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Some Observations on the Photoluminescence of Doped β-Galliumsesquioxide

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The luminescence of single crystalline and powder specimens of β-Ga_2O_3 has been studied in the temperature range 5–300°K. The investigations were carried out on nominally pure samples and samples doped with various cations. In addition to the intrinsic uv emission a blue and a green emission occurred. On the basis of luminescence and electronic conductivity data the blue emission is ascribed to the recombination of an electron in a $V_O^\times$ or $Ga_i^\times$ center and a hole trapped in a gallium ion vacancy. The data on the green luminescence do not permit any definitive conclusions to be drawn regarding the nature of this emission.

1. Introduction

The crystal structure of β-Ga_2O_3 has been described by Geller (*1*). The structure is monoclinic and belongs to space group *C*2/*m*. There are two kinds of Ga^{3+} ions, one in tetrahedral, the other in octahedral coordination. Depending on the growth conditions β-Ga_2O_3 can be either an insulator or an *n*-type semiconductor (*2–4*). At low temperatures photoconductivity is observed upon excitation in the fundamental absorption band (*5*).

In a previous paper (*5*) we reported on the ultraviolet luminescence of β-Ga_2O_3 single crystals and powders. This intrinsic emission was attributed to the recombination of an electron and a self-trapped hole or to the recombination of a hole and a self-trapped electron. In that paper we mentioned also the occurrence of a blue and green emission in doped β-Ga_2O_3. These emissions were reported earlier by Blasse and Bril (*6*) and by Herbert *et al.* (*7*). Herbert *et al* reported a blue emission emitted by nominally pure β-Ga_2O_3 powder after heat treatment, and a green emission in β-Ga_2O_3 doped with Si^{4+} and Zn^{2+}. The importance of impurities and of the heat treatment procedure was mentioned. Blasse and Bril investigated the influence of many different dopants on the luminescence properties. No explanation for the observed emissions was given, although it was recognized that β-Ga_2O_3 has properties similar to those of the ZnS-type phosphors.

In this paper we present results of investigations on doped β-Ga_2O_3 crystals and powder specimens. In addition to giving the excitation and emission spectra we comment on phenomena such as afterglow and thermoluminescence.

2. Experimental

The melting point of β-Ga_2O_3 is (2068 ± 20)°K (*8*). Nominally pure and doped crystals were grown by the Verneuil method using β-Ga_2O_3 powder (Alusuisse 99.99% pure) as starting material. The growth of the crystal was terminated by stopping the powder flow and lowering the crystal in the burner. It took

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about 7 min for the crystal to be removed from the muffle. Then the flame was extinguished and the crystal was left to cool to room temperature. More details about the crystal growth will be given elsewhere (*9*).

The dopants added to the crystals were Be, Mg, Si, and Zr in concentrations ranging from 100 to 1000 ppm. They were introduced as oxides. Undoped crystals were colorless or light blue. All as-grown Si- or Zr-doped crystals were blue, whereas all as-grown Be- or Mg-doped crystals were colorless. Thin platelets were cleaved from the boules along the (100) plane. Typical dimensions were 2 × 6 × 0.3 mm^3.

The luminescence of β-Ga_2O_3 powders (99.99% pure and 99.9999% pure) was measured on powders that had not received any pretreatment and on powders that had been fired at 1200° or 1400°C in air or nitrogen. Firing was carried out in alundum crucibles. As dopant to the powders Li Ag, Be, Ca, Cd, Cu, Fe, Mg, Mn, Pb, Zn, Al, B, In, Ge, Sn, Si, or Zr was added. The dopants were introduced as oxides in concentrations ranging from 100 to 5000 ppm. The experimental setup for the luminescence measurements has been described elsewhere (*5*).

3. Results

3.1. Emission Spectra

3.1.1. Crystals. A blue emission could be excited in addition to the uv emission in all blue-colored undoped crystals and in all (blue-colored) as-grown crystals that had been doped with Si or Zr. Within the experimental error this emission was identical for undoped, Si- or Zr-doped crystals. When these crystals were heated at 1200°C in nitrogen or air the blue color and the blue luminescence disappeared regardless of whether the crystals were cooled slowly or rapidly from 1200°C to room temperature. The blue color is associated with an absorption in the ir region of the spectrum. We attribute this absorption to the presence of free charge carriers (*4*). Crystals doped with Mg or equal amounts of Mg and Zr were colorless and showed no blue emission. However, we often noticed that although the crystals showed no visible emission, the polycrystalline material deposited on the ceramic pedestal and on the single crystal during the crystal growth showed a bright blue luminescence.

