Cathodo-luminescence of Samarium as Applied to the Structural Studies of Alumina. IV. On Alumina yielded by Thermal Decomposition of Hydrated Crystals of Aluminium Salts

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(Received May 16, 1955)

Introduction

Thermal decompositions of aluminium salts, such as aluminium nitrate, ammonium alum and others come frequently into consideration for the practical preparation of alumina, particularly free from silica. Crystals of hydrated aluminium nitrate, hydrated aluminium sulphate and ammonium alum are, on being heated, dissolved in their water of crystallisation; they intumesce, lose volatile constituents and produce alumina as residue, while hexahydrated crystals of aluminium chloride are decomposed to anhydrous alumina without melting.

The present authors have applied cathodo-luminescence spectrum of samarium to elucidate the thermal decomposition process of some hydrated aluminium salts.

Samarium-bearing samples of alumina have been prepared from the aluminium salts either by thermal decomposition in the presence of samarium or by the introduction of samarium into decomposition products, which were yielded through suitable thermal treatments of hydrated aluminium salts. Luminescence spectra given by these samples of alumina have been investigated under cathode-ray excitation and the results are reported in the present paper.

Experimental results and discussions relating to them are described separately on samples of alumina, according to different combinations of the procedures for the imbedment of samarium and those for the thermal decomposition.

1) On Alumina derived from Calcination of Hydrated Crystals of Aluminium Salts, to which Samarium was previously added

Experimental Procedure

As much as 2.7, 1.7 and 2.0 ml. of a 1% aqueous solution of samarium nitrate was directly added to each 10g. of crystals of aluminium nitrate enneahydrate, aluminium sulphate octodecahydrate and aluminium chloride hexahydrate respectively, which were subsequently calcined at a certain temperature between 800 and 1000°C, or in a direct flame of coal gas mixed with oxygen. The quantity of the samarium nitrate solution to be added was so chosen that samarium calculated as oxide would amount approximately to 1% for the resulting alumina. Luminescence spectrograms of these samarium-bearing aluminas were taken under the excitation by cathode-rays and are schematically shown in Figs. 1—3. A superior quality of alumina has hitherto been prepared very often by a calcination of ammonium alum(1), since the alum can readily be purified through repeated crystallisations in an aqueous solution. A series of experiments similar to those mentioned above has been carried out on alumina derived from the ammonium alum, and the results are given in Fig. 4.

Results and Discussion

The cathodo-luminescence spectrum tends to vary from the prototype I to the prototype II, as the calcination temperature has been elevated, and the samples of alumina produced by the calcination at moderately high temperatures yield cathodo-luminescence spectra of the prototypes I and II overlapped with each other. An alumina, produced by calcining the hydrated crystals of aluminium nitrate at 800°C in the presence of samarium, gives a cathodo-luminescence spectrum of the typical prototype I, as shown schematically in Fig. 1, (a). Luminescence bands belonging to the *prototype II, namely bands at* 609, 618 and 624 mμ, commence to appear after the alumina was heated at about 900°C (Fig. 1, b) and become fairly intense after heated at 950°C (Fig. 1, c). Its luminescence spectrum changes almost completely to the prototype II, when the sample of alumina was calcined at 1000°C, but a diffuse luminescence band with the intensity-maximum at about 600 mμ, a characteristic one to the prototype I, still remains (Fig. 1, d). With the increased calcination temperature, two cathodo-luminescence bands become at first perceptible at 608 and 613 mμ, in a spectral region around 610 mμ, before a transition from the prototype I to the prototype II sets in, and a band at 609 mμ begins subsequently to appear, is increased rapidly in its intensity and at last surpasses the intensity of the above two bands (compare Fig. 1, b, c and d).

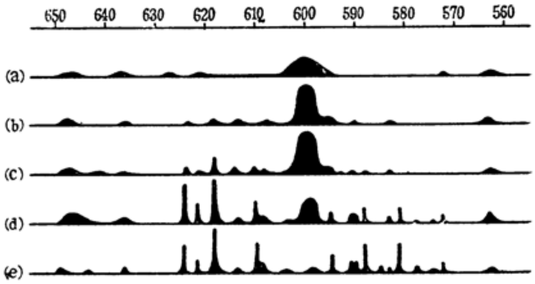

Fig. 1. Schematic representation of cathodo-luminescence spectrum given by samarium-bearing alumina, which was derived from calcination of aluminium nitrate enneahydrate in the presence of samarium.

