Halogenide geschaffenen Zentren (z. B. S-Fehlstellen, Zinkleerstellen oder Cl$^-$-Ionen) die grüne Lumineszenz bei kleineren Konzentrationen nicht ausgeschlossen werden, es tritt aber gleichzeitig die langwellige Bande mit steigender Aktivatorkonzentration immer mehr hervor. Das heißt aber, daß nur ein Teil der vielleicht vorgegebenen Zinkleerstellen durch Indium besetzt wird. — Da die orange-rote Emission mit Indium und Kupfer schon bei kleinen Kupferkonzentrationen auftritt, außerdem sich durch einen Diffusionsvorgang bei relativ niedrigen Temperaturen erzielen läßt und unempfindlich gegen Sauerstoff und Halogen-Ionen ist, ergibt sich eine klare Unterscheidung von der roten Kupferemission, wie sie von FROELICH [4] gefunden wurde.

Man muß also hier wirklich Indium als Koaktivator ansehen, der nicht nur die Aufgabe einer Ladungskompensation hat, sondern mit Kupfer ein neues Leuchtzentrum bildet. Es liegt nahe, diese langwellige orange-rote Emission einem Assoziationszentrum Indium-Kupfer im Sinne von PRENER und WILLIAMS [8] zuzuordnen. Doch bedarf es weiterer Untersuchungen, um diese Annahme zu stützen.

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

Anhydrous Zinc Borate as a Host Crystal in Luminescence*

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(Z. Naturforschg. **16 a**, 920—927 [1961]; eingegangen am 3. Mai 1961)

The best results for preparing Zinc Borate luminophors are obtained by thermal treatment from melts of ZnO : B_2O_3 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 B_2O_3 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 $OZn_4(BO_2)_6$—possesses a crystalline structure of the Sodalite (ultramarine) type. Each unit cell contains two molecules of metaborate. 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 wit the change of the Mn emission band (orange → green) and a simultaneous valency conversion $Mn^{>2+} \rightarrow Mn^{2+}$.

As, Sb, and Bi activated cubic Zinc Borates also create well defined emission bands. Arsenic incorporates as As^{5+}, antimony as Sb^{3+} and Sb^{5+}, whereas bismuth as Bi^{3+}. 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 curves [1–3], differential thermal analysis [4, 5], quench techniques and phase diagrams [5, 6], X ray diffraction patterns [4, 5, 7], chemical analysis [3, 5], and so on. Most authors give

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* Herrn Prof. Dr. N. RIEHL zum 60. Geburtstag gewidmet.

[1] N. A. TOROPOV and P. F. KONOVALOV, Dokl. Akad. Nauk, SSSR **66**, 1105 [1945].

[2] F. DE CARLI, Atti Accad. Lincey (6) **5**, 41 [1927].

[3] R. TOURNAY, C. R. Acad. Sci., Paris **203**, 558 [1936].

[4] YU. S. LEONOV, Dokl. Akad. Nauk, SSSR **114**, 976 [1957].

[5] D. E. HARRISON and F. A. HUMMEL, J. Electrochem. Soc. **130** (9), 491 [1956].

[6] E. INGERSON, G. W. MOREY and O. F. TUTTLE, Amer. J. Sci. **246**, 31 [1948].

[7] H. E. SWANSON and E. TATGE, J. Res. Nat. Bur. Stand., Wash. **46**, 321 [1951].

more than two compounds (Table 1).

Reported Zinc Borates (molar ratio $ZnO : B_2O_3$)	Authors	Wt%	
		ZnO	B_2O_3
1 : 4	8	22,61	77,39
1 : 3	1	28,03	71,97
1 : 2	9	36,88	63,12
2 : 3	8	43,79	56,21
3 : 4	8	46,71	53,29
1 : 1	1, 2, 4, 5, 6, 7, 8	53,89	46,11
5 : 4	8	59,36	40,64
3 : 2	2, 3, 8, 10, 11, 12	63,67	36,33
2 : 1	2, 8	70,03	29,97
5 : 2	5, 6	74,50	25,50
3 : 1	1, 4, 8, 13	77,80	22,19

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] reinvestigated 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 H_3BO_3 were used to prepare various $ZnO : B_2O_3$ of different molar ratios. Boric acid was melted in a Pt crucible until complete conversion into B_2O_3. Known amounts of ZnO were added to this B_2O_3 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 contentration (0 – 50%) a great immiscibility region was present[22]. Melts with ZnO content higher than about 68%, when quenched, gave milky glassis of yellow luminescence under 2537 Å and violet emission under C. R. excitation. Both dominant colours exhibited moderate afterglow.

