Anhydrous Zinc Borate as a Host Crystal in Luminescence*

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The best results for preparing Zinc Borate luminophors are obtained by thermal treatment from melts of ZnO : B₂O₃ in proper molar proportions. Compositions between 50% and 61% ZnO give transparent glasses, which yield separable cubic crystals by devitrification. A compound of molar relation 4 ZnO : 3 B₂O₃ not reported in the literature is deduced from a re-examination of the chemical and structural constitution of these crystals. This compound—more properly expressed O₂Zn₆(BO₃)₆—possesses a crystalline structure of the Sodalite (ultramarine) type. Each unit cell contains two molecules of metabolate. This crystal shows a violet emission band under 2537 Å and cathode ray excitation.

When the molar ratio is 2 : 1 (70% ZnO), or higher, the devitrification gives no single crystal, but a product of yellow luminescence under 2537 Å excitation consisting of a glassy phase and crystals which are not cubic. Preparations of intermediate composition show the presence of both phases (cubic and non-cubic) each one associated with its luminescent band. Upon heating a non-cubic Zinc Borate in hydrogen part of the Zinc is lost by reduction and subsequent volatilization, thus incurring a change to the cubic structure as a consequence of the composition change. The Manganese has a valence of 2+, when incorporated to the cubic crystals, and gives rise to a strong green emission whereas the resulting luminescence in the non-cubic phase is orange and the valence is greater than 2+. No direct influence of the firing atmosphere on the valency of the activator has been found in the preparation of such products. When the orange-emitting phosphor is heated in a reducing atmosphere, however, the structural change from non-cubic to cubic is always associated with the change of the Mn emission band (orange → green) and a simultaneous valency conversion Mn²⁺ → Mn³⁺.

As, Sb, and Bi activated cubic Zinc Borates also create well defined emission bands. Arsenic incorporates as As⁵⁺, antimony as Sb⁵⁺ and Bi⁵⁺, whereas bismuth as Bi³⁺. A speculation is made for the explanation of these effects.

The literature on anhydrous Zinc Borates is confusing. These high temperature products have been investigated by means of heating curves¹-³, differential thermal analysis⁴,⁵, quench techniques and phase diagrams⁵,⁶, X ray diffraction patterns⁴,⁵,⁷, chemical analysis⁵,⁶, and so on. Most authors give klare Unterscheidung von der roten Kupferemission, wie sie von FROELICH⁴ gefunden wurde.


Herrn Dr. H. ORTMANN möchte ich an dieser Stelle für die Überlassung von gefällitem chlorfreiem ZnS und für Diskussionen danken.

* Herrn Prof. Dr. N. RHIE zu seinem 60. Geburtstag gewidmet.
² F. DE CARLI, Atti Accad. Lincei (6) 5, 41 [1927].
more than two compounds (Table 1).

<table>
<thead>
<tr>
<th>Reported Authors</th>
<th>Zinc Borates (molar ratio ZnO: B₂O₃)</th>
<th>We%</th>
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<tbody>
<tr>
<td>ZnO</td>
<td>B₂O₃</td>
<td>Authors</td>
</tr>
<tr>
<td>1: 4</td>
<td>8</td>
<td>22,61</td>
</tr>
<tr>
<td>1: 3</td>
<td>1</td>
<td>28,03</td>
</tr>
<tr>
<td>1: 2</td>
<td>9</td>
<td>36,88</td>
</tr>
<tr>
<td>2: 3</td>
<td>8</td>
<td>43,79</td>
</tr>
<tr>
<td>3: 4</td>
<td>8</td>
<td>46,71</td>
</tr>
<tr>
<td>1: 1</td>
<td>1, 2, 4, 5, 6, 7, 8</td>
<td>53,89</td>
</tr>
<tr>
<td>5: 4</td>
<td>8</td>
<td>59,36</td>
</tr>
<tr>
<td>3: 2</td>
<td>2, 3, 8, 10, 11, 12</td>
<td>63,67</td>
</tr>
<tr>
<td>2: 1</td>
<td>2, 6</td>
<td>70,03</td>
</tr>
<tr>
<td>5: 2</td>
<td>5, 6</td>
<td>74,50</td>
</tr>
<tr>
<td>3: 1</td>
<td>1, 4, 8, 13</td>
<td>77,80</td>
</tr>
</tbody>
</table>

Table 1. Zinc Borate compounds given in the literature.