Calcination was made at 800, 900, 950, 1000°C and in coal gas-oxygen flame for (a), (b), (c), (d) and (e) respectively.

Fig. 2, (a) and (b) show schematically the cathodo-luminescence spectra given by the samarium-bearing aluminas, which were prepared in the presence of samarium through the calcination of the hydrated aluminium sulphate at 800 and 900°C respectively, while Fig. 3, (a) illustrates that of a samarium-

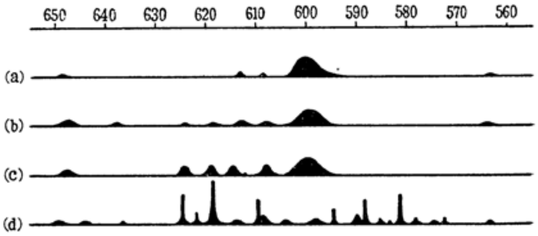

Fig. 2. Schematic representation of cathodo-luminescence spectrum given by samarium-bearing alumina, which was derived from calcination of aluminium sulphate octodecahydrate in the presence of samarium.

Calcination was made at 800, 900, 1000°C and in coal gas-oxygen flame for (a), (b), (c) and (d) respectively.

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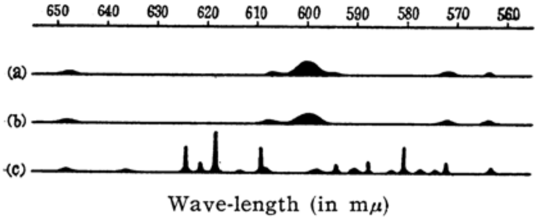

Fig. 3. Schematic representation of cathodo-luminescence spectrum given by samarium-bearing alumina, which was derived from calcination of aluminium chloride hexahydrate in the presence of samarium.

Calcination was made at 800, 1000°C and in coal gas-oxygen flame for (a), (b) and (c) respectively.

bearing alumina derived similarly by treating the hydrated aluminium chloride at 800°C.

The aluminas derived by the roasting from the hydrated aluminium sulphate and the hydrated aluminium chloride, undergo a transition toward α-modification with difficulty. To get the cathodo-luminescence spectrum of the prototype II is hardly possible, so far as the temperature of the calcination has not exceeded 1000°C (Fig. 2, c and Fig. 3, b), but it is attained through roasting in a direct flame of coal gas mixed with oxygen (Fig. 2, d and Fig. 3, c).

In the before-mentioned case of the alumina derived from the hydrated aluminium nitrate, the cathodo-luminescence spectrum of this prototype II was, however, seen in its fairly complete form, being overlapped with luminescence bands of the prototype I, after treated at 950°C (Fig. 1, c).

It might reasonably be presumed that proper structural transitions would, in some respects, be disturbed when the hydrated aluminium salts are thermally decomposed in the presence of foreign ions, namely samarium ions in the present case. This anticipation is realized by the observation that there appears an intermediate stage of alumina capable of showing luminescence bands at 608 and 613 mμ, but wanting a band at 609 mμ in its cathodo-luminescence spectrum (Fig. 1, b, Fig. 2, a, b and c).

Finally, crystals of ammonium alum were calcined over a blast flame of coal gas-air. Samarium was added to the resulting product and then the calcination was repeated over the blast flame. The cathodo-luminescence spectrum given by this sample of samarium-bearing alumina was found to consist mainly of the prototype I, accompanied by some luminescence bands of the prototype II situating at 588, 609, 618 and 624 mμ (Fig. 4, a).

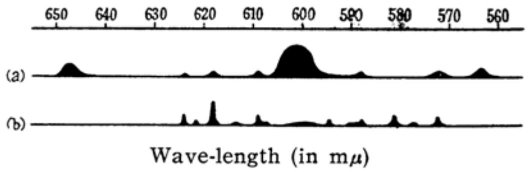

Fig. 4. Schematic representation of cathodo-luminescence spectrum given by samarium-bearing alumina, which was derived from calcination of ammonium alum in the presence of samarium.