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-

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[8] H. M. Cyr, Comprehensive Inorg. Chemistry, 4. — M. Cannon and R. C. Brasted, van Nostrand, New York 1948, p. 48.

[9] V. M. Gugel and V. L. Levshin, Bull. Akad. Sci. SSSR, Ser. Phys. **9**, 269 [1945].

[10] Er. Mallard, C. R. Acad. Sci., Paris **105**, 1260 [1887].

[11] H. LeChatelier, C. R. Acad. Sci., Paris **113**, 1034 [1891].

[12] R. Paris and P. Mondain, C. R. Acad. Sci., Paris **202**, 2075 [1936].

[13] L. Ouvrard, C. R. Acad. Sci., Paris **130**, 335 [1900].

[14] D. H. Kabakjian, Phys. Rev. **51**, 365 [1937].

[15] S. T. Henderson, Proc. Roy. Soc., Lond. A **137**, 323 [1939].

[16] J. T. Randall, Proc. Roy. Soc., Lond. A **170**, 272 [1939].

[17] H. W. Leverenz, An Introduction to Luminescence of Solids, J. Wiley, New York 1950, pp. 222 and 234.

[18] M. Curie, Trans. Faraday Soc. **35**, 114 [1939].

[19] L. Brüninghaus, J. Phys. Radium **12**, 398 [1931].

[20] F. A. Kröger, Some Aspects of the Luminescence of Solids, Elsev. Publ., Amsterdam 1948, p. 61.

[21] S. Terol and M. J. Otero, Anal. Real Soc. Esp. Fís. Quím. (Madrid) **48** (B), 750 [1952].

[22] S. Terol and M. J. Otero, III Reunión Internacional de Estado Sólido, Madrid 1956, p. 703.

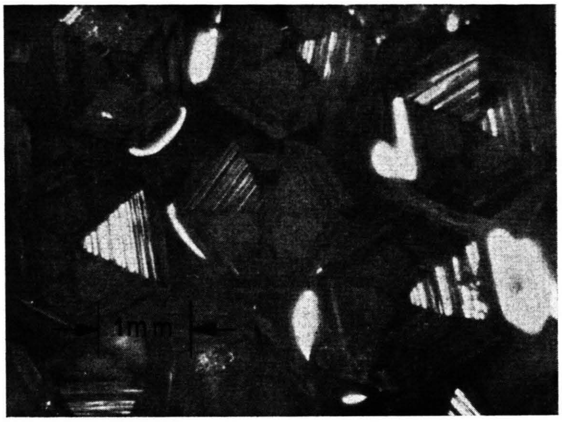

Fig. 1. Cubic single crystals of Zinc Borate grown from the melts.

mids with the crystal faces as their bases and the apeces 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_2. 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 mμ (Fig. 2). The examination by X ray diffraction gave a clear cubic structure with a lattice constant $a = 7.493 \pm 0.005$ Å.

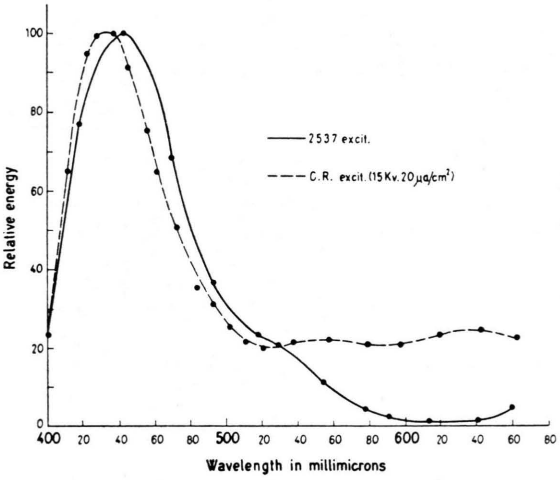

Fig. 2. Emission curves of pure cubic Zinc Borate at room temperature (arbitrary scales).

No single crystal was formed by annealing glasses of about 70% ZnO, or higher, between 800 – 900 °C. Instead a needle shaped white bulk, consisting of a glassy product and a crystalline phase which was not cubic, was obtained. When irradiated with low (2537 Å) and high (C. R.) energy, the emission colours were the same as those observed before annealing, but with a longer phosphorescence. Fig. 3 shows the emission curves under 2537 Å excitation (a strong yellow band peaked at 555 mμ and a weak violet band), and the cathodoluminescence (a strong violet band peaked at 410 mμ and a weak yellow band). Glassy and crystalline phases were easily soluble in dilute HCl, and all attempts of separation were fruitless.

