Three Prototypes for the Cathodo-luminescence Spectra of Praseodymium in Various Forms of Alumina

By Eiichi IWASE, Seijiro NISHIYAMA and Toshiaki ISONO

(Received February 23, 1955)

Introduction

The structures of aluminas and alumina-hydrates have recently been the subject of extensive researches, the X-ray diffraction method being, as is well known, almost always employed for this purpose. The present authors have tried, in the course of the studies on the similar problems, to apply a spectrographic method of the cathodo-luminescence brought about by a certain rare earth, either praseodymium or samarium, which was imbedded in the various specimens of alumina, and have found this method fairly effective in solving such yet indistinct problems. This paper presents the finding of the three prototypes for the cathodo-luminescence spectra given by the praseodymium-bearing alumina, and at the same time the structural interpretations as well as the preparations for the samples of alumina corresponding to the yielding of these three luminescence prototypes.

Materials and Experimental Procedures

Three samples of alumina containing praseodymium were prepared as follows.

Sample 1.—The hydrous alumina gel was precipitated with ammonia from the solution of aluminium sulphate, washed by decantation, filtered, and dried at about 110°C. This dried gel was soaked with a solution of praseodymium nitrate and then ignited at about 900°C for 1 hr.

Sample 2. — Crystals of aluminium nitrate ennea-hydrate were partially calcined at about 180°C until they became fine powders, which were then soaked with a solution of praseodymium nitrate and ignited at 1200–1300°C.

Sample 3. — Crystals of alumina-trihydrate produced by Bayer process, namely hydrargillite were previously calcined at about 800°C for 1 hr. The thermally decomposed product was soaked with a solution of praseodymium nitrate and then ignited at about 900°C for 1 hr.

The amount of praseodymium to be introduced was always made about 1% as oxide to the resulting sample of alumina.

The three samples mentioned above were submitted to the cathode-ray bombardment in a small Urbain tube and their luminescences thus yielded were spectrographically investigated by employing a glass-prism spectrograph of Feuss.

Experimental Results

Fig. 1, (a), (b) and (c) shows schematically the results of the investigations on the cathodo-luminescence spectra given by the samples 1, 2 and 3 respectively. The relative intensities of the luminescence bands were estimated visually, and indicated by the heights in the figures.

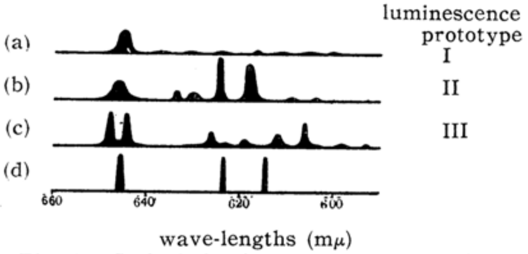

Fig. 1. Cathodo-luminescence spectra of praseodymium-bearing aluminas.

These three luminescence spectra have quite different and readily distinguishable appearances, and may be regarded as the three prototypes for the cathodo-luminescence spectra due to the praseodymium ions exisiting in various kinds of alumina.

The luminescence spectra given by the samples 1, 2 and 3 are, for convenience, called the luminescence prototypes I, II and III respectively.

Discussions

It has generally been considered that a certain rare earth element imbedded in a colorless inorganic ground-material of definite chemical composition, will give rise to a fixed luminescence spectrum. A few exceptions have, however, been reported: When the europium or samarium is present in either magnesia or calcium sulfide, the luminescence spectrum given by one of these rare earths differs in its details rather widely, depending on the manner of preparations for the luminescent materials, although the ground-materials have the same chemical composition[1].

---

[1] P. Pringsheim; "Fluorescence and Phosphorescence", Interscience publishers, Inc., New York, (1949), p. 470.

The luminescence of praseodymium mentioned here may provide a further noteworthy example of these interesting exceptional cases.

Rohden[2] described a definite luminescence spectrum for the praseodymium-bearing alumina as shown in Fig. 1, (d). It is concluded, from the comparison of Rohden's data with the three luminescence prototypes found by the present authors, that Rohden's spectrum seems to correspond to the prototype II.

The feature of the luminescence bands yielded by a rare earth, which has been introduced in a crystalline ground-material, is mainly determined by the transitions between electronic levels of the rare earth ion. The individual luminescence bands corresponding to these transitions may be influenced by the Stark effect owing to the electric field of the surrounding ions, and also to some extent by the lattice vibrations of the ground-material[3]. Thus the crystal structure of the ground-material would be expected to produce, in some cases, rather remarkable effects upon the feature of luminescence spectrum.

X-ray diffraction photographs have been taken of the samples 1, 2 and 3 in a Debye-Scherrer powder camera using copper K_α filtered radiation, and the results obtained are schematically illustrated in Fig. 2.

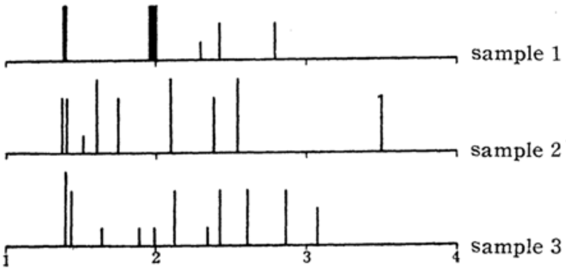

Fig. 2. Graphical representations of X-ray diffraction data for aluminas.