In crystals to which a high concentration (~1000 ppm) of Zr or Si had been added a green emission was observed in addition to the blue emission. In crystals doped with 200 ppm Be only a green emission was present which could not be distinguished from the green emission from Zr- or Si-doped crystals. Typical emission spectra of the blue and the green emission are presented in Fig. 1. In contrast to the intensity of the blue emission the intensity of the green emission band could not be influenced by heat treatment of the crystals at 1200°C.

Measurements on different parts of the crystals revealed that the blue emission is emitted homogeneously over the surface. The same holds for the green emission in Be-doped crystals. However, it was observed even visually that the green emission in Zr- or Si-doped crystals was restricted to certain parts of the samples. With a microscope the presence of gas bubbles and inclusions was established, especially in certain parts of the heavily doped crystals. The occurrence of the green

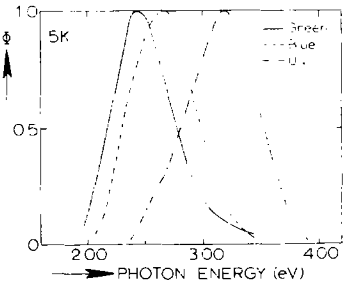

FIG. 1. Spectral energy distribution of the emission of Zr-doped β-Ga_2O_3 crystals at 5°K. Φ gives the radiant power per constant energy interval in arbitrary units. —·— A crystal doped with 100 ppm of Zr upon 4.92 eV excitation. --- A crystal doped with 100 ppm of Zr upon 4.46 eV excitation. —— A crystal doped with 1000 ppm of Zr upon 4.46 eV excitation.

emission, however, could not be related to the presence of these crystal imperfections.

Since Mn causes a bright green luminescence in several gallates (*10–12*), we checked whether the green emission in β-Ga_2O_3 could be due to the presence of Mn impurity. Therefore crystals with 100 ppm of Mn dopant were grown. In some crystals Zr was added as charge compensator. The latter crystals were colorless, indicating that Mn does not evaporate during the crystal growth process, but is in fact incorporated into the host lattice. Apart from the uv emission no emission was observed in the Mn-doped crystals.

3.1.2. Powders. The powder samples showed three emissions, viz. a uv, a blue, and a green one. The intensity of the blue and the green emission could be influenced by the nature of the dopant and the method used to prepare the powders. Since different batches of material with 99.99% purity showed different behavior with respect to heat treatment and doping, the experiments were continued with 99.9999% pure β-Ga_2O_3 powder. Results of emission spectroscopical analyses of this powder are given in Table I. For comparison results of an analysis on a single crystal are included. The starting material showed a weak green luminescence. After heat treatment at 1200°C this luminescence had disappeared regardless of the ambient in which the heat treatment was carried out. If the 99.9999% pure powder was ground in an agate ball-mill before the heat treatment at 1200°C a bright blue emission was induced. In addition to this blue emission a weaker green emission could be excited (cf. Sect. 3.2). The intensity of the blue emission decreased markedly if the heat treatment was carried out at 1400°C. Emission spectroscopical analyses revealed that if the β-Ga_2O_3 powder is ground in agate for about 20 min, relatively high concentrations of Si (~200 ppm) are introduced.

Doped powders were prepared in two different ways: Before the heat treatment the mixture of β-Ga_2O_3 and dopant was either ground in an agate ball-mill for 20 min or, in order to avoid the introduction of Si, it was shaken thoroughly in a plastic box. In Table II the results of experiments with different dopants and different preparation conditions have been summarized. In the samples that were ground in an agate ball-mill the presence of the blue emission cannot be related to the introduction of the dopant, since the blue emission is caused by grinding in agate and subsequent heat treatment only. The presence of an intense green emission, however, is clearly related to the introduction of the dopant. The most efficient green emission is obtained by the introduction of Be. Ge, Sn, and to a lesser extent, Li also promote this emission. Fe and Cu both act as a killer for the