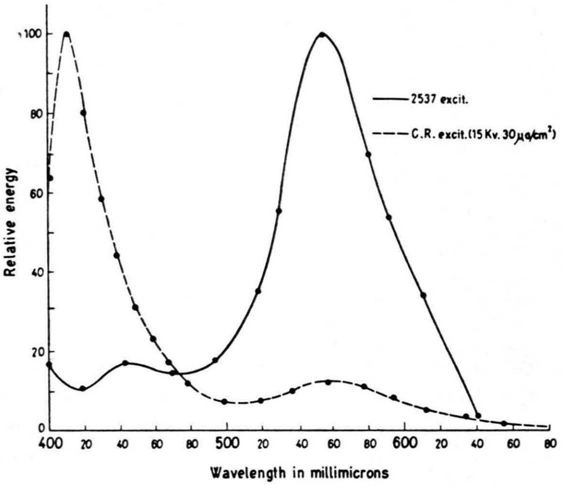

Fig. 3. Emission curves of non-cubic Zinc Borate at room temperature (arbitrary scales).

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 B_2O_3 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[23]. The results are given in Table 2 as average values of 10 titrations, together with the standard deviation (σ). (Proceedural details are omitted here[24].)

Method	%ZnO	σ(%)
Volumetric	61,01	0,19
Gravimetric	60,99	0,18
Potentiometric	61,04	0,10
	61,0% (mean value)	

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

B_2O_3 was titrated against standard alkali in the presence of mannitol with phenolphtalein 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 B_2O_3 ($\sigma = 0.14\%$).

The results pointed toward the $4\,ZnO : 3\,B_2O_3$ relation as the most probable compound.

A first structural analysis[25] of the cubic single crystals through Patterson projections gave 8 atoms of Zn per unit cell. Such a number, together with the data given above, allowed an easy check on the compound $4\,ZnO : 3\,B_2O_3$ as the most approximate "formula-weight".

From

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

the number (n) of molecules per unit cell

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

was calculated for some Zinc Borate compositions given in the literature. These are compared with the proposed $4\,ZnO : 3\,B_2O_3$ (Table 3).

Molecular ratio $ZnO : B_2O_3$	Molecular Weight (Pm)	%ZnO	%B_2O_3	n
3 : 4	522.70	46.71	53.29	2.04
1 : 1	151.02	53.89	46.11	7.07
5 : 4	685.46	59.36	40.64	1.56
3 : 2	383.42	63.67	36.33	2.78
4 : 3	534.44	60.91	39.09	**1.99**

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

No compound appeared as satisfactory as $4\,ZnO : 3\,B_2O_3$. Its B_2O_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[25] 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 $OZn_4(BO_2)_6$ 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).

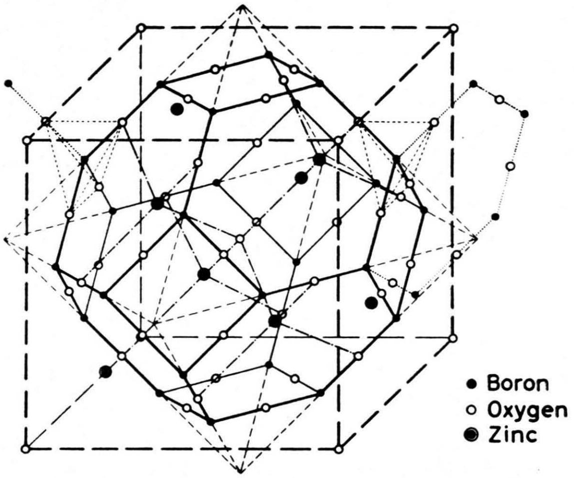

Fig. 4. The unit cell of $OZn_4(BO_2)_6$, drawn not to scale. For simplicity the oxygens tetrahedrally surrounding each boron are depicted at the middle point of each edge, but these oxygens are not coplanar with the hexagonal faces. "Cavity" oxygen is located at the center—and corners—of the unit cell.

3. *Activation with Manganese*

The incorporation of manganese was carried out by melting the mixture $B_2O_3 + ZnO(MnO_2)$ 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 luminance for $5 \cdot 10^{-3}$ at/mol Mn.