KABAKJIAN \(^{14}\) reports the pure metaborate 1:1 as a violet emitter phosphor. HENDERSON \(^{15}\) refers to the ortoborate 3:1, RANDALL \(^{16}\) to the 2:1, etc. LEVERENZ \(^{17}\) outlines the cathodoluminescence spectra of pure 1:1 and 3:1 Zinc Borate, and presents the emission curves for molar ratios of 3:1, 2:1, 3:2, and 1:1 with manganese activator. CURIE \(^{18}\) investigates the crystalline compound 3:2 as a base for Mn activation, and reports that different emission colours are obtained depending upon whether preparation is performed in oxygen (green), or in a non-oxidizing atmosphere (orange). This is just the reverse of what was found by other investigators \(^{19}\).

By contrast KRÖGER \(^{20}\) states that he observed no influence of the atmosphere on Mn activated Zinc Borates, and attributes these colour changes to differences in the crystal structure (all still containing divalent manganese). HARRISON and HUMMEL \(^{5}\) re-investigated the 1:1 and 5:2 Zinc Borates. They concluded that these molar ratios are compounds and detected for each one both low and high temperature polymorphic forms: the α-5:2(Mn) fluoresces orange and the β-1:1(Mn) fluoresces green under both 2537 Å and C.R. excitation. The authors of the present paper at first thought \(^{21}\), that only the compounds 3:2 and 2:1 existed but further work carried out with more detail enabled them to draw other conclusions.

In this paper a survey is given of the chemical and structural constitution of pure Zinc Borate after a careful reinvestigation of such products by means of chemical analysis and X ray diffraction work. A contribution of other authors about the crystallographic characterization - based in our data - of the cubic system is mentioned. Activation of Zinc Borate is achieved and good phosphors are obtained with Mn and 5-B group metals. An investigation of the valency degree and concentration of each activator in the crystals enables one to make some speculation about the ability of the lattice to admit foreign ions as luminescent activators.

### Experimental

1. **Synthesis, luminescence and X ray examination of pure Zinc Borates**

Highly purified ZnO and H₂BO₃ were used to prepare various ZnO : B₂O₃ of different molar ratios. Boric acid was melted in a Pt crucible until complete conversion into B₂O₃. Known amounts of ZnO were added to this B₂O₃ and then heated at 1100 °C until the ZnO was dissolved.

Transparent glasses were obtained for ZnO contents between 50 and 61%, which did not show any fluorescence under 2537 Å excitation. For lower concentration (0—50%) a great immiscibility region was present \(^{22}\). Melts with ZnO content higher than about 68%, when quenched, gave milky glasses of yellow luminescence under 2537 Å and violet emission under C.R. excitation. Both dominant colours exhibited moderate after-glow.

A devitrification occurred by annealing transparent glasses at 850 °C and single crystals grew from the glass. Hexagonal-like faces were visually observed. Microstereoscopic examination revealed growth pyra-
mids with the crystal faces as their bases and the apices inside the crystals (Fig. 1). These crystals were isolated by dissolving the matrix glass in dilute HCl and were rhombododecahedrons of about 2 mm and density 4.22. The response to 3650 Å excitation was very weak, but under 2537 Å a violet emission of long afterglow appeared. The emission curve consists of a narrow band peaked at about 435 μm (Fig. 2). The examination by X ray diffraction gave a clear cubic structure with a lattice constant α = 7.493 ± 0.005 Å.

Preparations of intermediate composition between 61 and 68% ZnO gave both phases, cubic and not cubic, after annealing. Each one showed its typical luminescent band. The molar ratio 2 : 1 (70% ZnO) never gave the cubic phase. Since all compositions between those of 2 : 1 and 3 : 1 showed the same non-cubic X ray pattern and some additional ZnO lines for 3 : 1 preparation were observed, it might mean that “2 : 1” is a compound.

