

Fluorescence and Structure of Barium Zirconium Trisilicate

G. BLASSE AND A. BRIL

*Philips Research Laboratories, N.V. Philips Gloeilampenfabrieken,
Eindhoven, Netherlands*

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The compound $\text{BaZrSi}_3\text{O}_9$ is isomorphous with benitoite. Under cathode-ray excitation it shows an emission with a maximum at 285 nm. This emission is ascribed to the Zr^{4+} ions. Activation with Ti^{4+} or Eu^{2+} yields efficient photoluminescent phosphors. It is further shown that the blue-green emission observed for a number of zirconium compounds is due to Ti^{4+} impurities and that the Zr^{4+} emission itself lies in the ultraviolet.

1. Introduction

The ternary system $\text{BaO-ZrO}_2\text{-SiO}_2$ has been investigated by Galkin and Chukhlantsev, who reported the existence of two ternary metal oxides, viz., $\text{BaZrSi}_3\text{O}_9$ and $\text{Ba}_2\text{Zr}_2\text{Si}_3\text{O}_{12}$ (1). X-ray powder diagrams were given. Shulgin et al. (2, 3) studied the fluorescence of pure and trivalent rare-earth activated $\text{BaZrSi}_3\text{O}_9$. The pure silicate was reported to show emission in 480-500 nm region. A similar emission has also been reported for ZrO_2 and $\text{Ba}_2\text{ZrP}_2\text{O}_9$ (4). Sarver (5), however, showed that the emission of ZrO_2 is due to Ti^{4+} impurities and that pure ZrO_2 does not fluoresce. A completely different emission, overlooked in Refs. (4, 5), is given by ZrP_2O_7 . This compound fluoresces efficiently under cathode-ray excitation with an emission band peaking at 285 nm as reported many years ago by Brill and Klasens (6).

When we found that $\text{BaZrSi}_3\text{O}_9\text{-Eu}^{2+}$ is an efficient Eu^{2+} -phosphor, we were prompted to investigate this so-called "zirconium host-lattice emission" further. As anticipated by Sarver (5) it was found that the blue-green emission of zirconium compounds is due to Ti^{4+} impurities and that pure zirconium compounds give an ultraviolet emission or no emission at all.

2. Experimental

Samples were prepared by firing intimate mixtures of BaCO_3 , ZrO_2 , and SiO_2 at temperatures between 1300 and 1400°C for at least three days. Ti-free ZrO_2 was prepared by repeated recrystallization of

zirconium oxychloride from HCl solution followed by decomposition of the oxychloride at 1000°C (5). The formation of $\text{BaZrSi}_3\text{O}_9$ is accelerated if 5% of the Ba in the starting mixture is used as BaF_2 . Replacement of small amounts of Ba by Sr also facilitates the reaction.

The firing atmosphere was always air except if Eu^{2+} was applied as activator. Then an atmosphere consisting of $\text{N}_2 + 5\% \text{H}_2$ was used. X-ray analysis was carried out with $\text{CuK}\alpha$ radiation using a Philips diffractometer.

The optical measurements were performed as already described (7).

3. Results and discussion

3.1. Structure of $\text{BaZrSi}_3\text{O}_9$

In the powder diagram of our $\text{BaZrSi}_3\text{O}_9$ samples some lines are lacking that are present in the diagrams reported in Ref. (1). On the other hand, we observed an additional line with $d = 5.00 \text{ \AA}$. From our diagram it becomes clear that $\text{BaZrSi}_3\text{O}_9$ is isomorphous with benitoite [$\text{BaTiSi}_3\text{O}_9$ with hexagonal lattice parameters $a = 6.60 \text{ \AA}$, $c = 9.71 \text{ \AA}$ (8)]. The lattice parameters of $\text{BaZrSi}_3\text{O}_9$ are $a = 6.75 \text{ \AA}$, $c = 10.00 \text{ \AA}$. This structure consists of Si_3O_9 rings with the Ba^{2+} and Zr^{4+} ions in trigonally distorted octahedra.

3.2. Optical Properties of $\text{BaZrSi}_3\text{O}_9$

Pure $\text{BaZrSi}_3\text{O}_9$ shows no emission under 254 nm excitation due to the fact that only radiation with $\lambda < 220 \text{ nm}$ is absorbed. The compound can be

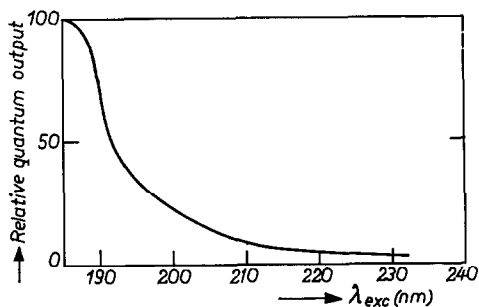


FIG. 1. Excitation spectrum of the uv emission of $\text{BaZrSi}_3\text{O}_9$.

excited with short-wavelength ultraviolet radiation (see Fig. 1) or cathode-ray excitation (Fig. 2). The emission consists of a broad band peaking at about 285 nm. The efficiency for cathode-ray excitation is relatively high (see Table I). The fluorescence of $\text{BaZrSi}_3\text{O}_9$ is, therefore, comparable to that of ZrP_2O_7 .

