JOURNAL OF SOLID STATE CHEMISTRY 3, 452–457 (1971)

Luminescence of Alkaline Earth Yttrium and Lanthanum Phosphate-Silicates with Apatite Structure

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Received February 5, 1971

The following compositions having the apatite structure were prepared:

$$\mathrm{Me}^{\mathrm{II}}_{2+x}\mathrm{Me}^{\mathrm{III}}_{8-x}(\mathrm{SiO}_4)_{6-x}(\mathrm{PO}_4)_x\mathrm{O}_2, \quad (0 \leqslant x \leqslant 6) \quad (\mathrm{I})$$
$$\mathrm{Me}^{\mathrm{II}}_{3+x}\mathrm{Me}^{\mathrm{III}}_{6-x}(\mathrm{SiO}_4)_{6-x}(\mathrm{PO}_4)_x, \quad (0 \leqslant x \leqslant 1.5) \quad (\mathrm{II})$$
$$\mathrm{Me}^{\mathrm{II}}_{4+x}\mathrm{Me}^{\mathrm{III}}_{6-x}(\mathrm{SiO}_4)_{6-x}(\mathrm{PO}_4)_x\mathrm{O}, \quad (0 \leqslant x \leqslant 6) \quad (\mathrm{III})$$

with $\mathrm{Me}^{\mathrm{II}}$ = Ca, Sr, Ba, Mg, Zn or Cd and $\mathrm{Me}^{\mathrm{III}}$ = Y or La. Among these are several new compounds; e.g., $Zn_2La_8(SiO_4)_6O_2$, $BaMgY_8(SiO_4)_6O_2$, $Zn_2Y_8(SiO_4)_6O_2$, $Cd_2Y_8(SiO_4)_6O_2$, $Ca_4La_5(SiO_4)_5(PO_4)$ and $Ba_4La_5(SiO_4)_5(PO_4)$. The crystallographic parameters were determined and their luminescence studied.

The most efficient activator proved to be trivalent antimony, especially in compositions of type I. At 77°K an emission band at about 400 nm was observed in many of the apatites.

Introduction

Many inorganic compounds have the structure of the mineral apatite $Ca_{10}(PO_4)_6F_2$. The most important group consists of the type $\mathrm{Me}_{10}(\mathrm{X}^{\mathrm{V}}\mathrm{O}_4)_6\mathrm{Z}_2$, in which $\mathrm{Me}^{\mathrm{II}}$ stands for Ca, Sr, Ba, Cd, Pb and Mn, X^{V} for P, As, V and Z for F, Cl and OH. The XO_4 anions may be partially or totally replaced by SO_4, CrO_4, SiO_4 and GeO_4, requiring the simultaneous substitution of monovalent ions (Na,K) or trivalent cations (Al, Fe and rare earths), respectively, for the divalent cations. Reviews of compounds with apatite structure can be found in the recent theses by Hoekstra (*1*), Kreidler (*2*), and Grisafe (*3*).

Several compounds that have the apatite crystal structure show luminescence, especially those of the type $\mathrm{Me}^{\mathrm{II}}_{10}(\mathrm{PO}_4)_6\mathrm{Z}_2$ (Z = F or Cl). To this group belongs the most important lamp phosphor $Ca_{10}(PO_4)_6(F,Cl)_2$ — Cahalophosphate — activated by Sb^{3+} and Mn^{2+}, developed in 1942 by McKeag (*4*).

Schwarz (*5*) prepared several new compounds with the apatite structure, viz., $La_{9.33}(SiO_4)_6O_2$ (IV) and $La_{8.67}(SiO_4)_6O$ (V). Substituting Sr for a part of the La also gives compounds with the apatite crystal structure, viz., $Sr_2La_8(SiO_4)_6O_2$ (VI), $Sr_3La_6(SiO_4)_6$ (VII), and $Sr_4La_6(SiO_4)_6O$ (VIII).

