# *Cathodo-luminescence of Samarium as Applied to the Structural Studies of Alumina. II. On the Alumina Produced from Hydrous Alumina Gels*

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## Introduction

Investigations of X-ray powder diffraction patterns showed that hydrous alumina gels freshly produced by a rapid precipitation from cold solutions of aluminium salts are amorphous[1,2]. The hydrous alumina gels are, on calcination, converted to $\gamma$-alumina in a wide sense[3,4] through poorly crystallised boehmite, and with progressively increased temperatures, a gradual ordering of cubic close-packed oxygen network takes place, aluminium ions entering into the network by thermal diffusion preferably much more into octahedral than tetrahedral interstices. A low-temperature form of the $\gamma$-alumina may be regarded as a modification possessing imperfect and disordered lattices. A complete ordering of aluminium ions is achieved in the cubic close-packed oxygen network by a heat treatment at just below the temperature required for producing $\alpha$-alumina. This state was called $\theta$-alumina by Stumpf et al.[5] and is considered to be a well-crystallised form of the $\gamma$-alumina[6]. The arrangement of oxygen ions varies, on further heating at much elevated temperatures, from cubic to hexagonal close-packing, resulting in the $\alpha$-alumina or corundum modification of alumina. In this paper an account is given on the mode of changes in a cathodo-luminescence spectrum of samarium ions brought about by heat treatments of samarium-bearing aluminas which have been derived from various alumina hydrogels, and effects of the heat treatments upon the so-called $\gamma$-$\alpha$ transformation of alumina are explained.

## Experimental Procedure and Results

Hydrous alumina gels were precipitated by means of neutralisation with ammonia from the solution of one of the following aluminium salts, namely nitrate, sulphate and chloride. These precipitates were washed with water several times on filters, and dried at about 110°C. One gram of each sample of the hydrous alumina gels thus obtained was soaked with 1 ml. of a samarium nitrate solution (the concentration of samarium in this solution is 1% calculated as samarium oxide), dried on a water bath, and ignited at a certain elevated temperature. The resulting samples of samarium-bearing alumina were subjected to cathode-ray bombardment, and cathodo-luminescence spectrograms were taken with a small glass-prism spectrograph of Feuss. The alumina obtained by the ignition at about 930°C for thirty minutes showed, when the aluminium nitrate was employed for the preparation of hydrous alumina gel, broad diffuse luminescence bands belonging to the luminescence prototype I[7], while that at 1000°C for one hour comparatively sharp line-like bands characteristic of the luminescence prototype II[7] (Photo. 1, a). The luminescence spectrum of the prototype I was, however, seen persistently in

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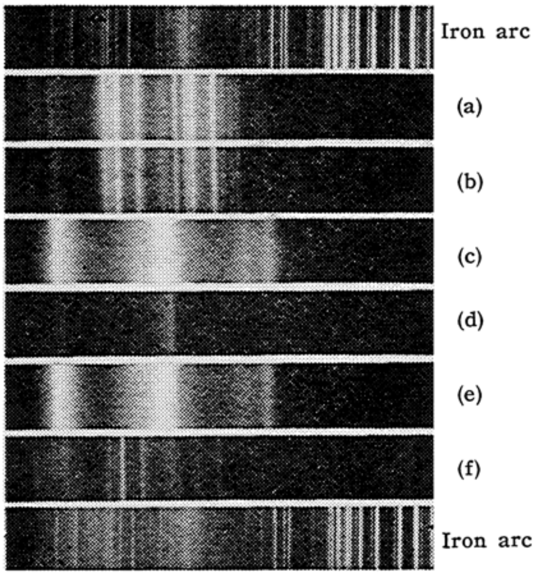

Photo. 1. Reproduction of the cathodo-luminescence spectra of samarium-bearing aluminas derived from various precipitated alumina hydrogels.

Alumina hydrogels were prepared by adding ammonia to solutions of aluminium nitrate (a), (b), of aluminium chloride (c), (d) and of aluminium sulphate (e), (f) respectively. The hydrogels were, after being soaked with a solution of samarium nitrate, converted to alumina by calcination at 1000°C (a), (c), (e) and by roasting in a direct flame of coal gas mixed with oxygen.

the case of alumina derived from either aluminium chloride or aluminium sulphate, without accompanying any band of the prototype II, even though heat treatment had been done at 1000°C for one hour or 1100°C for fifteen minutes (Photo. 1, c and e).

