminas in the transformation series associating with the original dehydration product of the hydrargillite have the weak (400) line, while the γ-, δ- and θ-aluminas in the transformation series associating with the boehmite have the intense (400) line, as can be seen from the results of X-ray investigations by Stumpf, Thibon, Brown and Day listed in Table I. It is concluded from the foregoing considerations that the occurrence of the two distinct series in the course of the thermal transformation of the hydrargillite might be ascribed to the possibility of aluminium ions in choosing one of the two different ways to enter into the interstices of the oxygen network of cubic close-packing.

The remarkable prototype III for the cathodo-luminescence spectrum of samarium ions is obtained, when these ions are imbedded in an alumina, which is presumably constituted of the aluminium ions occupying the

---

[23] R. Brill, *Z. Krist.*, **83**, 323 (1932); H.B. Barlett, *J. Am. Ceram. Soc.*, **15**, 361 (1932); G.H. Hagg und G. Soderholm, *Z. phys. Chem.*, [B], **29**, 88 (1935); E.J.W. Verwey, *J. Chem. Phys.*, **3**, 592 (1935); G. Ervin, *Acta Cryst.*, **5**, 106 (1952).

tetrahedral interstices of cubic close-packed oxygen network.

The packing effect of the introduced samarium ions in stabilising this special configuration of alumina is considered to resemble that of sodium or others in the formation of the β- and ζ-aluminas24), but the samarium ions in the former case serve at the same time as an activator for causing the cathodo-luminescence. The fixation, of this alumina-configuration, caused by the packing of samarium ions is so firm that the most intense band characteristic of the luminescence prototype III, namely a band situated at 597 mμ persists to be intense in the cathodo-luminescence spectrum, mixing with bands of the prototype II, although afterwards the sample has been roasted at a high temperature in a direct flame of coal gas-oxygen. This fact indicates that the tight fixation of the above-mentioned structure remains tenaciously in some local parts after an extremely intense heat treatment, which brings about a fundamental structural change of alumina into the corundum configuration.

It is finally shown that this cathodo-luminescence spectrum of samarium may be utilised for conjecturing how an activated alumina for the chromatographic use could be prepared. The well-known sample of E. Merck's aluminium oxide, which was standardised for a chromatographic adsorption analysis according to Brockmann, is directly soaked with the solution of samarium nitrate and then ignited over a blast flame of the mixture of coal gas and air. It gives a samarium-luminescence spectrum of the pure prototype III under the excitation by the cathode-ray bombardment. This prototype of the samarium-luminescence spectrum can scarcely ever be obtained in its pure form, except the alumina derived from the hydrargillite of Bayer process. A conclusion might, therefore, be drawn that this activated alumina would possibly have been prepared by heating the purified alumina-trihydrate of Bayer process at moderately high temperatures.

Summary

Results of investigations are summarised as follows on the cathodo-luminescence spectra of samarium ions imbedded in various samples of aluminas, which were thermally derived from hydrargillite.

The transformation from γ- to α-modification of alumina takes place according as the temperature for heat treatment of the hydrargillite is elevated, at whose dried state the samarium ions have been impregnated.

After the hydrargillite was subjected to a previous heat treatment at the temperature range between 250 and 900°C, impregnated with the samarium ions and then calcined over a blast flame of coal gas mixed with air, it gives a characteristic cathodo-luminescence spectrum, which was designated by one of the present authors as the prototype III. The configuration of the alumina giving rise to luminescence bands of this prototype under the excitation by the cathode-rays is when once formed, stable and persistent for heat treatments of much elevated temperatures.

The activated alumina standardised after Brockmann can give, after being impregnated with the samarium ions, the particular cathodo-luminescence spectrum of the prototype III owing to the above-said ions. The appearance of this luminescence spectrum in its pure form is of use for choosing a material as well as for finding an activation method in the preparation of the alumina suitable for the chromatographic purpose.

The dual transformation conception postulated recently by Day on the thermal decomposition of the hydrargillite was elucidated from a structural point of view. The luminescence prototype III of samarium ions seems to be due to the special configuration of alumina, such as χ- and κ-modifications, in which the aluminium ions occupy preferably the tetrahedral rather than the octahedral interstices of oxygen network ofcubic close-packing.

This research has been financed by the Scientific Encouragement Grant of the Ministry of Education, to which the authors' thanks are due.

Scientific Research Institute, Ltd.
Komagome, Bunkyo-ku, Tokyo

---

24) A.F. Wells, "Structural Inorganic Chemistry", Clarendon Press, Oxford (1945), p. 335; H.B. Barlett, *J. Am. Ceram. Soc.*, **15**, 361 (1932); E.J.W. Verwey, *Z. Krist.*, **91**, 66 (1935).