Compounds with the apatite structure are also found after substitution of 1 Sr ion for 1 La ion and 1 PO_4 group for 1 SiO_4 group in compounds of the type VI, VII and VIII. This leads to the following types of compounds described by Schwarz (*5*):

$$Sr_{2+x}La_{8-x}(SiO_4)_{6-x}(PO_4)_xO_2 \ (\mathrm{IX}) \quad \text{with } 0 \leqslant x \leqslant 6;$$

$$Sr_{3+x}La_{6-x}(SiO_4)_{6-x}(PO_4)_x \ (\mathrm{X}) \quad \text{with } 0 \leqslant x \leqslant 1.5; \text{ and}$$

$$Sr_{4+x}La_{6-x}(SiO_4)_{6-x}(PO_4)_xO \ (\mathrm{XI}) \quad \text{with } 0 \leqslant x \leqslant 6.$$

We prepared the foregoing compounds of the types IX, X and XI, but also others in which Sr was partially or totally replaced by other divalent ions, viz. Ca, Ba, Mg, Zn, Cd and La by Y. In the type X group of compounds, La was totally replaced by Ce, Sm, Dy, Eu and Y, with $x = 1.5$. The cell constants of the synthesized products were determined. In addition, activation was carried out with various elements, viz. Sb, Bi, Ce, Eu, Tb, Sn, Mn and Pb. It was found that Sb is the most efficient activator in the relevant host lattices when excited with 254 nm radiation.

Experimental

The ingredients used in the reaction mixture were luminescent grade $CaHPO_4$, $SrHPO_4$, $BaHPO_4$,

$CaCO_3$, $SrCO_3$, $MgCO_3$, ZnO, $CdCO_3$, $BaCO_3$ and $(NH_4)_2HPO_4$; SiO_2 (aerosil) as obtained from the firm Degussa; La_2O_3 (99.9%) from the firm Auer Remy or Péchiney and Y_2O_3 (99.9%) from Péchiney. The activator elements were added as oxides, except Ce which was added as the oxalate, Mn (as the carbonate) and Bi (as the basic carbonate).

Since Sb_2O_3 may be volatilized at the heating temperature, in many cases the antimony was added as $2SrO \cdot Sb_2O_3$ (6), a compound which is stable up to 1200°C in an atmosphere of nitrogen. In the preparation of some of the Ca compounds $2CaO \cdot Sb_2O_3$ was used, which decomposes at the preparation temperature of the apatites (*6*).

The required amounts of the starting ingredients were thoroughly mixed and subsequently fired. In most cases we used a molar composition of the firing mixture with a deficiency of cations, just as the most efficient Ca-halophosphates are made with an excess of phosphate (*7*). In nearly all cases, however, the compositions of the phosphors in this paper are given as the theoretical ones.

In general, a double firing process was carried out at temperatures between 1200 and 1500°C. Most samples were made in the following way: The first heating was for 2 hr at 1350°C, the reaction products were ground, sieved and refired for 2 hr at 1350°C. The samples were prepared in air, but for Ce- and Sn-activation a slightly reducing atmosphere was used. In order to prevent the formation of pentavalent antimony compounds, the apatites activated with antimony were mostly heated in nitrogen. The nitrogen was humidified with water of room temperature, in order to facilitate the host lattice formation.

From most samples, X-ray diffraction patterns were taken, using CuKα radiation from a Philips diffractometer. The cell constants and their precision were computed by a least squares analysis on the 10–14 strongest diffraction lines in the powder diagram of the apatite lattice. This analysis was carried out with an Algol-60 program on an IBM 360/75 computer.

The experimental techniques for measuring the optical properties of the samples have been described previously (*8*).

Results and Discussion

Crystal Structure

Several new compounds (not described in the literature before) were made; e.g., of the type II (see abstract) with Ca, Ba and Mg. We did not succeed in obtaining BaY compounds with an apatite crystal structure, probably because the ionic radii of the Ba^{2+} and Y^{3+} ions are so different. Mixed compounds such as $Ba_2La_4Y_4(SiO_4)_6O_2$ and $BaMgY_8(SiO_4)_6O_2$, however, show the apatite structure.

