Cathodo-luminescence of Samarium as Applied to the Structural Studies of Alumina. I. Three Prototypes for the Luminescence Spectra of Samarium in Alumina

By Eiichi IWASE

(Received April 25, 1955)

Introduction

Studies on the structures of alumina and alumina-hydrate as well as their structural variations during dehydration and calcination have made steady and marked progress in recent years, being based mainly on the results of X-ray diffraction investigations. The present author has carried out over a number of years extensive investigations on the cathodo-luminescence spectra of certain rare earths, such as praseodymium and samarium, which were impregnated into a great variety of anhydrous alumina, derived from hydrargillite, bayerite and boehmite, or from hydrous alumina gels, or from hydrated crystals of aluminium salts.

Rohden¹⁾ as well as the present author²⁾ have already made spectrographic studies on the cathodo-luminescence of samarium imbedded in alumina and a different set of luminescence bands was assigned for it respectively. These two sets of the luminescence spectra for the samarium-bearing alumina are likely to correspond to an observation described in Lecoq de Boisbaudran's³⁾ classical work; namely the samarium imbedded in alumina gave two different cathodo-luminescence spectra, according as the calcination temperature was varied.

---

1) Ch. de Rohden, *Ann. chim.*, [9] 3, 362 (1915).

2) E. Iwase, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **34**, 770 (1938).

3) Lecoq de Boisbaudran, *Compt. rend.*, **105**, 258 (1887).

Rohden[4] proposed, on the other hand, one definite kind of cathodo-luminescence spectrum for praseodymium-bearing alumina. Three prototypes have, however, been brought forward quite recently by the present author and his collaborators[5] for cathodo-luminescence spectra of the praseodymium imbedded in various kinds of alumina, and some interpretations have also been given for their occurrences from a structural standpoint.

This paper presents three prototypes of the cathodo-luminescence spectra owing to samarium existing in three different kinds of alumina respectively, and shows the interdependence of the alumina-structure and the samarium-luminescence spectrum, since cathodo-luminescence bands due to the samarium ions are, in general, much more intense than those due to the praseodymium ions in solid inorganic ground-materials.

TABLE I

CATHODO-LUMINESCENCE SPECTRA OF SAMARIUM-BEARING ALUMINA

Prototype I		Prototype II		Prototype III	
Wave-length (mμ)	Intensity	Wave-length (mμ)	Intensity	Wave-length (mμ)	Intensity
656 651	w	661 658.5	w	656 654	w
646 (maximum)	s	650 648	ww	649.5 644.5	w w
644 635	w	644.5 642	ww	625 623	s
		637 635	ww	621.5 620	s
621		624.5 623	s	616 615	m
		622 620.5	m	613 612	s
	m	619 616.5	ss	611 609.5	s
		614.5 612	w	609 607	s
		610 608.5 606.5	s m	606 604	m
604		604.5 602	ww	603 602	m
599.5 (maximum)	ss	600 596	ww	600 598 596.5 593	w ss w
594		595 593.5	m		
		591 590	m	589.5	
		590 589	m		ww
	w	588.5 587 586	s ww	587	
		585 582.5	ww	583.5 582.5	w
581		581 580	s	581 580	w
		578 576.5	ww	578 577	ww
574		575 573.5	ww		
	s	572	w	571.5	m
568				568	ww
567	ww			566	ww
565				562.5	m
560.5	m			561	m
551				553.5	ww
547	w			548.5	ww
545	w				
542.5				542.5	ww
541	m				
540.5	ww				

---

[4] Ch. de Rohden, *Ann. chim.*, [9] 3, 360 (1915).

[5] E. Iwase, S. Nishiyama and T. Isono, This Bulletin, 28, 345 (1955).

Experimental

Three samples of samarium-bearing alumina were prepared by the following methods.

Sample 1: The hydrous alumina gel was precipitated by the addition of ammonia to a cold solution of aluminium sulphate. After being washed with water and dried at 110°C, the gel was soaked with a solution of samarium nitrate and then ignited at about 900°C for one hour.

Sample 2: Crystals of aluminium nitrate enneahydrate were partially calcined at about 180°C until they became porous masses, which were ground to fine powders, soaked with the solution of samarium nitrate and roasted at 1200°C or above.

Sample 3: Fine granular crystals of the hydrargillite obtained by the Bayer process, namely crystals of alumina-trihydrate, were previously calcined at a suitable temperature, for example 800°C for one hour. The anhydrous alumina thus obtained was, after the solution of samarium nitrate had been added, ignited at about 900°C for one hour.