Transparent ($4\,ZnO : 3\,B_2O_3 : 5 \cdot 10^{-3}$ Mn) and opaque ($2\,ZnO : 1\,B_2O_3 : 5 \cdot 10^{-3}$ Mn) glasses showed weak orange luminescence under 2537 Å excitation with some afterglow. The annealing of the former at 850 °C

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[23] (a) Volumetric titrations were carried out by using standard potassium ferrocyanide solution and uranyl acetate as an external indicator. (b) In the gravimetric determinations were weighed Zn samples as $ZnNH_4PO_4$. (c) An standard potassium ferrocyanide, and an electronic potentiometer were used for the potentiometric titration and platinum served as the indicator electrode.

[24] S. Terol and M. J. Otero, Anal. Real Soc. Esp. Fís. Quím. (Madrid) **57**, (B) 343 [1961].

[25] P. Smith, S. G. Blanco and L. Rivoire, Z. Krist. (in press).

for 2 hours gave cubic Zinc Borate (Mn) with a strong green luminescence (a narrow band peaked at 540 mμ) under 2537 Å and C. R. excitation, with phosphorescence of long decay. The same thermal treatement for the latter resulted in the mixture of glassy and non-cubic (Mn) phases with enhanced orange response (a broad band peaking about 595 mμ) 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.

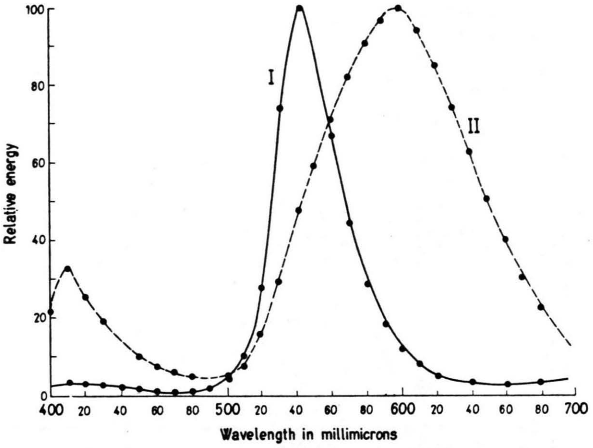

Fig. 5. Cathodoluminescence emission spectra of Zinc Borate (Mn) (arbitrary scales).
I. Cub. $\mathrm{OZn_4(BO_2)_6}$: $5\cdot10^{-3}$ Mn under 15 KV 13 μa cm^{-2} C. R.,
II. Non-cubic. 2 ZnO : 1 $\mathrm{B_2O_3}$: $5\cdot10^{-3}$ Mn under 15 KV 10 μa cm^{-2} C. R..

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 $\mathrm{MnO_2}$ — 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 $\mathrm{MnO_2}$ [26]. 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 descomposition of the matrix compound gave rise to a change from non-cubic to cubic structure. This was associated with the valency conversion $\mathrm{Mn}^{>2+} \rightarrow \mathrm{Mn}^{2+}$ 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 [27].

Arsenic was added as $\mathrm{As_2O_3}$ and $\mathrm{As_2O_5}$. In both cases most of the arsenic [28] in the crystals was $\mathrm{As^{5+}}$, which indicated the oxidation of the $\mathrm{As_2O_3}$. 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-

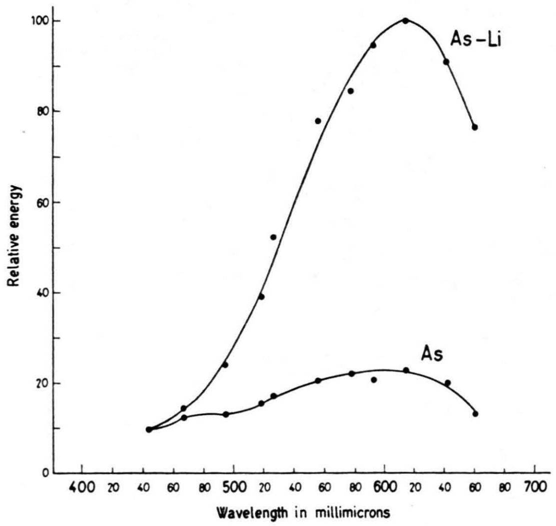

Fig. 6. Emission curves of As activated cub. $\mathrm{OZn_4(BO_2)_6}$ under 2537 Å excitation (curves drawn with the same scale). 10^{-1} at/mol As added. Lower curve: As found in crystals = 1,30%, Upper curve: As found in crystal = 1,33%.