A prolonged heating (more than 20 hours) in air of this high Zn content yellow phosphor (2 : 1) at 850°–900° gave rise to some crystallites of violet luminescence and cubic structure, this denotes a conversion from non-cubic to cubic structure, which showed the high stability of the latter at such temperature. Upon heating in hydrogen atmosphere, the structural change was speeded, because of the loss of part of the Zn (composition change) by reduction and subsequent volatilization.

No influence upon the ZnO content or on the lattice constant has been observed among the cubic crystals obtained from any glass composition.

2. Characterization of cubic phase

Selected cubic crystals were investigated by chemical analysis in order to determine the ZnO and B₂O₃ contents. Samples were prepared by melting the weighed crystals in a Pt crucible at 1000 °C for only 1 minute and dissolving the resultant glass in dilute HCl.
ZnO has been determined in three ways. The results are given in Table 2 as average values of 10 titrations, together with the standard deviation ($\sigma$). (Procedural details are omitted here.)

<table>
<thead>
<tr>
<th>Method</th>
<th>%ZnO</th>
<th>$\sigma$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumetric</td>
<td>61.01</td>
<td>0.19</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>60.99</td>
<td>0.18</td>
</tr>
<tr>
<td>Potentiometric</td>
<td>61.04</td>
<td>0.10</td>
</tr>
<tr>
<td>(mean value)</td>
<td>61.0%</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Analytical determination of ZnO in cubic Zinc Borate (average of 10 titrations).

$\text{B}_2\text{O}_3$ was titrated against standard alkali in the presence of mannitol with phenolphthalein as indicator. Zinc was separated from the solution as carbonate before determination, and the liquid was finally boiled to remove CO$_2$. An average of 10 titrations gave 39.09% of $\text{B}_2\text{O}_3$ ($\sigma = 0.14\%$).

The results pointed toward the 4 ZnO : 3 $\text{B}_2\text{O}_3$ relation as the most probable compound.

A first structural analysis of the cubic single crystals through Patterson projections gave 8 atoms of Zinc per unit cell. Such a number, together with the data given above, allowed an easy check on the compound 4 ZnO : 3 $\text{B}_2\text{O}_3$ as the most approximate "formula-weight".

From

$$\varrho = \frac{n \cdot m}{v} = \frac{n \cdot m \cdot 1.66 \times 10^{-24}}{a^3 \cdot \text{cm}^3} \text{g}$$

the number ($n$) of molecules per unit cell

$$n = \frac{1068.19}{P \cdot m}$$

was calculated for some Zinc Borate compositions given in the literature. These are compared with the proposed 4 ZnO : 3 $\text{B}_2\text{O}_3$ (Table 3).

<table>
<thead>
<tr>
<th>Molecular ratio, ZnO : $\text{B}_2\text{O}_3$</th>
<th>Molecular Weight (Pm)</th>
<th>%ZnO</th>
<th>%$\text{B}_2\text{O}_3$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 : 4</td>
<td>522.70</td>
<td>46.71</td>
<td>53.29</td>
<td>2.04</td>
</tr>
<tr>
<td>1 : 1</td>
<td>151.02</td>
<td>53.89</td>
<td>46.11</td>
<td>7.07</td>
</tr>
<tr>
<td>5 : 4</td>
<td>685.46</td>
<td>59.36</td>
<td>40.64</td>
<td>1.56</td>
</tr>
<tr>
<td>3 : 2</td>
<td>383.42</td>
<td>63.67</td>
<td>36.33</td>
<td>2.78</td>
</tr>
<tr>
<td>4 : 3</td>
<td>534.44</td>
<td>60.91</td>
<td>39.09</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Table 3. Number ($n$) of molecules per unit cell.