The samarium introduced into the above-mentioned samples of alumina, serves as an activator to cause the cathodo-luminescence, and its concentration was adjusted to be nearly 1% calculated as oxide for a ground-material, namely alumina in the present cases.

These samples of samarium-bearing alumina were subjected to cathode-ray bombardment in a small Urbain tube and their luminescence was spectrographically investigated by employing a Feuss glass-prism spectrograph.

Results

Table I shows results of the cathodo-luminescence spectra given by the samples 1, 2 and 3. Relative intensities of the luminescence bands were estimated visually and indicated by the following symbols; ss(very strong), s(strong), m(medium), w(weak) and ww(very weak).

These luminescence spectra are reproduced in Photos. 1, 2 and 3. They are schematically given in Fig. 1, (a), (b) and (c) in order to facilitate comparisons. Luminescence spectra of the samples 1, 2 and 3 have quite different and readily distinguishable appearances, and thus may be designated as the three prototypes I, II and III respectively for the cathodo-luminescence spectra due to the samarium ions, which have been imbedded in different modifications of alumina. The prototype I of samarium-luminescence spectrum is composed of several broad diffuse bands, while the prototypes II and III are composed of a number of relatively sharp line-like bands.

Discussion

The sample 1 of samarium-bearing alumina is found, on one hand, giving the cathodo-luminescence spectrum of the prototype I (Fig. 1, a, and Photo. 1) and, on the other

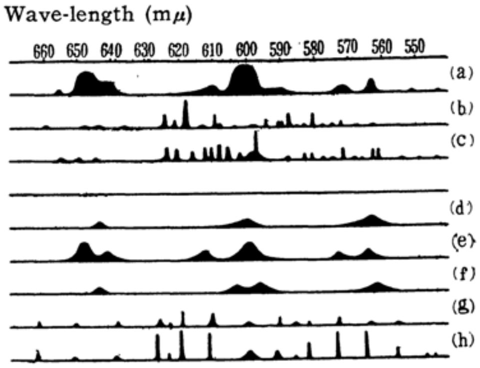

Fig. 1. Schematic representation of luminescence spectra due to samarium in alumina and in water.

Cathodo-luminescence spectrum of prototype I (a), of prototype II (b), and of prototype III (c), Luminescence spectrum of Al_2O_3-Sm calcined at low temperatures (Lecoq de Boisbaudran) (d), of Al_2O_3-Sm (Iwase) (e), of aqueous solution of $SmCl_3$ (Lecoq de Boisbaudran) (f), of Al_2O_3-Sm calcined at elevated temperatures (Lecoq de Boisbaudran) (g), and of Al_2O_3-Sm (Rohden) (h).

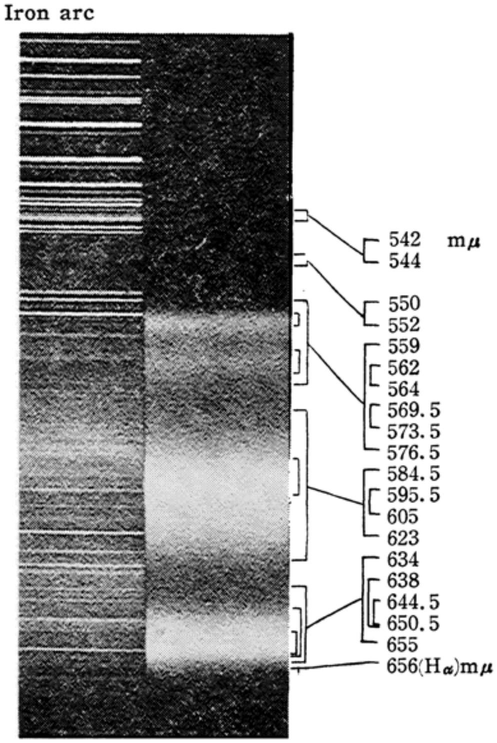

Photo. 1. Prototype I of the cathodo-luminescence spectrum of samarium-bearing alumina.