TABLE I

REPRESENTATIVE EXAMPLES OF THE IMPURITY CONTENTS (mole ppm) OF 99.9999% PURE β-Ga_2O_3 POWDER AND A β-Ga_2O_3 SINGLE CRYSTAL

Element	Powder (99.9999% pure)	Single crystal
Ag	~0.4	~2
Al	10	20
Ba	<1	<1
Be	<10	<10
Bi	<5	<5
Ca	<20	50
Cd	<15	<15
Co	<5	<5
Cu	<1	<1
Cr	<2	<2
Fe	<10	50
Ge	<13	<13
In	<8	<8
Mg	<10	20
Mn	<2	<2
Mo	<3	<3
Nb	<10	<10
Ni	<8	<8
Pb	<5	<5
Si	<20	~200
Sn	<8	<8
Sr	<5	<5
Ti	<4	<4
V	<13	<13
Zr	<10	<10

TABLE II

INFLUENCE OF THE DOPANT ON THE COLOR OF THE VISIBLE EMISSION OF β-Ga_2O_3 POWDERS[a]

	Dominant Emission Band Excluding the uv Emission Band ground		not ground	
Dopant	N_2	air	N_2	air
—	B	B	—	—
Li	B(G)	B(G)	—	—
Ag	B	B	—	—
Be	G	G	G	G
Ca	B	B	—	—
Cd	B	B	—	—
Cu	—	—	—	—
Fe	—	—	—	—
Mg	B	B	—	—
Pb	B	B	—	—
Zn	B	B	—	—
Al	B	B	—	—
B	B	B	—	—
In	B	B	—	—
Ge[b]	B(G)	B(G)	G(B)	G
Sn[b]	B/G	G(B)	B(G)	G(B)
Si	B	B	—	—
Zr	B	B	—	—

[a] All powders were heat treated at 1200°C. When the samples were ground in an agate ball-mill the concentration of the dopant varied from 500 to 4000 ppm. If the samples were not ground (shaken in a plastic box) the concentrations were usually 4000 ppm. If two emission bands were present, the band with the lowest intensity is given in parentheses.

[b] Samples doped with Ge or Sn were often inhomogeneous.

blue emission. In Fe-doped powders there was not even any uv emission. In samples prepared by shaking the mixture in a plastic box and subsequent heat treatment the occurrence of luminescence can be accounted for only by the introduction of the dopant. In unground samples Be promotes the green emission, whereas Sn and Ge promote the blue and the green emission. Only in the case of undoped or Ge- or Sn-doped powders did we notice an influence of the ambient during firing on the luminescence characteristics. Firing in nitrogen slightly promotes the blue emission, whereas firing in air promotes the green emission. All powders were either rapidly or slowly cooled from 1200°C to room temperature. We found no clear relation between the cooling rate and intensity or color of the emissions. The intensity of the green emission also decreased if the firing was carried out at 1400 instead of 1200°C, but to a lesser extent than that of the blue emission.

The most striking differences between our results on single crystals and powders were as follows:

(1) In the powders the blue emission is present after firing at 1200°C.

(2) The addition of Mg to the powder samples has no negative influence on the intensity of the blue emission.

3.2. *Excitation Spectra*

The excitation spectra at 5°K of the blue and the green emission of Zr-doped crystals have been depicted in Fig. 2. Contrary to the uv emission these emissions can be excited at low temperatures with energies lower than the energy of the bandgap only. The excitation spectra of the blue and the green emission differ in the sense that the latter has a tail on the low energy side. The maxima of the excitation bands (hereafter referred to as the defect excitation bands) coincide. At 5°K the maximum is at 4.70 eV. All measurements

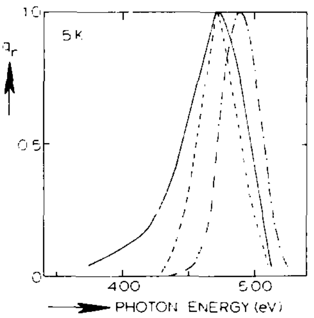

FIG. 2. Relative excitation spectra of Zr-doped β-Ga_2O_3 crystals at 5°K. q_r denotes the relative quantum output. —·— Excitation spectrum of a crystal doped with 100 ppm of Zr, observed at 3.26 eV. --- Excitation spectrum of a crystal doped with 100 ppm of Zr, observed at 2.70 eV. —— Excitation spectrum of a crystal doped with 1000 ppm of Zr, observed at 2.63 eV.