No compound appeared as satisfactory as 4 ZnO : 3 $\text{B}_2\text{O}_3$. Its $\text{B}_2\text{O}_3$ and ZnO contents differ by only less than 0.2% from those values found by analysis. Its $n$ value is the best approximation to an integral multiple of one “formula-weight". On the other hand only this compound (for $n = 2$) is quite consistent with the previously statemented 8 atoms of Zinc predicted in the Patterson diagrams.

On the basis of the above data, a further crystallographic study was carried out in order to investigate the atomic positions from Patterson and Fourier projections. The structure of cubic anhydrous Zinc Borate is similar to that of the Sodalite (ultramarine) confirming the 4 : 3 ratio and assigning the definitive formula $\text{OZn}_4(\text{BO}_2)_6$ as opposed to the 3 : 2 and 1 : 1 supported by most authors. Like the Sodalite, the structure of cubic Zinc Borate is a three-dimensional framework (Fig. 4).

![Fig. 4. The unit cell of $\text{OZn}_4(\text{BO}_2)_6$, drawn not to scale. For simplicity the oxygens tetrahedrally surrounding each boron are depicted at the middle point of each edge, but these oxygens are not coplanar with the hexagonal faces. "Cavity" oxygen is located at the center—and corners—of the unit cell.](image)

3. Activation with Manganese

The incorporation of manganese was carried out by melting the mixture $\text{B}_2\text{O}_3$ + ZnO (MnO$_2$) at 1100 °C and followed by crystallization. Two molar relations for Zinc Borate matrix were experienced: (a) 4 : 3 and (b) 2 : 1. The addition of the activator gave an optimum luminescence for $5 \times 10^{-2}$ at/mol Mn.

Transparent (4 ZnO : 3 $\text{B}_2\text{O}_3$ : $5 \times 10^{-3}$ Mn) and opaque (2 ZnO : 1 $\text{B}_2\text{O}_3$ : $5 \times 10^{-3}$ Mn) glasses showed weak orange luminescence under 2537 Å excitation with some afterglow. The annealing of the former at 850 °C
for 2 hours gave cubic Zinc Borate (Mn) with a strong green luminescence (a narrow band peaked at 540 m/z) under 2537 Å and C. R. excitation, with phosphorescence of long decay. The same thermal treatment for the latter resulted in the mixture of glassy and non-cubic (Mn) phases with enhanced orange response (a broad band peaking about 595 m/z) under both 2537 Å and C. R. excitation (Fig. 5). The phosphorescent decay was also prolonged. Note the weak violet band from traces of unactivated substance present in the “2 : 1” phase.

Fig. 5. Cathodoluminescence emission spectra of Zinc Borate (Mn) (arbitrary scales).

I. Cub. OZn₄(B₆O₃)₆ : 5 · 10⁻³ Mn under 15 KV 13 μA cm⁻² C. R.,
II. Non-cubic. ZnO : 1 B₂O₃ : 5 · 10⁻³ Mn under 15 KV 10 μA cm⁻² C. R.

Manganese incorporates into the cubic crystals as divalent, since it showed no oxidizing power toward KI + HCl. The same test for the mixture of non-cubic (Mn) and glassy (Mn) phases gave values almost of the same order as those found upon just the same amounts of MnO₂—previously heated at 1100 °C—used in the activation. Should the manganese ion be present in the non-cubic phase as 2⁺ and in the glassy phase as > 2⁺, the oxidizing power found in the whole mixture would be considerably lower than that tested separately in MnO₂. Hence, the non-cubic phase contains manganese in an oxidation state higher than 2⁺.

No influence of the firing atmosphere has been found in the crystallization of cubic Zinc Borate (Mn) either on the luminescence or on the valence of manganese. Upon heating an orange-emitting phosphor (2 : 1 : Mn) in a reducing atmosphere, however, the decomposition of the matrix compound gave rise to a change from non-cubic to cubic structure. This was associated with the valency conversion Mn²⁺ → Mn³⁺ and caused the change of the emission band from orange to green.