TABLE I

UNIT-CELL DIMENSIONS OF SOME NEWLY SYNTHESIZED APATITES

Type of composition[a]	Formula	*a* (Å)	*c* (Å)	*c*/*a*
I	$Ca_8La_2(PO_4)_6O_2$	9.43	6.89	0.731
	$Ba_8La_2(PO_4)_6O_2$	9.76	7.32	0.750
	$BaMgY_8(SiO_4)_6O_2$	9.35	6.70	0.717
	$Zn_2Y_8(SiO_4)_6O_2$	9.43	6.79	0.720
	$Zn_2La_8(SiO_4)_6O_2$	9.69	7.14	0.736
	$Cd_2Y_8(SiO_4)_6O_2$	9.39	6.77	0.721
II	$Ca_3La_6(SiO_4)_6$	9.67	7.15	0.740
	$Ca_3Y_6(SiO_4)_6$	9.35	6.78	0.725
	$Ca_{4.5}La_{4.5}(SiO_4)_{4.5}(PO_4)_{1.5}$	9.60	7.09	0.738
	$Sr_{4.5}Eu_{4.5}(SiO_4)_{4.5}(PO_4)_{1.5}$	9.52	7.02	0.738
	$Ba_{4.5}La_{4.5}(SiO_4)_{4.5}(PO_4)_{1.5}$	9.77	7.31	0.749
III	$Ca_4La_6(SiO_4)_6O$	9.66	7.16	0.741
	$Mg_4Y_6(SiO_4)_6O$	9.30	6.63	0.713

[a] Type of composition:

I	$Me^{II}_{2+x}Me^{III}_{8-x}(SiO_4)_{6-x}(PO_4)_xO_2$	$(0 \leqslant x \leqslant 6)$
II	$Me^{II}_{3+x}Me^{III}_{6-x}(SiO_4)_{6-x}(PO_4)_x$	$(0 \leqslant x \leqslant 1.5)$
III	$Me^{II}_{4+x}Me^{III}_{6-x}(SiO_4)_{6-x}(PO_4)_xO$	$(0 \leqslant x \leqslant 6)$

The unit-cell dimensions of some of the newly synthesized apatites are given in Table I. It was found that the addition of antimony in the amount as used for the activation does not alter the cell constants of the apatite crystal lattice. The Mg-compounds show the lowest values of the *a* and *c* axes, whereas these values increase with increasing ionic radius of the Me^{II} ion. Both the *a* and *c* axes are larger in the La compounds (ionic radius of La: 1.15 Å) than in the corresponding Y compounds (ionic radius of Y: 0.93 Å); e.g.,

	a (Å)	*c* (Å)	*c*/*a*
$Ca_2Y_8(SiO_4)_6O_2$	9.36	6.78	0.724
$Ca_2La_8(SiO_4)_6O_2$	9.67	7.15	0.739

More details about the unit-cell dimensions of the newly synthesized apatites will be published elsewhere.

Luminescence

In our investigation we found in some cases a weak luminescence (with 254 nm excitation) in the apatites, without the addition of an activator. A more efficient luminescence, however, was observed after the addition of activator ions such as Bi, Ce, Pb, Sn, Mn, Eu, Tb and Sb. Since antimony gives the most efficient luminescence, we will treat some properties of the apatites activated with antimony.

Most of the apatites synthesized by us are soluble in boiling 6 N HCl, enabling the Sb^{3+} content in the finished phosphor to be determined in the usual way (in the solution cooled to room temperature) with a bromometric titration (*9*). It was found that during the preparation of the phosphor a large amount (in most cases more than 50%) of the added amount of the antimony is lost.

Usually 0.2 mole of Sb/mole of apatite is added. Of the various types of antimony-activated apatites,

TABLE II

Efficiencies of Various Sb-Activated Compounds with the Apatite Crystal Structure[a] [b]

				Emission	
Type	Compounds	*r*(%)[c]	*q*(%)[d]	λ max (nm)	$\Delta\lambda_{1/2}$ (nm)[e]
I	$Ca_2Y_8(SiO_4)_6O_2$	18	53	460	145
	$Cd_2Y_8(SiO_4)_6O_2$[f]	14	14	475	190
	$Sr_2La_8(SiO_4)_6O_2$	15	33	520	160
	$Ca_2Y_8(SiO_4)_{5.9}(PO_4)_{0.1}O_2$	17	60	460	165
	$Ca_{3.5}Y_{6.5}(SiO_4)_{4.5}(PO_4)_{1.5}O_2$	25	56	460	190
	$Ca_5Y_5(SiO_4)_3(PO_4)_3O_2$	34	35	465	165
	$Sr_{3.5}La_{6.5}(SiO_4)_{4.5}(PO_4)_{1.5}O_2$[f]	16	37	545	190
	$Sr_5La_5(SiO_4)_3(PO_4)_3O_2$[f]	19	21	540	180
	$Sr_2Y_4La_4(SiO_4)_6O_2$	15	30	485	190
	$CaSrY_8(SiO_4)_6O_2$	14	42	445	150
	$CaMgY_8(SiO_4)_6O_2$	21	41	445	150
II	$Ca_{4.5}Y_{4.5}(SiO_4)_{4.5}(PO_4)_{1.5}$[f]	16	20	465	165
	$Sr_3La_6(SiO_4)_6$	14	25	520	160
III	$Ca_4Y_6(SiO_4)_6O$	16	30	460	145
	$Ca_{5.5}Y_{4.5}(SiO_4)_{4.5}(PO_4)_{1.5}O$	18	28	465	200