Extremely remarkable differences were observed in cathodo-luminescence spectra of samples of alumina derived from the various alumina hydrogels mentioned above, after being roasted intensely in a direct flame of coal gas mixed with oxygen. The alumina produced by neutralisation of aluminium nitrate solution showed, needless to say, the luminescence spectrum of the pure prototype II (Photo. 1, b), since this had already been attained by calcination at 1000°C, a much lower temperature than that of the present calcination. The alumina derived from the solution of aluminium chloride exhibited, however, a mixed luminescence spectrum of the prototypes I and III (Photo. 1, d), and that from the solution of aluminium sulphate a mixed luminescence spectrum of the prototypes II and III (Photo. 1, f).

It is worthy of note that the most intense luminescence band of the prototype III situated at 596.5∼598.0 mμ was seen in the cases of alumina, which had been prepared by precipitation from the solution of aluminium chloride and that of sulphate, and by subsequent ignition in a direct flame of coal gas mixed with oxygen. This luminescence band commenced to appear, after heat treatment had been made at 1200°C for fifteen minutes in the case of alumina derived from the solution of aluminium sulphate. The intensity of cathodo-luminescence bands belonging to the prototype I was decreased in the case of alumina produced from the solution of aluminium chloride, when roasting had been repeated in a direct flame of coal gas mixed with oxygen.

There were observed two luminescence bands at 648∼650 mμ and 642∼644.5 mμ in a spectral region between 640 and 650 mμ. It is to be mentioned that the former band was more intense than the latter in the case of alumina derived from the nitrate solution, while the order of intensity was reversed in the case of alumina derived from the solution of chloride or sulphate.

Samarium was directly added to dried alumina hydrogels in the experiments so far described. Investigations of cathodo-luminescence spectra of samarium are now being carried out on samarium-bearing samples of alumina, which have been prepared by an addition of samarium at various intermediate stages of thermal decomposition from the hydrous to the anhydrous alumina.

The hydrous alumina gel produced by precipitation with ammonia, was submitted to a previous heat treatment at a certain temperature between 200 and 1000°C. The thermally decomposed samples thus obtained have been soaked with the solution of samarium nitrate and then ignited for one hour over a blast flame of coal gas mixed with air. The samarium-bearing samples of alu-

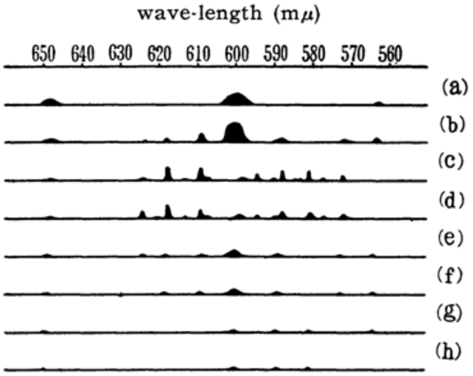

Fig. 1. Schematic representation of cathodo-luminescence spectrum of samarium-bearing alumina derived from the precipitated hydrogel.

Hydrous alumina gels were prepared from a solution of aluminium nitrate by precipitation with ammonia. Prior to the addition of samarium, the alumina gels were dried at 110°C (a), heated for 1 hr. at 200°C (b), at 230°C (c), at 270°C (d), at 300°C(e), at 400°C (f), at 700°C (g), and for 15 min. at 1000°C (h) respectively. All these were finally ignited in a blast flame of coal gas mixed with air.

mina derived from the solution of aluminium chloride or sulphate give always a cathodo-luminescence spectrum belonging to the prototype I, whereas this is not the case with those obtained from the solution of aluminium nitrate. A noteworthy phenomenon has been witnessed with the latter samples. Hydrous alumina gels yielded from the solution of aluminium nitrate, have been washed simply on filters as usual, heated at a temperature either below 200°C or above 400°C, soaked with the solution of samarium nitrate, and then ignited over a blast flame of coal gas mixed with air. These samples of alumina show samarium-luminescence spectra of the prototype I, as can be seen in Fig. 1, (a), (g) and (h).

When previous heat treatment was made at a moderately elevated temperature, namely between 230 and 270°C, and the other experimental conditions mentioned above were maintained, the resulting samples of samarium-bearing alumina give cathodo-luminescence spectra of the plain prototype II (Fig. 1, c and d), although the temperature of final heat treatment was considerably lower than that normally required for the $\gamma$-$\alpha$ transformation of alumina.

Experiments quite similar to those described above reveal, with thoroughly purified samples of hydrous alumina gels, that such a striking phenomenon is not encountered, the luminescence spectra being of the prototype I, so far as final ignition has been made over a blast flame of coal gas mixed with air.

Finally, results of investigations are described on hydrous alumina gels produced by immersing for a sufficiently long time crystals of aluminium nitrate enneahydrate, aluminium sulphate octodecahydrate, aluminium chloride hexahydrate and ammonium alum in concentrated solutions of ammonia respectively. The hydrous alumina gels resulting from these reactions were removed from the liquors, washed with water, dried at 110°C, soaked with the solution of samarium nitrate, and then ignited.