The structural change cubic → non-cubic, or the color change green → orange, was never observed after crystallizing at 800 — 900 °C. On the contrary, when the orange-emitting phosphor is heated in air for long periods, some cubic crystals (green-emitting) appear again. This is evidence that the emission, as well as the valence of manganese, are not a direct effect of the preparation atmosphere, but rather the consequence of the adjustment of the manganese ion in a particular lattice.

4. Activation with As, Sb, and Bi

These elements have been introduced, like manganese, by crystallization of glasses containing As, Sb or Bi. In this section an account is given on the luminescent effects observed in cubic crystals when activated by these activators alone and coactivated by lithium.

Arsenic was added as As₂O₃ and As₂O₅. In both cases most of the arsenic in the crystals was As⁵⁺, which indicated the oxidation of the As₂O₃. By prolonged annealing at 850 °C (crystallization) all arsenic was found in the pentavalent state and gave rise to a broad emission yellow-orange band under 2537 Å with long afterglow. The emission curves of Fig. 6 were taken from samples prepared with just the same amount of As added (0.1 at/mol = 1.38%). The presence of lithium (1 at/mol added) in the crystal increases ap-

Fig. 6. Emission curves of As activated cub. OZn₄(B₂O₃)₆ under 2537 Å excitation (curves drawn with the same scale).

10⁻¹ at/mol As added. Lower curve: As found in crystals = 1.30%, Upper curve: As found in crystal = 1.33%.

As — Li

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preciably the concentration of $\text{As}^{5+}$ and enhances the luminescent response and suppresses the visual phosphorescence.

The influence of lithium for retaining $\text{As}^{5+}$ in crystals is more appreciable when the portions of As are higher. From an addition of 1 at/mol, 6.4%. As was found, whereas the same added amount in the presence of lithium gave about 8% As. These high contents, however, did not give good phosphors (quench concentration).

Antimony, added as $\text{Sb}_2\text{O}_3$, incorporates to the crystal in both states $\text{Sb}^{3+}$ and $\text{Sb}^{5+}$. The concentration of the pentavalent ion is nearly 2 or 3 times that of the trivalent ion. The luminescence of this system under 2537 Å excitation consists of two emission bands (blue and yellow) with moderate and long afterglow. The additional lithium behaves here as in the As activation (Fig. 7).

Bismuth was added as $\text{Bi}_2\text{O}_3$ and was detected in the crystal only as trivalent. The amount for this element permitted by the crystal was lower than those for As and Bb. Three emission bands for this system have been recorded (blue, yellow and orange) with fast phosphorescent decay. Lithium also increases the emission intensity. The Bi-Li system under 3650 Å excitation shows a much larger efficiency than under 2537 Å excitation. In Fig. 8 emission curves for Bi and Bi-Li under 3650 Å are compared. The violet band for the unactivated cubic Zinc Borate is noticed in the Bi curve. The blue band of Bi-Li curve, which peaks at about 460 mµ, is the strongest one observed in all preparations with 5-B metals as activators in cubic Zinc Borate.

All luminescent results with As, Sb and Bi activated cubic Zinc Borate are summarized in Table 4. The relative peak outputs have been obtained by visual photometry using a Macbeth type photometer equipped with interference filters.