[a] 0.2 atoms of Sb added per mole of apatite.
[b] Excitation with 254 nm radiation;
[c] r = diffuse reflection.
[d] q = quantum efficiency;
[e] $\Delta\lambda_{1/2}$ = halfwidth of the emission spectrum.
[f] Newly synthesized compounds.

Note: The quantum efficiency of the phosphors was determined from the emission spectra in comparison with that of $MgWO_4$ (NBS 1027 standard phosphor). For the NBS phosphor, the value of the quantum efficiency as measured by Bril (*13*) was taken, viz., 85%.

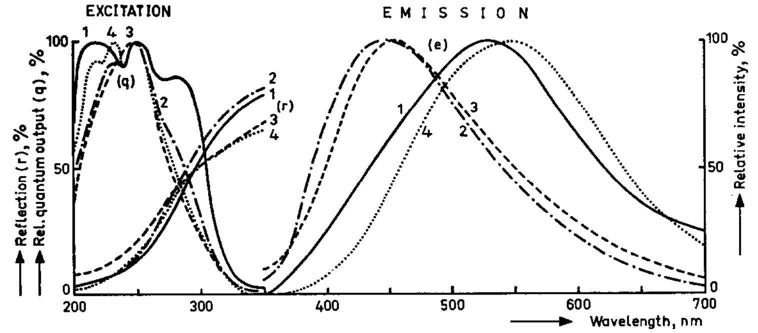

FIG. 1. Diffuse reflection spectra (r), excitation spectra (q) and spectral energy distribution (mainly 254 nm excitation) of the emission (e) of some antimony-activated apatites, as measured at room temperature.

Curve	Compound
1	$Ca_2La_8(SiO_4)_6O_2$-$Sb_{0.2}$
2	$Sr_2Y_8(SiO_4)_6O_2$-$Sb_{0.2}$
3	$Mg_2Y_8(SiO_4)_6O_2$-$Sb_{0.2}$
4	$Sr_3La_6(SiO_4)_6$-$Sb_{0.1}$

the most efficient ones are found in the type $Me^{II}_{2+x}Me^{III}_{8-x}(SiO_4)_{6-x}(PO_4)_xO_2$, with $x = 0$, Me^{II} = Ca and Sr, and Me^{III} = La and Y.

The quantum efficiencies of some of the antimony-activated phosphors with apatite structure are given in Table II. With Me^{II} = Ba, Zn and Cd only weakly luminescent products are obtained (with 254 nm excitation).

In general, the intensity of the luminescence (254 nm excitation) of the phosphors decreases with increasing amounts of PO_4 groups present. With more than 3 PO_4 groups per mole of apatite hardly any antimony is dissolved in the apatite lattice and, consequently, the luminescence intensity of such phosphors is low. The luminescence of the Sb^{3+}-activated phosphors cannot be excited by cathode rays.

The antimony-activated apatites show a broad emission band with a maximum from 445 to 545 nm and a halfwidth of 150 to 230 nm. As the excitation band has its maximum at about 250 nm, the phosphors can be readily excited by the 254 nm radiation of a low-pressure mercury discharge lamp. The diffuse reflection, excitation and emission spectra of some of these phosphors are shown in Fig. 1.

Activation with Sb and Mn

Both in $Ca_2Y_8(SiO_4)_6O_2$ and in $Sr_2La_8(SiO_4)_6O_2$, partial substitution of manganese for the host lattice cations gives rise to a weak emission band at about 580 nm. (Peak height about 10% of that of NBS standard phosphor 1027 = $MgWO_4$). If antimony is also added, the intensity of the manganese emission band increases, probably due to energy transfer from antimony to manganese. This follows from the fact that the excitation spectrum of the Mn emission band is identical with that of the Sb emission band and that the ratio of the intensities of the Mn emission band and of the Sb emission band increases with increasing amounts of Mn added.