Calcination was made in coal gas-air and coal gas-oxygen flames for (a) and (b) respectively.

According to Gorbunova[2], alumina obtained by calcination of ammonium alum at about 1100°C consists exclusively of γ-modification, and the transformation of the γ- to α-modification starts at 1150 or 1155°C, while Rinne[3] stated that the resulting alumina is composed of the γ-modification so long as the calcination temperature of ammonium alum is maintained below 1220°C. For a completion of the γ-α transformation, ammonium alum should be roasted above 1220°C according to Gorbunova[2], and it should be roasted at 1300°C according to Guseva[4]. However, the cathodo-luminescence spectrum of samarium indicates that the alumina derived from the calcination of ammonium alum is composed of the γ-modification mixed with some amounts of the α-modification, although the calcination has been made at a temperature far below that necessary for the yielding of the γ-α transformation.

The samarium-bearing alumina mentioned above gives, after being calcined strongly in a direct flame of coal gas-oxygen, a cathodo-luminescence spectrum of the genuine prototype II (Fig. 4, b), and thus the complete transformation toward the α-modification is now surely attained.

2) On the Alumina yielded in the Presence of Samarium through Calcination of Primarily Decomposed Products of Various Aluminium Salts

Experimental Procedure

Hydrated crystals of aluminium salts were heated at appropriate temperatures and the solution of samarium nitrate was added to resulting masses, which were then dried at 110°C and ignited over a blast flame of coal gas-air in order to ensure the expellation of volatile matters. Previous heat treatments prior to the introduction

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[2] O.E. Gorbunova and L.I. Vaganova, *Khim. Referat. Zhur.*, **2**, 31 (1939); *C.A.*, **34**, 2228 (1940).

[3] F. Rinne, *Neues Jahrb. Mineral. Geol. Beilage Bd. A*, 58, 43 (1928).

[4] P.G. Guseva and A.S. Ivanov, *Khim. Referat. Zhur.*, **2**, 85 (1939); *C.A.*, **34**, 3025 (1940).

of samarium, were made at 180, 500 and 700°C with crystals of aluminium nitrate enneahydrate, at 500, 700, 1100 and 1200°C with those of aluminium sulphate octodecahydrate, and at 200, 550, 1000 ond 1200°C with those of aluminium chloride hexahydrate respectively. These products were soaked with the solution of samarium nitrate and converted to anhydrous alumina by ignition over a blast flame of coal-gas mixed with air. The samples of samarium-bearing alumina thus prepared were subjected to cathode-ray bombardment, and spectrograms of the luminescence are schematically illustrated in Figs. 5–7.

Results and Discussion

It is concluded from the investigations on cathodo-luminescence spectra shown in Figs. 5–7 that, irrespective of the same final heat treatment at a comparatively low temperature, considerable distinctions are seen in the feature of the samarium-luminescence spectrum, depending upon the kinds of starting hydrated aluminium salts and the mode of their previous heat treatments. The configuration of the alumina giving rise to the luminescence prototype II, namely the α-alumina structure, seems to be much more readily produced by thermal decomposition of aluminium nitrate enneahydrate than by that of aluminium sulphate octodecahydrate and of aluminium chloride hexahydrate.

According to Parravano5) three waters of crystallisation were, on the heating of aluminium nitrate enneahydrate, expelled at 73.5°C and the resulting hexahydrate, $Al(NO_3)_3 \cdot 6H_2O$ changed then to a basic salt, $4Al_2O_3 \cdot 3N_2O_5 \cdot 14H_2O$ at 140°C. This basic salt was decomposed to anhydrous alumina at 200°C.

The decomposition of the hydrated aluminium nitrate is now found to proceed as far as 86% by a previous heat treatment at 180°C, namely 20°C below the temperature necessary for the production of anhydrous alumina. This partially decomposed product exhibits, after being mixed with the solution of samarium nitrate and ignited over a blast flame of coal gas-air, such a cathodo-luminescence spectrum as an overlap of the prototypes I and II, in which bands of the former prototype are remarkably intense (Fig. 5, a).

A conversion to the anhydrous alumina was already completed, when a previous heat treatment had been carried out at 500°C. Samarium was introduced into this decomposed product, which was then subjected to a final heating over a blast flame of coal gas-air. The cathodo-luminescence spectrum given by this sample was almost entirely of the prototype II (Fig. 5, b).