Characteristic emission from zirconium compounds is in itself not unexpected, since many compounds containing highly charged ions with np^6nd^{10} configuration are known to fluoresce (e.g., Ti^{4+} , Nb^{5+} , W^{6+}). The absorption and emission transitions are ascribed to charge transfer transitions between the O^{2-} anions and the central metal ion. Jørgensen (9) stated that for peroxy complexes these transitions move to longer wavelengths in the series $\text{Zr}^{4+} < \text{Ta}^{5+} < \text{W}^{6+} < \text{Nb}^{5+} < \text{Mo}^{6+} < \text{Ti}^{4+} < \text{V}^{5+}$, and in fluorescent oxides an analogous sequence seems to be valid which according to our experience (10, 11) should be $\text{Zr}^{4+} < \text{Nb}^{5+} \approx \text{W}^{6+} \approx \text{Ta}^{5+} < \text{Ti}^{4+} \approx \text{V}^{5+} < \text{Mo}^{6+}$. The differences are small but Zr^{4+} and Mo^{6+} are clear extremes with ultraviolet and orange emission, respectively. A general property of these fluorescent centres is the large Stokes shift of their emission (12,000–16,000 cm^{-1}).

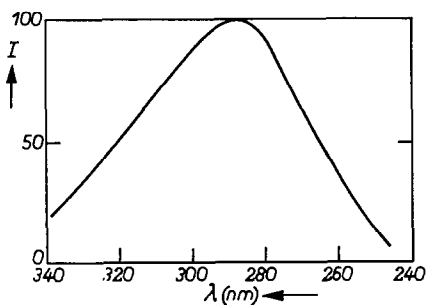


FIG. 2. Spectral energy distribution of the emission of $\text{BaZrSi}_3\text{O}_9$ under c.r. excitation. I gives the radiant power per wavelength interval in arbitrary units.

TABLE I
EFFICIENCIES OF PHOSPHORS INVESTIGATED

Composition	$\eta(\%)^a$	$q(\%)^a$	$q_{\text{max}}(\%)^a$
$\text{BaZrSi}_3\text{O}_9$	5	—	—
$\text{BaZrSi}_3\text{O}_9\text{-Ti (0.5\%)}$	3	40	40
$\text{Ba}_{0.99}\text{Eu}_{0.01}\text{ZrSi}_3\text{O}_9$	5	40	50
$\text{Ba}_2\text{ZrP}_2\text{O}_9$	0.5	—	—
ZrO_2	< 0.1	—	—
ZrP_2O_7	6	—	—

^a η —radiant efficiency for cathode-ray excitation (20 kV);

q —quantum efficiency for 250–270 nm excitation;

q_{max} —maximum value of the quantum efficiency in the ultraviolet region.

This holds also for zirconium. No accurate value can be given, since the excitation band is situated at or beyond the wavelength limit of the apparatus used. It can be deduced from our data, however, that the shift has at least a value of 17,000 cm^{-1} , but is probably even larger.

Since uv emission from the Zr^{4+} centre has now been observed for two compounds (ZrP_2O_7 and $\text{BaZrSi}_3\text{O}_9$) it may be expected for other Zr^{4+} compounds as well. No emission was observed for ZrO_2 (uv and c.r. excitation). This runs probably parallel to the observation that oxides like Nb_2O_5 , WO_3 and TiO_2 do not fluoresce either. Pure $\text{Ba}_2\text{ZrP}_2\text{O}_9$ shows an uv emission band with a maximum at about 350-nm under cr excitation. It seems probable that this is also emission from a Zr^{4+} centre.

It remains to be investigated why $\text{BaZrSi}_3\text{O}_9$ and $\text{Ba}_2\text{ZrP}_2\text{O}_9$ are described as blue-green emitting phosphors in the literature (2, 3, 4), Sarver (5) has convincingly shown that the reported blue-green emission of ZrO_2 is due to Ti^{4+} impurities. Also Kröger (12) has described a number of Ti^{4+} -activated zirconates with blue to green emission. Therefore, we investigated Ti^{4+} -activated $\text{BaZrSi}_3\text{O}_9$.

3.3. Optical Properties of $\text{BaZrSi}_3\text{O}_9\text{-Ti}$

The phosphor $\text{BaZrSi}_3\text{O}_9\text{-Ti (0.5\%)}$ shows efficient blue-green emission under 254 nm and c.r. excitation. For 365-nm excitation a very weak emission is observed with a maximum shifted to longer wavelengths. Figure 3 shows the spectral energy distribution for these excitations. The excitation spectrum of the blue-green emission is given in Fig. 4.