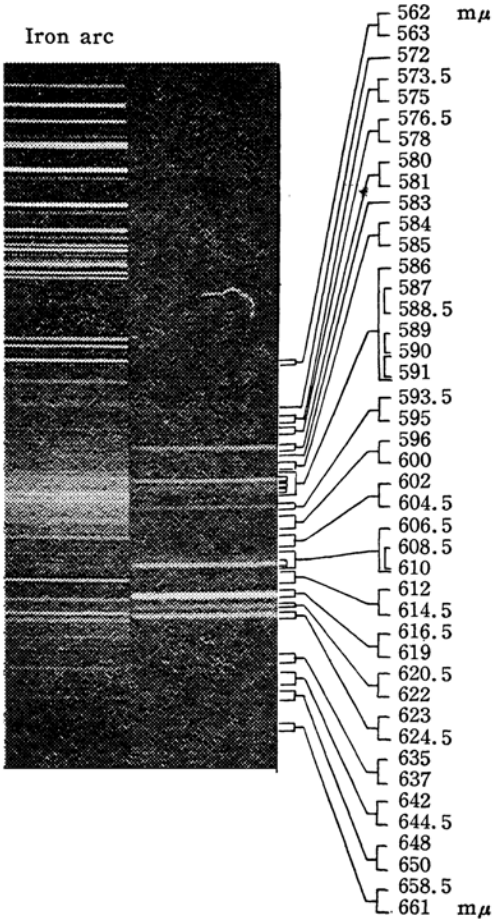

Photo. 2. Prototype II of the cathodo-luminescence spectrum of samarium-bearing alumina.

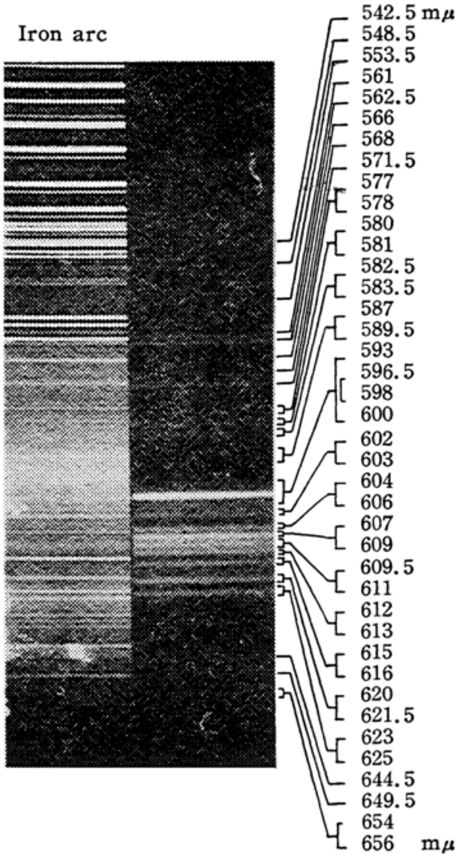

Photo. 3. Prototype III of the cathodo-luminescence spectrum of samarium-bearing alumina.

hand, having the structure of γ-modification as revealed by an X-ray investigation[5]. This luminescence prototype may simply accounted for by the luminescence spectrum caused by the excitation of samarium ions in solution, since the present author has confirmed that samarium ions distributing at random in an optically isotropic substance, for example in an ordinary glass, show a cathodo-luminescence spectrum quite akin to that of the prototype I (Photo. 4). The γ-modification of alumina is considered to be, in harmony with the above statement, constructed from the oxygen-ion network of cubic close-packing with aluminium ions distributing in a statistical way over its whole interstices evenly[6].

Additional examples for this luminescence prototype are supplied by samarium-bearing alumina prepared by means of the calcination at low temperatures, as already described by Lecoq de Boisbaudran[3] (Fig. 1, d) as well as the present author[2] (Fig. 1, e), and by a solution of samarium chloride, as shown by Lecoq de Boisbaudran[3] (Fig. 1, f).

The luminescence spectrum of the prototype II (Fig. 1, b and Photo. 2) is decisively produced by samarium ions imbedded in a corundum structure, in which oxygen ions are arranged in hexagonal close-packing, because a study of the X-ray diffraction pattern has revealed that the sample 2 is really α-modification of alumina[5]. The cathodo-luminescence spectrum of samarium-bearing alumina calcined at greatly elevated temperatures belongs to this prototype, according to observations by Lecoq de Boisbaudran[3] (Fig. 1, g) and Rohden[1] (Fig. 1, h).

In addition to the above-mentioned two luminescence prototypes another conspicuous luminescence spectrum is obtained, which seems overlooked by the investigators. This new luminescence spectrum may be designated as the prototype III for the luminescence spectrum of samarium ions existing in an

---

[6] E. J. W. Verwey, *Z. Krist.*, 91, 68 (1935).