Cathodo-luminescence spectra of the prototype I were always obtained with samarium-bearing samples subjected to a moderate ignition over a blast flame of coal gas-air. These samarium-bearing samples showed, after ignited intensely in a direct flame of coal gas mixed with oxygen, cathodo-luminescence spectra of the prototype II, but a luminescence spectrum of the prototype III[7] appeared overlapping that of the prototype II in the cases of samarium-bearing alumina derived from hydrated crystals of aluminium chloride and aluminium sulphate.

## Discussion

According to Biltz's X-ray investigations[8], hydrous alumina gels yielded through neutralisation of a solution of aluminium sulphate with ammonia gave $\gamma$-modification of alumina, when subjected to heat treatments between 150 and 500°C. Hansen[9] also stated that hydrous alumina gels derived from a solution of aluminium chloride by precipitation with ammonia, was converted to the $\gamma$-alumina, when calcined at temperatures between 600 and 1000°C. A thermal transformation was said to proceed gradually from $\gamma$- to $\alpha$-alumina, and various temperatures were given for this transformation namely 950°C or higher[10], 1000°C[11], above 1000°C[12] and 1000~1200°C[13].

From the present authors' investigations on the feature of the cathodo-luminescence spectrum it is found that alumina gels derived from solutions of various aluminium salts show some differences in the temperature for the $\gamma$-$\alpha$ transformation, when samarium was added to the dried original hydrogels and the thermal transformation was caused in the presence of the samarium; the alumina hydrogel derived from a solution of aluminium nitrate is transformed into the $\alpha$-modification at temperatures between 930 and 1100°C, while that from a solution of aluminium chloride or sulphate is so far unable to be transformed by an intense heat treatment at 1100°C. Weiser[14] stated that a remarkable difference in the size of the constituting particles was confirmed by X-ray studies between the hydrous alumina gels produced from aluminium nitrate and those from either aluminium sulphate or chloride. This statement seems to deserve to be referred to in connection with the above-mentioned observations. There are also marked distinctions in the cathodo-luminescence spectrum between the alumina derived from a solution of aluminium chloride and that from a solution of aluminium sulphate, both samples of alumina being roasted at more elevated temperatures.

A peculiar configuration, namely the $\kappa$-modification of alumina, begins to be formed in some parts of the alumina derived from a solution of aluminium sulphate by heat treatment at 1200°C for fifteen minutes, the configuration being responsible for giving rise to the most intense luminescence band of the prototype III. This particular configuration is locally produced in corundum structure, when a much stronger heat treatment is made in a direct flame of coal gas

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mixed with oxygen. Thus the alumina obtained here does not consist of the simple corundum. The resulting alumina is composed of the mixture of $\gamma$- and $\kappa$-modifications, when the hydrogel derived from a solution of aluminium chloride has been subjected to an intense roasting in a direct flame of coal gas mixed with oxygen. The amount of its $\gamma$-ingredient is decreased by repeated heat treatments.

It was already presumed by one of the present authors⁷⁾ that the luminescence bands of the prototype III are perceptible, when the samarium ions exist in such an alumina that its constituting aluminium ions are situated favourably in tetrahedral rather than in octahedral interstices of cubic close-packed oxygen network. Verwey¹⁵⁾ compared the X-ray diagram of an ordinary spinel with that of the $\gamma$-alumina prepared by careful heating of aluminium hydroxide, which had been precipitated with ammonia, and thus arrived at a conclusion that octahedral interstices of the oxygen network are not filled up by aluminium ions in this $\gamma$-alumina. Hence, his conclusion is concordant with the postulation presented by one of the present authors, which has been deduced from investigations of the cathodo-luminescence spectra of samarium ions.

In short, the studies on the cathodo-luminescence spectra of samarium indicate that samples of alumina produced by neutralisation of solutions of aluminium nitrate, sulphate and chloride with ammonia, have constructions different from one another. This fact might naturally be related to the complicated characters shown by various kinds of alumina hydrogel, when they are employed as catalysts in some chemical reactions.