Luminescence at Various Temperatures

Measuring the spectral energy distribution of the phosphors at 77°K, we observed in many cases an intense emission band at about 400 nm as may be

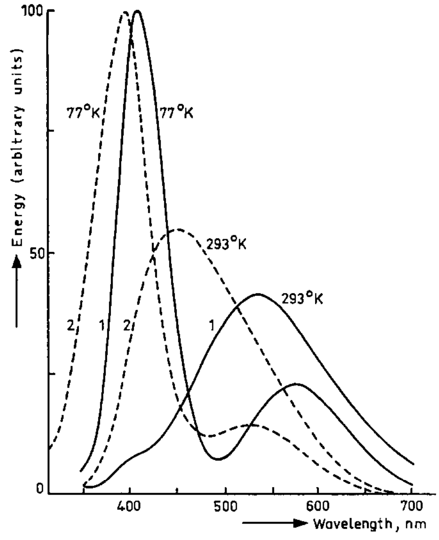

FIG. 2. Emission spectra (mainly 254 nm excitation) of antimony-activated $Sr_2La_8(SiO_4)_6O_2$ (curves 1) and $Ca_2Y_8(SiO_4)_6O_2$ (curves 2) as measured at 77° and 293° K.

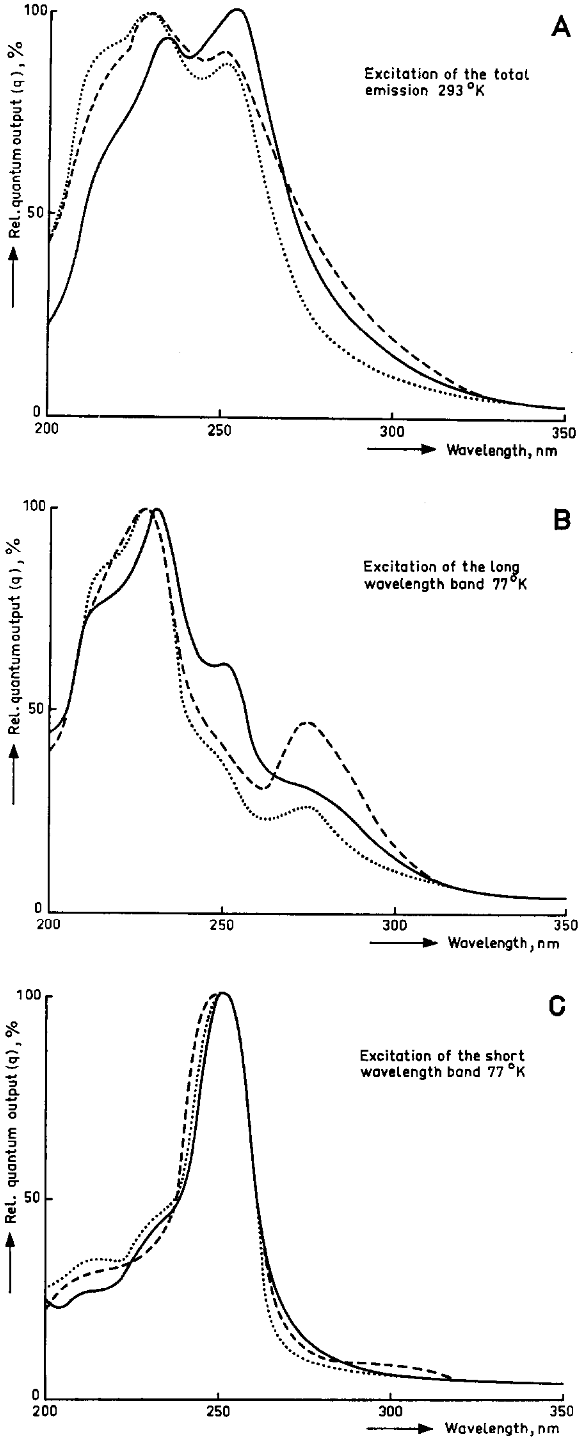

FIG. 3. Excitation spectra of $Ca_2Y_8(SiO_4)_6O_2\text{-}Sb_x$ at 293° K (A) and at 77°K of the long wavelength emission band (B) and of the short wavelength emission band (C). solid curves: $x = 0.01$; dashed curves: $x = 0.20$; dotted curves: $x = 0.40$.

seen in Fig. 2. Moreover, in $Mg_2Y_8(SiO_4)_6O_2$-Sb a small subband at 350 nm was observed at 77°K.