<table>
<thead>
<tr>
<th>Activators</th>
<th>Fluorescence (2537 Å excit.)</th>
<th>Phosphorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed Bands</td>
<td>Relative Peak Outputs.</td>
</tr>
<tr>
<td>Without</td>
<td>Violet</td>
<td>Long</td>
</tr>
<tr>
<td>As</td>
<td>Yellowish-orange</td>
<td>6</td>
</tr>
<tr>
<td>As-Li</td>
<td>Yellowish-orange</td>
<td>25</td>
</tr>
<tr>
<td>Sb</td>
<td>1. Blue</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2. Yellow</td>
<td>40</td>
</tr>
<tr>
<td>Sb-Li</td>
<td>1. Blue</td>
<td>530</td>
</tr>
<tr>
<td></td>
<td>2. Yellow</td>
<td>130</td>
</tr>
<tr>
<td>Bi</td>
<td>1. Blue</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>2. Yellow</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3. Orange</td>
<td>3</td>
</tr>
<tr>
<td>Bi-Li</td>
<td>1. Blue</td>
<td>360</td>
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<tr>
<td></td>
<td>2. Yellow</td>
<td>80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluorescence (3650 Å excit.)</th>
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</thead>
<tbody>
<tr>
<td>Bi</td>
<td></td>
</tr>
<tr>
<td>1. Blue</td>
<td>10</td>
</tr>
<tr>
<td>2. Yellow</td>
<td>8</td>
</tr>
<tr>
<td>3. Orange</td>
<td>10</td>
</tr>
<tr>
<td>Bi-Li</td>
<td></td>
</tr>
<tr>
<td>1. Blue</td>
<td>1000</td>
</tr>
<tr>
<td>2. Yellow</td>
<td>270</td>
</tr>
<tr>
<td>3. Orange</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 4. Luminescence of As, Sb and Bi activated cubic Zinc Borate.
Discussion

Only two essential crystalline structures have been found for Zinc Borate: one (low Zn content) is cubic, with the composition $\text{OZn}_4(\text{BO}_2)_6$, and the other (high Zn content) is non-cubic.

The two crystalline structures are associated with typical luminescent bands. The violet band which is observed in both pure structures under C. R. excitation seems to be related with the anionic group because of the high strength of the BO$_4$ tetrahedra. The increase of Zn content might fragment the 3-dimensional lattice of linked BO$_4$ tetrahedral groups and give rise to a new luminescence under low energy excitation (2537 Å) which is shifted to the longer wavelength side (yellow) in the non-cubic form.

The difference observed between the peaks of the violet bands of the pure cubic (435 mμ) and non-cubic (410 mμ) structures, under C. R. excitation, might be explained by the lessening of the bond Zn-O (oxygen from BO$_4$) in the non-cubic form and subsequent contraction of the BO$_4$ tetrahedra.

The experiences with manganese give evidence that this activator only incorporates into the cubic structure — most probably as a substitute for Zn — as a divalent ion (green-emitting), whereas a valence $>2+$ is tolerated by the glassy and non-cubic phases (orange-emitting). Most authors attribute the Mn luminescence in host crystals to the environment more than to the oxidation state. This may be the case for manganese in Zinc Silicates which shows two coordination types: tetrahedral environment (green-emitting) and hexahedral coordination (yellow-emitting), but both containing divalent manganese. Manganese in Zinc Borates shows two emission colours, each one apparently associated with different valency states although it may also involve a change in the coordination number.

Manganese in Zinc Borate glasses has been found in a valence $>2+$, its conversion to divalent ion in the process of devitrification indicates an adjustment to the growing cubic crystals with spontaneous reduction. A suggestion given to us would explain this conversion by the sequence of reactions:

$$\begin{align*}
\text{a) } & 2 \text{Mn}^{3+} \text{ (glass)} \rightarrow \text{Mn}^{2+} \text{ (cubic crystals)} + \text{Mn}^{4+} \text{ (glass)}, \\
\text{b) } & 2 \text{MnO}_2 \xrightarrow{850\text{°C}} \text{Mn}_2\text{O}_3 + \frac{1}{2} \text{O}_2.
\end{align*}$$

Such a reduction proceeds until all glassy phase is changed to cubic crystals.

The most interesting part of this paper is perhaps the characterization of the cubic phase. The multiple closed chains of linked BO$_4$ tetrahedra form a baskets-like framework containing many cavities large enough to accommodate positive and negative ions. Oxygen vacancies in BO$_4$ tetrahedra are not probably because of the high strength of this framework. If long phosphorescence means trapped electrons or positive holes, one concludes that some “cavity” oxygen — or Zn — might preferably volatilize without a great energy change in the system.