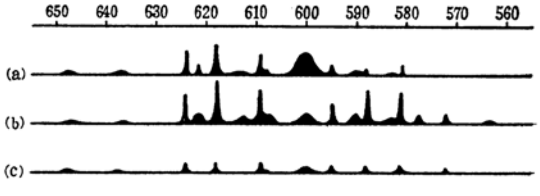

Fig. 5. Schematic representation of cathodo-luminescence spectrum given by samarium-bearing alumina, which was derived from calcination of aluminium nitrate enneahydrate.

Temperature of previous heating prior to the introduction of samarium was 180, 500 and 700°C for (a), (b) and (c) respectively. Final heat treatment was all made in a coal gas-air flame.

On heating octodecahydrated crystals of aluminium sulphate, anhydrous sulphate was formed at about 460°C6), and this was decomposed to alumina and sulphuric oxide gas at much more elevated temperatures, for which various numerical figures were presented, namely 650∼8506), 7605) and 850∼900°C7).

Samarium was added to anhydrous aluminium sulphate yielded by a previous heat treatment of the hydrated aluminium sulphate at 500°C. A samarium-bearing alumina derived by heating this product over a blast flame of coal gas-air gives a cathodo-luminescence spectrum of the typical prototype I (Fig. 6, a).

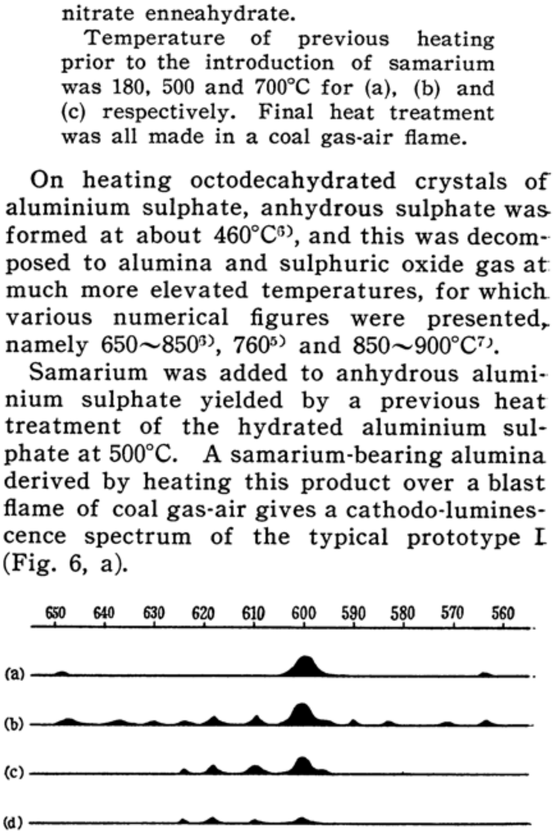

Fig. 6. Schematic representation of cathodo-luminescence spectrum given by samarium-bearing alumina, which was derived from calcination of aluminium sulphate octodecahydrate.

Temperature of previous heating prior to the introduction of samarium was 500, 700, 1100 and 1200°C for (a), (b), (c) and (d) respectively. Final heat treatment was all made in a coal gas-air flame.

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5) N. Parravano and G. Malquori, *Atti II congresso naz. chim. pura applicata*, **1926**, 1131; *C.A.*, **22**, 2119 (1928).

6) Y. Asada, *Bull. Inst. Phys. Chem. Reseach*, Tokyo, **17**, 1308 (1938).

7) S. Bretsznajder, *Przemyst Chem.*, **22**, 285 (1938); *C.A.*, **33**, 3974 (1939).

When a heat treatment prior to the introduction of samarium has been made at 700°C, a partially decomposed basic aluminium sulphate is probably produced. The samarium-bearing alumina obtained by roasting this product over a blast flame of coal gas-air, shows feeble luminescence bands of the prototype II in addition to fairly intense luminescence bands of the prototype I (Fig. 6, b). This means that the above-mentioned sample of alumina consists of a mixture of the γ- and α-modifications, although Day[8] stated that the alumina obtained by calcining the hydrated crystals of aluminium sulphate at 1000°C is wholly the pure γ-modification. It is to be mentioned that a complete disappearance of luminescence bands of the prototype I is not attained even by intense heat treatments at 1100 and 1200°C in the case of aluminium sulphate octodecahydrate (Fig. 6, c and d).