were carried out with unpolarized radiation. If the temperature is raised, the excitation bands of the blue and the green emission shift to lower energies as does the intrinsic excitation band of the uv emission. Above 120°K the blue and the green emission can also be excited in the lowest interband transition as is indicated, by the fact that the intrinsic excitation band appears in the excitation spectra of these emissions above 120°K. This points to the onset of energy migration after excitation in the band–band transition. At 300°K no significant difference is observed between the excitation spectra of the blue, the green, and the uv emission.

The intensity ratio of the green to the uv emission at 300°K for Zr-doped crystals is larger for 4.92 than for 4.46 eV excitation. In a previous paper (*5*) we demonstrated that the excitation spectra are connected with two absorption bands, one with the electrical vector (E) of the incident radiation parallel to the b-axis and one with the electrical vector perpendicular to the b-axis. The band with $E \parallel b$ lies at higher energy. Excitation at 4.46 eV at room temperature leads mainly to absorption of radiation with $E \perp b$. Obviously energy migration to the green centers at 300°K is more efficient after excitation with $E \parallel b$ than after excitation with $E \perp b$.

The excitation spectra obtained on powder samples are essentially the same. Because polarization of the incident radiation does not affect the excitation bands measured on powder samples, these bands are narrower (cf. Ref. (*5*)). Moreover it is noteworthy that in powder samples that show a bright blue emission on excitation in the interband transition at 300°K the blue emission cannot be excited at 5°K either by irradiation in the intrinsic absorption band or by irradiation at lower energies in the defect excitation band. If these powder samples are excited at low temperatures in the defect excitation band (e.g., 4.46 eV) only a weak green emission is observed. In measurements on powder samples that showed both the blue and the green luminescence, it was noticed that on excitation at lower energies (~4.10 eV) at 300°K the green emission can be excited selectively. (cf. Fig. 3).

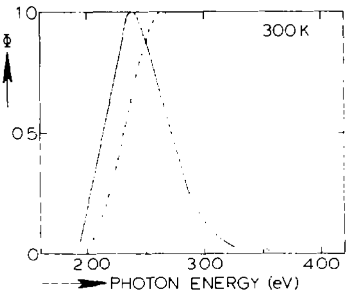

FIG. 3. Spectral energy distribution of the emission of β-Ga_2O_3 powder at 300°K. The 99.9999% pure powder was ground in an agate ball-mill and subsequently heat treated at 1200°C. Φ gives the radiant power per constant energy interval in arbitrary units. ---: Excitation at 4.92 eV. ——: Excitation at 4.13 eV.

In measuring the excitation spectra we did not encounter the problems mentioned by Blasse and Bril (*6*). Although an afterglow was clearly present, its intensity was too low in relation to the intensity of the luminescence to hinder our measurements of the excitation spectra.

3.3. Temperature Dependence of the Luminescence

The position of the maxima of the three emission bands was determined by fitting the emission spectra to the sum of two or three Gaussian curves. Within the experimental error the position of the maximum and the half-width of the blue and the green emission band remained constant in the temperature range 5–300°K. The maximum of the blue emission band was found at (2.65 ± 0.02) eV, and the maximum of the green emission band at (2.39 ± 0.02) eV. the half-widths were (0.68 ± 0.02) eV and (0.53 ± 0.02) eV, respectively. The intensity of the exciting radiation was varied over two decades, but this did not cause any significant change in the peak positions.

We investigated the energy migration by measuring the emission spectra of the uv and the blue emission at different temperatures

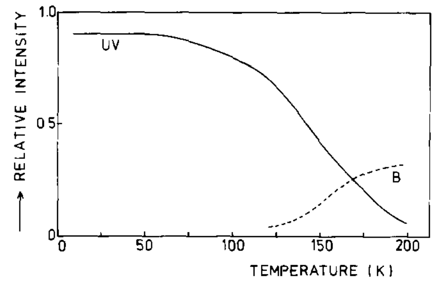

FIG. 4. Temperature dependence of the intensity of the maxima of the uv and the blue emission of β-Ga_2O_3 (measured on a powder specimen) upon excitation in the maximum of the intrinsic excitation band.