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[26] S. Terol and M. J. Otero, Anal. Real Soc. Esp. Fís. Quím. (Madrid) **55** (A) 117 [1959].

[27] S. Terol and M. J. Otero, Anal. Real Soc. Esp. Fís. Quím. (Madrid) **57** (A) (in press).

[28] (a) $\mathrm{As^{3+}}$ — or $\mathrm{Sb^{3+}}$ — was determined by oxidation with potassium bromate. (b) $\mathrm{As^{5+}}$ is distilated as $\mathrm{As^{3+}}$ from a reducing solution containing conc. HCl, KBr and hydrazine sulfate, while passing a current of pure nitrogen. Titration of $\mathrm{As^{3+}}$ before and after distilation gives $\mathrm{As^{5+}}$. (c) $\mathrm{Sb^{5+}}$ is treated with conc. HCl and KI, the iodine liberated being titrated with standard sodium thiosulphate.

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

The influence of lithium for retaining 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 Sb_2O_3, incorporates to the crystal in both states Sb^{3+} and 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).

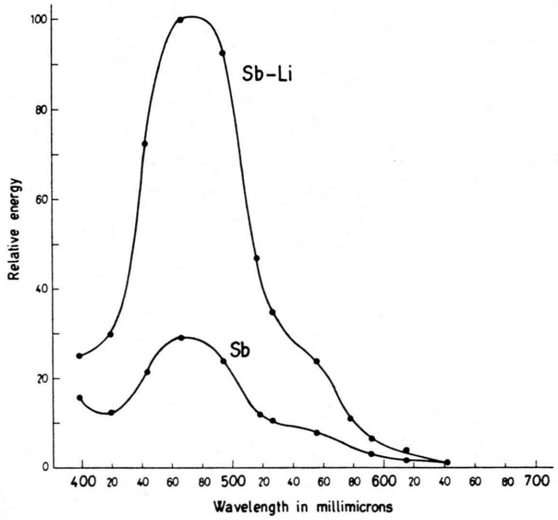

Fig. 7. Emission curves of Sb activated cub. $OZn_4(BO_2)_6$ under 2537 Å excitation (curves drawn with the same scales). 10^{-2} at/mol Sb added. Lower curve: Sb found in crystals= 0,26%, upper curve: Sb found in crystals=0,30%.

Bismuth was added as Bi_2O_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 fo 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 equiped with interference filters.

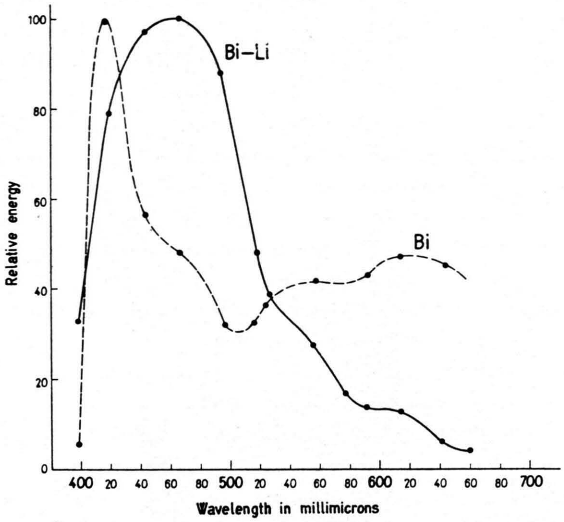

Fig. 8. Emission curves of Bi activated cubic Zinc Borate under 3650 Å excitation (arbitrary scales). 10^{-3} at/mol Bi added as Bi_2O_3.

Activators	Fluorescence (2537 Å excit.)		Phosphorescence
	Observed Bands	Relative Peak Outputs.	
Without	Violet		Long
As	Yellowish-orange	6	Long
As-Li	Yellowish-orange	25	Fast Decay
Sb	1. Blue	150	Moderate
	2. Yellow	40	Long
Sb-Li	1. Blue	530	Short
	2. Yellow	130	Very Short
Bi	1. Blue	15	Fast Decay
	2. Yellow	3	Fast Decay
	3. Orange	3	Fast Decay
Bi-Li	1. Blue	360	Fast Decay
	2. Yellow	80	Fast Decay
	Fluorescence (3650 Å excit.)		
Bi	1. Blue	10	Fast Decay
	2. Yellow	8	Fast Decay
	3. Orange	10	Fast Decay
Bi-Li	1. Blue	1000	Fast Decay
	2. Yellow	270	Fast Decay
	3. Orange	130	Fast Decay

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 $OZn_4(BO_2)_6$, 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 wave length 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 rather than to the oxidation state. This may be the case for manganese in Zinc Silicates[29] 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[30] would explain this conversion by the sequence of reactions

a) $2\,Mn^{3+}$ (glass) $\rightarrow$ Mn^{2+} (cubic crystals) $+ Mn^{4+}$ (glass),

b) $2\,MnO_2 \xrightarrow{850^\circ C} Mn_2O_3 + \frac{1}{2}\,O_2$.