An impregnation of samarium ions may possibly stabilise the transient stage caused by thermal decomposition of hydrous alumina gels, and these stages would, in some cases, remain fixed in samples of anhydrous alumina obtained by the subsequent calcination at just below the temperature necessary for production of the $\alpha$-modification, since the large samarium ions might pack structural defects yielded during the course of thermal destruction of the hydrous alumina gels. This expectation is usually not fulfilled in the cases of hydrous alumina gels produced by precipitation with ammonia, irrespective of the different kinds of aluminium salts employed for the preparation of these alumina gels, the $\gamma$-modification of alumina being always obtained, which is confirmed by the feature of the cathodo-luminescence spectrum of the impregnated samarium. However, the intermediate configurations caused by suitable thermal treatments are, in the case of hydrous alumina gels derived from a solution of aluminium nitrate, likely made fixed by the impregnated samarium ions. The hydrous alumina gel in question was previously heated at a medium temperature, namely between 230 and 270°C for one hour, and the impregnation of samarium ions was made for the purpose of stabilising the intermediate configuration thus yielded. The samarium-bearing alumina resulting from a subsequent ignition in a blast flame of coal gas-air, gives a cathodo-luminescence spectrum of the plain prototype II, although the temperature of final heat treatment has been considerably lower than that normally required for the $\gamma$-$\alpha$ transformation of alumina. An X-ray diffraction investigation has also shown that this sample of alumina consists of the $\alpha$-modification. It should accordingly be presumed that the configuration yielded intermediately through the special heat treatment, closely resembles the structure of the $\alpha$-modification of alumina, which is fixed by the packing of the impregnated samarium ions.

The content of water and that of ammonium nitrate, the latter being the by-product of the neutralisation reaction, are estimated for the original sample of this hydrous alumina gel to be 1.00 and 0.39 g. of the resulting alumina respectively, while the water content is, in the samples partially decomposed by the special previous heat treatments at 230 and 270°C, reduced to 0.31 and 0.26 g. respectively and the ammonium nitrate content is also reduced to 0.30 and 0.06 g. respectively. The hydrous alumina gels mentioned above were produced by a simple washing on filters and not entirely free from the reaction by-products. In the case of hydrous alumina gel produced by neutralisation with ammonia, of a solution of aluminium nitrate, the reaction by-product, namely the ammonium nitrate remaining in the gel, seems to act, when its amount is moderate, as something like a mineraliser for accelerating the transformation into the $\alpha$-modification on being heated at much lower temperatures. A series of experiments indicates that such a striking effect is scarcely ever observed with the carefully purified samples of hydrous alumina gels.

The purified samples derived from a solution of aluminium nitrate were, after ammonium nitrate had been added to each of them in varying amounts, subjected to a mild heat treatment at 250°C for one hour, soaked

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15) E. J. W. Verwey, *Z. Krist.*, **91**, 69 (1935).

with the solution of samarium nitrate, and then calcined over the flame of coal gas mixed with air. All the resulting samples of samarium-bearing alumina show nothing but the cathodo-luminescence spectrum of the prototype I. Thus it becomes apparent that no extraordinary effect is produced, once the ammonium nitrate intimately held in the original alumina hydrogel has been removed, and a subsequent addition of ammonium nitrate can no more act as a special mineraliser for yielding the $\alpha$-modification of alumina.

## Summary

Hydrous alumina gels were prepared from both solutions and crystals of a number of aluminium salts, in the former case by precipitation with ammonia and in the latter by direct immersion in concentrated ammonia liquor. Samarium ions were impregnated in these hydrous alumina gels or in their transition phases resulting from the previous thermal treatment of various temperatures. The feature of the cathodo-luminescence spectrum was investigated on the samarium-bearing alumina produced from the above-mentioned samples by a final heat treatment.

Spectrographic measurements of the cathodo-luminescence reveal that the heating of the hydrous alumina gels derived from a solution of aluminium nitrate results in their conversion to the $\alpha$-alumina, while the heating of those from solutions of aluminium chloride and sulphate does not give the genuine $\alpha$-modification. This was confirmed by the fact that the most intense band of a particular luminescence prototype III as designated by one of the present authors was observed in the cathodo-luminescence spectra.

The $\gamma$-$\alpha$ transformation of alumina occurs at temperatures far below its transition temperature when a suitable amount of ammonium nitrate, the by-product of the neutralisation reaction, was caused to remain by heating the precipitated hydrous alumina gel, which was derived from a solution of aluminium nitrate at a moderately elevated temperature.

Similar remarkable results were, however, not obtained with hydrous alumina gels derived from solutions of aluminium chloride and sulphate, and also with the gel derived from a solution of aluminium nitrate, if the latter gel had been made free from the reaction by-product. An addition of ammonium nitrate to the purified alumina gels can no more regenerate the ability to accelerate the $\gamma$-$\alpha$ transformation.

It is interesting to note that hydrous alumina gels obtained by immersing crystals of aluminium nitrate enneahydrate, aluminium chloride hexahydrate, aluminium sulphate octodecahydrate and ammonium alum in concentrated ammonia liquor for a sufficiently long time behave themselves, on being heated, in a somewhat similar way to those obtained by precipitation from the solutions of the foregoing aluminium salts.

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