Arsenic goes into the crystal as As$^{5+}$ in small concentrations and gives rise to a weak yellow band of long afterglow. No Arsenic Borate has been reported, but some Magnesium and Zinc Arseniates have. The crystalline compound BAsO$_4$ with the Cristobalite structure has also been reported in which BO$_4$ tetrahedral groups alternate with other AsO$_4$ tetrahedra. Therefore, it seems reasonable to assume that the As enters the anionic group as it does in Zinc Silicates. Thus, substitution of arsenic for boron in a fourfold coordination might be quite possible resulting in the formula

$$\text{OZn}_{4(4-x)}(\text{B}_{(1-x)}^{3+} \text{O}_2)_6,$$

$$\text{As}_{5+x}(x)$$

where As$^{5+}$, replacing B$^{3+}$, causes one Zn vacancy in the crystal for each As$^{5+}$ atom incorporated, the positive holes being attracted to such vacant lattice points (long afterglow). An other possibility for As incorporation would also be by the replacement of boron (2 B vacancies for each 3 As$^{5+}$)

$$\text{OZn}_{4+}(\text{B}_{(1-x)-2/3x}^{3+} \text{O}_2)_6,$$

$$\text{As}_{5+x}(x)$$

but this scheme seems less probable because of the formation energy of B-tetrahedra as the major framework support. Either scheme, however, explains the stopping of the solubility of As in the crystal; the free energy change involved in the formation of a vacancy is quite large. In this system the presence of lithium enhances the yellow band and suppresses the phosphorescence which lends sup-

32 G. E. Schulze, Z. physik. Chem. (B) 24, 215 [1939].
port to the charge compensation theory. To account for this effect it may be necessary to assume that the Zn vacancies are occupied by Li\(^{1+}\), thereby increasing the As solubility and removing traps, according to

\[
\text{OZn}^{2+}_{(4-x)} \left(\text{Bi}^{3+}_{(1-x)} \text{O}_2\right)_6 \\
\text{Li}^{1+}_{(2-x)} \text{As}^{5+}_{(x)}
\]

The incorporation of antimony gives two bands (Fig. 7). The Li coactivation also enhances the intensity and considerably reduces the phosphorescence. Such a behaviour is like that of As and the structural scheme would be similar. A question is that of the simultaneous presence of Sb\(^{3+}\) and Sb\(^{5+}\). According to the literature\(^{35,36}\) the bands might be correlated with the valency states (yellow for Sb\(^{3+}\) in cationic or cavity position and blue for Sb\(^{5+}\) as substitute for boron).

Trivalent bismuth gives three weak bands. The phosphorescent decay is very fast (no trapping effect) which might indicate that Bi\(^{3+}\), whatever may be the manner of incorporating, does not create vacancies. It is hardly expected that Bi\(^{3+}\) ion \((r = 1.2 \text{ Å})\) could be a substitute for B\(^{3+}\) \((r = 0.2 \text{ Å})\) because of size and polarization properties. It would seem more reasonable to assume Bi\(^{3+}\) at interstitial (cavity) positions. The relatively very low concentrations permitted by the crystal and the weakness of its emission bands which allows the conservation of the base crystal violet band (Fig. 8) speak in favour of it. The presence of lithium as a coactivator enhances the blue Bi-band. On the other hand the increase of response when exciting this Bi-Li system by u.v. of low energy (3650 Å) seems to be in agreement with the picture of Bi as interstitial since in such a position the vibrational frequency of an impurity ion is lower than that of the lattice atoms.

Hence the scheme would be

\[
\text{OZn}^{2+}_{(4-x)} \left(\text{BO}_2\right)_6 \\
\text{Li}^{1+}_{(x)} \\
\text{Bi}^{3+}_{(x/3)}
\]

where the \(x \text{Li}^{1+}\) replaces \(x \text{Zn}^{2+}\) and establishes the defect of \(x \) positive charges to be compensated by \(x/3 \text{Bi}^{3+}\) ions.

The foregoing considerations might also be applied to the cubic crystal with isomorphous additions for the base material (i.e. Si\(^4\), P\(^4\) ... for B\(^4\) and Cl, S, ... for cavity 0) thereby opening up future research for multiple ion substitutions.

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