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[31]. 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[32] 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[33, 34]. Thus, substitution of arsenic for boron in a fourfold coordination might be quite possible resulting in the formula

$$O\,Zn^{2+}_{(4-x)} \left| \begin{array}{l} \left(B^{3+}_{(1-x)}\,O_2\right)_6 \\ As^{5+}_{(x)} \end{array} \right.$$

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+})

$$O\,Zn^{2+}_{4} \left| \begin{array}{l} \left(B^{3+}_{(1-x-2/3x)}\,O_2\right)_6 \\ A^{5+}_{(x)} \end{array} \right.$$

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 what lends sup-

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[29] S. H. Linwood and W. A. Weyl, J. Opt. Soc. Amer. **32**, 443 [1942].

[30] R. Ward, Private communication.

[31] A. F. Wells, Structural Inorganic Chemistry, Clarendon Press, Oxford 1950, p. 591.

[32] G. E. Schulze, Z, physik. Chem. (B) **24**, 215 [1939].

[33] H. C. Froelich and G. R. Fonda, J. Phys. Chem. **46**, 878 [1942].

[34] J. H. Schulman, J. Appl. Phys. **17**, 902 [1946].

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 trapps, according to

$$\begin{array}{c|l} \mathrm{O\,Zn}^{2+}_{(4-2x)} & \left(\mathrm{B}^{3+}_{(1-x)}\,\mathrm{O}_2\right)_6 \\ \mathrm{Li}^{1+}_{(2x)} & \mathrm{As}^{5+}_{(x)} \end{array}$$

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 ($r = 1{,}2$ Å) could be a substitute for B^{3+} ($r = 0{,}2$ 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

$$\begin{array}{c|l} \mathrm{O\,Zn}^{2+}_{(4-x)} & (\mathrm{BO}_2)_6 \\ \mathrm{Li}^{1+}_{(x)} & \\ \mathrm{Bi}^{3+}_{(x/3)} & \end{array}$$

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

The foregoing considerations might also be applied to the cubic crystal with isomorphous additions for the base material (i. e. SiO_4, PO_4 ... for BO_4 and Cl, S, ... for cavity 0) thereby opening up future research for multiple ion substitutions.

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[35] D. E. KINNEY, J. Electrochem. Soc. **102**, 676 [1955].

[36] W. L. WANMEKER, J. Phys. Radium **17**, 636 [1956].

Präzisionsmessung der niederenergetischen Neutronen-Einfang-Gammastrahlung bei Gd^{156}, Gd^{158}, Sm^{150}, Sm^{153} und Eu^{152}

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Herrn Prof. Dr. N. RIEHL *zum 60. Geburtstag gewidmet*

Es werden genaue Energiewerte der niederenergetischen Gammastrahlen angegeben, welche die Kerne Gd^{156}, Gd^{158}, Sm^{150}, Sm^{153} und Eu^{152} kurz nach ihrer Erzeugung durch Neutroneneinfang aussenden. Die gemessenen Werte werden mit den Energiewerten verglichen, die nach dem kollektiven Modell zu erwarten sind.

Am Reaktor FRM wurden die Isotope $_{64}Gd^{155}$, $_{64}Gd^{157}$, $_{62}Sm^{152}$, $_{63}Eu^{151}$ und das Element $_{62}Sm$ bestrahlt und mit dem Kristallspektrometer [1] die bei der n,γ-Reaktion entstehenden weichen γ-Strahlen erneut (vgl. Anm. [2]) ausgemessen. Die Linien, die man dabei erwartet, sind hauptsächlich Übergänge innerhalb der Grundzustandsrotationsbande, allgemein den Niveaus, die dicht über dem Grundzustand

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[1] O. SCHULT, Z. Phys. **158**, 444 [1960].

[2] J. T. WASSON, Z. Naturforschg. **15 a**, 276 [1960].