At 77°K the excitation spectra of both the short wavelength and the long wavelength emission bands of antimony-activated $Ca_2Y_8(SiO_4)_6O_2$ were measured. Figure 3 shows that the short wavelength emission band has its maximum excitation at about 250 nm and the long wavelength emission band at about 230 nm. Therefore, with 254 nm excitation at 77°K the 400 nm emission band dominates.

At 293°K the excitation spectrum is a superposition of the excitation spectra of the two emission bands as measured at 77°K. Since now the long wavelength emission band dominates, a shift of its excitation band towards longer wavelengths must be supposed. Moreover, the short wavelength emission band is strongly quenched at 293°K, as observed, for instance, in $Sr_2La_8(SiO_4)_6O_2$-Sb and in $Ca_2Y_8(SiO_4)_6O_2$-Sb.

An explanation of the two emission and excitation bands might be the presence of various (*3*) specific energy levels of the excited Sb^{3+} ions, as proposed by Butler and Jerome (*10*) in Sb^{3+}-activated Ca-halophosphate phosphors.

Some General Remarks and Conclusions

Efficient luminescence was observed with Sb as an activator, which, as will be remembered, is also the activator in the most important lamp phosphor Ca-halophosphate.

One of the intriguing phenomena of the present investigation is the origin of the 400 nm emission band observed in many of the new phosphors, e.g., those with Sb or Pb as an activator at 77°K. Moreover, this band was observed, though much more weakly, in many of the unactivated apatites also.

One explanation of the two emission bands at 77°K might be a distribution of the activator ions between the two unequal lattice sites present in the apatite crystal structure, as was found by Blasse and Bril (*11*) in Eu^{2+}-activated $Sr_{10}(PO_4)_4(SiO_4)_2$. The position of the 400 nm emission band, however, is virtually independent of the kind of activator added. This suggests that the matching luminescent centre is inherent in the host lattice, while by the incorporation of an activator ion a strong energy transfer to this centre takes place.

Since the apatites have a complicated crystal structure, it is difficult, with the present data, to elucidate the exact nature of the luminescent centres found. This is especially true since many of the apatites investigated by us, e.g., the types X and XI, contain both anion and cation vacancies.

In apatites which correspond to the normal lamp phosphor Ca-halophosphate—$Ca_{10}(PO_4)_6(F,Cl)_2$—colour centres can be formed with 185 nm radiation (*12*). Several unactivated samples made during this investigation seem to be even more susceptible to colour centre formation, since their reflection in the visible part of the spectrum decreases already by 300 nm irradiation, giving rise in some cases to brown coloured products.

It is clear that much more work has to be done to unravel the exact nature of the luminescent centres of the apatites mentioned, which may also provide greater insight into the luminescent centres in the conventional Ca-halophosphate phosphors.

Acknowledgment

The authors wish to express their thanks to Mr. E. P. J. de Meester for his assistance in preparing the phosphors, to Mr. C. Bakker for the optical measurements, and to Dr. A. Bril for the measurements of the efficiency of the phosphors.

References

1. A. H. Hoekstra, Thesis, Technical University, Eindhoven, 1967: also see *Philips Res. Rep. Suppl.* No. 2, 1968.

2. E. R. Kreidler, Thesis, Pennsylvania State University, Auttiar City, 1967. E. R. Kreidler and F. A. Hummel, *Amer. Mineralogist* **55**, 170 (1970).

3. D. A. Grisafe, Thesis, Pennsylvania State University, Auttiar City, 1968.

4. British Patent 578.192, 1942.

5. H. Schwarz, *Inorg. Nucl. Chem. Lett.* **3**, 231 (1967).

6. W. L. Wanmaker, A. H. Hoekstra, and J. G. Verriet, *Rec. Trav. Chim. Pays Bas* **86**, 537 (1967).

7. W. L. Wanmaker, *J. Phys. Radium* **17**, 636 (1956).

8. A. Bril and W. L. Wanmaker, *J. Electrochem. Soc.* **111**, 1363 (1964).

9. W. L. Wanmaker, A. H. Hoekstra, and M. G. A. Tak, *Philips Res. Rep.* **10**, 11 (1955).

10. K. H. Butler and C. W. Jerome, *J. Electrochem. Soc.* **97**, 265 (1950).

11. G. Blasse and A. Bril, *Phys. Lett.* *A***28**, 572 (1969).

12. E. F. Apple, *J. Electrochem. Soc.* **110**, 374 (1963).

13. A. Bril and W. Hoekstra, *Philips Res. Rep.* **16**, 356 (1961).