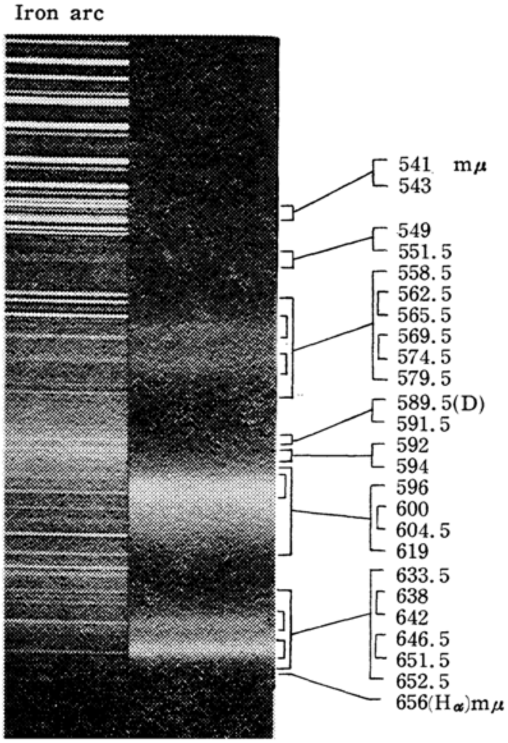

Photo. 4. Cathodo-luminescence spectrum of samarium-bearing glass.

alumina, and is seen in its pure form only with a sample of samarium-bearing alumina, which has been yielded from the hydrargillite by a suitable heat treatment, prior to the addition of samarium (Fig. 1, c and Photo. 3). Brown⁷⁾ and Day⁸⁾ have recently proposed that the hydrargillite should thermally be decomposed to the α-alumina through dual routes simultaneously, one proceeding directly through a sequence of virtually anhydrous aluminas, namely χ-and κ-modifications, and the other through boehmite followed by a series of other virtually anhydrous aluminas, namely γ-, δ-, and θ-modifications. Both of these two routes lead eventually to a common product, the α-alumina. There remains much to be proved, as to whether or not the formation of the boehmite is of primary nature⁷⁾⁸⁾⁹⁾¹⁰⁾ in this case, and further precise investigations seem necessary in this connection.

It has been confirmed, from an X-ray powder diffraction analysis⁵⁾, that the sample 3 of samarium-bearing alumina is almost completely composed of κ-modification. This κ-modification is assumed to be an intermediate alumina produced in one route of the dual thermal transformation from the hydrargillite to the α-alumina. Provided that the X-ray diffraction line in the immediate vicinity of 2.0 Å is caused by the reflection from (400) planes of a spinel lattice¹¹⁾, its estimated relative intensity would allow us to elucidate whether most of the aluminium ions take their seats in tetrahedral or octahedral interstices of the oxygen network of cubic close-packing. It may probably be concluded, for structural reasons quite similar to those previously made concerning the three prototypes for cathodo-luminescence spectra of praseodymium-bearing aluminas⁵⁾ that aluminium ions would fill tetrahedral in preference to octahedral interstices in the decomposition sequence leading directly through anhydrous aluminas. This is likely to be the reason why the luminescence spectrum of the prototype III appears in its genuine form only in the case of samarium-bearing alumina derived from the hydrargillite by a suitable previous heat treatment.

Almost all the luminescence spectra caused by samarium ions existing in numerous samples of anhydrous alumina, which have been obtained in various ways of preparation, may be interpreted as belonging to either one of the three prototypes mentioned above or their combinations.

Conclusion

Cathodo-luminescence spectra given by samarium ions, which have been imbedded in various samples of anhydrous alumina can, according to circumstances, be regarded as belonging to either one of the three luminescence prototypes, namely I, II and III, or their combinations.

It is concluded that the three ways of the reciprocal arrangements for oxygen and aluminium in the configuration of a groundmaterial, namely alumina in the present cases, may be closely related to the occurrence of these three fundamental spectral types for the samarium-activated luminescence.

The luminescence prototype II mentioned above is obtained with an alumina having the oxygen network of hexagonal close-packing, namely α-modification of alumina, while the luminescence prototypes I and III are caused by aluminas possessing the oxygen network of cubic close-packing.

Which of the last two prototypes of lumi-

---

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

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

9) T. Sato, *J. Chem. Soc. Japan, Ind. Chem. Section*, **55**, 66 (1952).

10) H.T. Tran et M. Prettre, *Compt. rend.*, **234**, 1366 (1952).

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

nescence is produced, depends probably upon the manner of aluminium ions in occupying the two sorts of interstices of the cubic close-packed oxygen network, namely octahedral and tetrahedral interstices. The luminescence prototype I is seen with γ-modification of alumina, in which aluminium ions are statistically distributed evenly throughout the two sorts of interstices mentioned above, whilst the luminescence prototype III is observed with κ-modification of alumina, where aluminium ions take, for the most part, their seats in the tetrahedral rather than in the octahedral interstices.

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

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