It will be seen that the X-ray diffraction patterns for the samples of alumina 1, 2 and 3 coincide almost entirely with those of γ-[4], α-[5] and κ-[6] modifications of alumina respectively.

The oxygen arrangement in alumina is hexagonal close-packed for α-modification, while it is cubic close-packed for the γ- and κ-modifications.

The aluminium ions of the α-modification are situated in the octahedral interstices of the oxygen networks, and this configuration of alumina yields decisively the luminescence prototype II of the praseodymium.

In the case of γ-modification the aluminium ions are said to be situated statistically in the octahedral and tetrahedral interstices of the cubic close-packed oxygen networks evenly, and it may therefore be assumed that the praseodymium ions introduced in this modification of alumina will also be distributed at random through these two kinds of interstices. The luminescence prototype I of the praseodymium given by the γ-modification of alumina may accordingly be considered as the luminescence spectrum of the praseodymium in solution.

It is also found that the praseodymium contained in an optically isotropic substance, namely ordinary glass emits the cathodoluminescence spectrum almost similar to that of the prototype I. This fact seems to support the above reasoning.

Ervin[7] has recently postulated the position occupied by aluminium ions in the oxygen networks of cubic close-packing, by taking the intensity of the line at 1.985–2.03 Å observed in X-ray diffraction patterns into considerations. This line is caused by the reflection from (400) planes of the spinel lattice, which include all the oxygen positions and the octahedral aluminium positions, but not the tetrahedral aluminium positions. It is to be remarked that this line is found to be weak in the κ-modification of alumina as compared with the γ-modification. Provided the postulation described above is valid for the κ- and γ- modifications of alumina, the conclusion may then be drawn that the aluminium ions in the κ-modification should be situated much more predominantly in the tetrahedral rather than the octahedral interstices of oxygen networks.

The praseodymium-luminescence of the prototype III can be seen distinctly only in the case of the praseodymium-bearing alumina, which has been derived from the hydrargillite through the special previous heat treatment.

The practical thermal decomposition of hydrargillite is, at the present, considered to proceed simultaneously through dual routes[8], the one through boehmite followed by a

---

[2] A. de Rohden, *Ann. chim.*, [9] **3**, 361 (1915).

[3] R. Tomaschek, *Acta Phys. Polonica*, **6**, 401 (1936).

[4] H. C. Stumpf, A. S. Russell, J. W. Newsome, and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1402 (1950).

[5] H. Thibon, J. Charrier and R. Tertian, *Bull. soc. chim. de Fr.*, [5] **18**, 387 (1951).

[6] J. F. Brown, D. Clark and W. W. Elliott, *J. Chem. Soc.*, **1953**, 86.

[7] G. Ervin, *Acta Cryst.*, **6**, 106 (1953).

[8] J. F. Brown, D. Clark and W. W. Elliott, *J. Chem. Soc.*, **1953**, 85; M. R. B. Day and V. J. Hill, *Nature*, **170**, 539 (1952); *J. Phys. Chem.*, **57**, 946 (1953).

series of virtually anhydrous alumina, namely γ-, δ- and θ-modifications, and the other directly through a sequence of other virtually anhydrous alumina, namely χ- and κ-modifications, both of these routes leading eventually to a common product, the α-modification. Irrespective of whether the formation of boehmite is of primary[9] or of secondary origin[10], it seems to be almost certain that the thermal decomposition of hydrargillite forks off in practice into two branches on the way of the transformation to the α-modification of alumina. In the route of conversion directly via the anhydrous aluminas, for example the κ-alumina, the aluminium ions tend to be arranged in the tetrahedral interstices of the cubic close-packed oxygen networks. This arrangement seems to be characteristic of the thermal transformation sequence derived from the hydrargillite and responsible for giving rise to the luminescence prototype III of praseodymium.

Conclusion

Almost all the cathodo-luminescence spectra given by the various preparations of the praseodymium-bearing alumina can be regarded as belonging to either one of the three prototypes (I, II and III) or their combinations.

The occurrence of these three fundamental spectral types for the praseodymium-luminescence may closely be related with the three ways for the reciprocal arrangements of oxygen and aluminium in the configuration of alumina.

The prototype II of the praseodymium-luminescence spectrum is obtained for the alumina with the oxygen network of hexagonal close-packing, namely the α-modification.

The alumina with the oxygen network of cubic close-packing, shows either the luminescence prototype I or III, depending upon the location of aluminium ions. The prototype I is seen in the γ-modification of alumina, where the aluminium ions are statistically distributed evenly throughout the two sorts of interstices of the oxygen network, namely octahedral and tetrahedral interstices, while the luminescence prototype III is yielded with the κ-modification of alumina, in which the aluminium ions take their seats in the tetrahedral rather than in the octahedral interstices.

In connection with the X-ray investigations here included thanks are due to Dr. M. Nakahira. The authors are also grateful to the Ministry of Education for the Scientific Research Encouragement Grant in aid of this work.

The Institute of Scientific Researches,
Komagome, Bunkyo-ku, Tokyo

---

[9] J. E. Brown, D. Clark and W. W. Elliott, *J. Chem. Soc.*, **1953**, 85.

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