When aluminium chloride hexahydrate is heated, it decomposes without melting[9].

According to Parravano[5], the thermal decomposition curve of aluminium chloride hexahydrate showed breaks at 122° and at 180°C, the latter corresponding to a decomposition to anhydrous alumina.

The resulting samarium-bearing alumina gives always the cathodo-luminescence spectrum of the prototype I (Fig. 7, a), when hexahydrated crystals of aluminium chloride was previously calcined at a temperature between 200 and 1000°C, and then soaked with the solution of samarium nitrate, followed by ignition over a blast flame of coal gas-air, while that previously calcined at 1200°C and then treated in a similar way shows the cathodo-luminescence spectrum of the pure prototype II (Fig. 7, b).

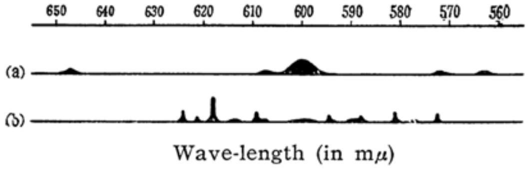

Fig. 7. Schematic representation of cathodo-luminescence spectrum given by samarium-bearing alumina, which was derived from calcination of aluminium chloride hexahydrate.

Temperature of previous heating prior to the addition of samarium was 550∼1000 and 1200°C for (a) and (b) respectively. Final heat treatment was all made in a coal gas-air flame.

Finally, samarium was introduced into decomposed products obtained by previous thermal treatments of crystals of ammonium alum at temperatures below 1200°C. When final heat treatment on these samarium-bearing samples had been made at a comparatively low temperature, namely over a blast flame of coal gas-air, the pure prototype I of the cathodo-luminescence spectrum was always seen. However, a transition to the pure prototype II took place in the cathodo-luminescence spectrum, if the temeperature of this heat treatment had been much more raised by using a direct flame of coal gas mixed with oxygen.

The foregoing studies on the cathodo-luminescence spectrum of samarium have revealed that the thermal decomposition to the α-alumina proceeds most readily for aluminium nitrate enneahydrate, and with difficulty for aluminium sulphate octodecahydrate and ammonium alum. The cathodo-luminescence of samarium is, in general, very weak for the alumina previously heated at considerably elevated temperatures as can be seen from a comparison of Fig. 5, (b) with (c), and from that of Fig. 6, (c) with (d) respectively. From these observations a conclusion might be drawn that it is likely to be difficult for samarium to enter into the configuration of an intensely calcined alumina.

Summary

Hydrated crystals of some aluminium salts, namely nitrate, chloride, sulphate and ammonium alum were subjected to heat treatments in the presence of a small amount of samarium ions. Cathodo-luminescence spectra were investigeted on the samarium-bearing aluminas thus resulted. A conversion of the luminescence spectrum takes place, as the temperature of the heat treatment has been elevated, from the prototype I to the prototype II, which corresponds to the γ-α transformation of an alumina. It was, however, confirmed that there are some differences in the facility of this conversion according to the kinds of aluminium salts employed for the preparation of alumina.

Some alterations were, furthermore, perceived in the intensity of luminescence bands situating in the vicinity of 610 mμ, when the hydrated crystals of aluminium nitrate were submitted to the heat treatments of various elevated temperatures.

Hydrated crystals of these aluminium salts were heated previously at various temperatures between 180 and 1200°C. After the addition of samarium ions, they were roasted.

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[8] M.K. Day and V.J. Hill, *J. Phys. Chem.*, **57**, 950 (1953).

[9] J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans & Co., London (1924), 5, p. 316.

The resulting samarium-bearing aluminas give rise to cathodo-luminescence spectra, which reveal that a conversion to the genuine α-modification proceeds most readily in the case of aluminium nitrate, while it occurs with difficulty in the cases of hydrated aluminium sulphate and ammonium alum. It seems to be hard for samarium ions to enter into the configuration of alumina, when previous thermal treatments of aluminium salts have been carried out at much elevated temperatures.

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

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