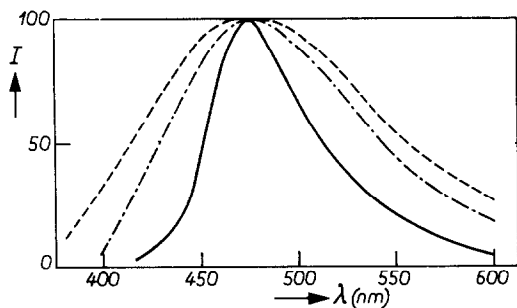


FIG. 3. Spectral energy distribution of $\text{BaZrSi}_3\text{O}_9\text{-Ti}$ (-----, 254-nm and c.r. excitation, -.-.-, 365-nm excitation) and of $\text{BaZrSi}_3\text{O}_9\text{-Eu}^{2+}$ (———, 254-nm excitation).

From these results it follows that the blue-green emission of $\text{BaZrSi}_3\text{O}_9$ described in Refs. (2, 3) is most likely due to Ti^{4+} impurities in $\text{BaZrSi}_3\text{O}_9$. Our own samples of $\text{BaZrSi}_3\text{O}_9$ prepared from 99.9% ZrO_2 also show this blue-green emission. No decision can be made at the moment whether the emitting Ti^{4+} centres consist of Ti^{4+} ions on Zr^{4+} sites or on Si^{4+} sites or both. The excitation and emission spectra seem to indicate the presence of two different centres. Kröger (12), however, has already shown that the Ti^{4+} centre in oxides fluoresces from two different levels.

The energy transfer from the Zr^{4+} centres to the Ti^{4+} centres is very effective. This follows from the fact that under host lattice excitation an intense blue-green emission is observed for all samples of $\text{BaZrSi}_3\text{O}_9$ prepared from ZrO_2 not purified by special methods. It remains to be discussed why this transfer has such a high probability. In our opinion this is due to the very large spectral overlap of the Zr^{4+} emission band and the Ti^{4+} absorption band (Figs. 2 and 4). The overlap integral will be roughly 1 eV^{-1} , so that the critical distance for this transfer will be about 35 \AA (the overlap region is

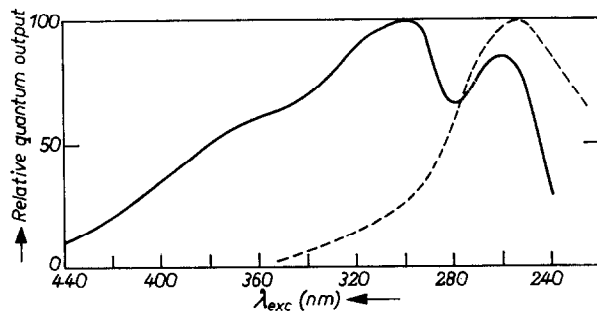


FIG. 4. Excitation spectrum of the blue-green emission of $\text{BaZrSi}_3\text{O}_9\text{-Ti}$ (---) and the blue-green emission of $\text{BaZrSi}_3\text{O}_9\text{-Eu}^{2+}$ (———).

situated at about 4 eV) if we use the same approximation as applied by Dexter (13).

This critical distance corresponds to a Ti^{4+} concentration of about 0.1% Ti. Due to the perfect spectral overlap radiative transfer will also occur, so that it is not surprising that the Ti^{4+} concentration must be considerably lower than 0.1% to prevent transfer from the Zr^{4+} centres to the Ti^{4+} centres. Also in the case of $\text{Ba}_2\text{ZrP}_2\text{O}_9\text{-Ti}$ the Zr^{4+} emission overlaps the Ti^{4+} excitation band very well.

Summarizing we conclude that the blue-green emission observed for many Zr^{4+} compounds will be due to Ti^{4+} impurities. Pure Zr^{4+} compounds can show emission in the ultraviolet. In many cases this emission cannot be excited by 254-nm radiation, since the Zr^{4+} compounds do not show absorption in this region.

3.4. Optical Properties of $\text{BaZrSi}_3\text{O}_9\text{-Eu}^{2+}$

We take this opportunity to report also the efficient luminescence of Eu^{2+} in $\text{BaZrSi}_3\text{O}_9$. The Eu^{2+} ions can be introduced easily in $\text{BaZrSi}_3\text{O}_9$ on Ba^{2+} sites. This phosphor shows efficient blue-green emission under 254 and 365-nm excitation and c.r. excitation (Table I). The spectral energy distribution of the emission is given in Fig. 3 and is seen to be narrower than the Ti^{4+} emission. The excitation spectrum of the Eu^{2+} emission is given in Fig. 4.

The bands in the excitation spectrum correspond to the crystal field components of the excited $5d$ level of the Eu^{2+} ion in the trigonally distorted octahedron. These are expected to be a (lower) triplet split by the trigonal field and a doublet. These features can indeed be recognized in Fig. 4. The cubic crystal-field splitting is estimated to be some $10,000 \text{ cm}^{-1}$ in reasonable agreement with our earlier work (14).

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