under excitation in the maximum of the intrinsic excitation band. The intensities of the two emissions have been given in Fig. 4 as a function of temperature. The temperature dependence of the intensity ratio of the green and the uv emission on excitation in the interband transition is the same as the temperature dependence of the blue and the uv emission. Energy migration becomes apparent at about 120°K, the temperature at which a change in the excitation spectra occurs (Sect. 3.2). In Fig. 5 the temperature quenching of the blue and the green emission is given. Excitation took place in the maximum of the excitation band of the blue and green emission bands. The blue emission quenches at lower temperatures than the green emission.

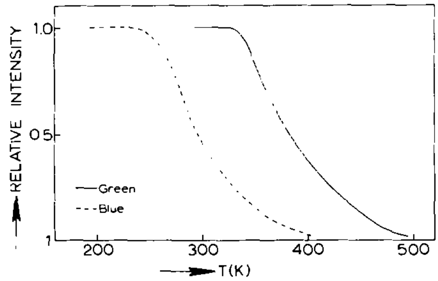

FIG. 5. Temperature dependence of the intensity of the blue (dashed line) and the green (solid line) emission as a function of temperature upon excitation in the maximum of the blue and the green excitation band, respectively.

3.4. *Decay, Afterglow, Thermoluminescence, and Optical Stimulation*

The decay of the blue emission was measured on powder samples upon irradiation in the intrinsic absorption band in the temperature range 200–300°K. The decay was observed up to 200 μsec after the excitation pulse (pulse duration 10 μsec). The intensity decreased hyperbolically with time, indicating a bimolecular recombination mechanism. In about 120 μsec the intensity decreased to $1/e$ times the intensity at the moment the excitation was terminated. The decay of the green emission could not be measured. Perhaps the reason was that the intensity of this emission was too low or that the decay time was shorter than 10 nsec (the shortest time measurable with the apparatus available (*5*)). For both emissions a low intensity afterglow could be measured easily, since during afterglow measurements no interference with the exciting radiation occurs. A relatively strong afterglow was observed in powder samples and undoped crystals. In as-grown Zr-doped crystals, however, the afterglow was almost absent, even at 5°K. This indicates that in Zr-doped crystals the traps are already filled with the extra electrons which are present in these crystals, as was shown previously (*4*). Obviously the afterglow in other samples is caused by recombination of holes with electrons that have been trapped. Apparently there is no afterglow caused by hole trapping. We ascribe this to the fact that the holes are self-trapped immediately. The uv emission is a result of the recombination of these self-trapped holes and electrons. In Fig. 6 a typical example of the afterglow at 80°K for an undoped crystal is plotted as $\log I$ vs $\log t$. The decrease of the intensity with time is neither exponential nor hyperbolic. The smooth line of the $\log I$ vs $\log t$ plot indicates a continuous trap distribution (*13*). At 80°K lifetimes (τ) of between 1 sec and 1 day correspond with trapdepths (E) between 0.14 and 0.22 eV (calculated from $1/\tau = se^{-\Delta E/kT}$ with $s = 10^9$ sec^{-1}).

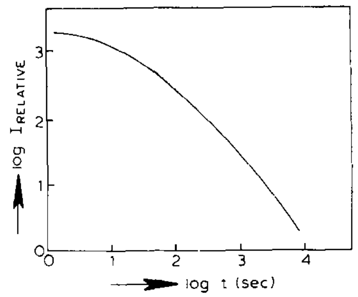

FIG. 6. Time dependence of the intensity (I) of the afterglow of an undoped β-Ga_2O_3 crystal, plotted as $\log I$ vs $\log t$. The measurement was carried out at 80°K after 4.92 eV excitation.

Thermoluminescence was studied on the same undoped crystal for which the afterglow is plotted in Fig. 6. Thermoluminescence occurred between 5 and 150°K. Since the temperature could not be varied continuously in this range, this observation is only qualitative. Trap depths (E) can be approximated with the formula $E(\text{eV}) \approx T^*/500$, where T^* is the position of the maximum (*14*). Consequently thermoluminescence peaks in the temperature range 5–150°K point to trap-depths between ~0.01 and ~0.30 eV in accordance with the trap depths derived from the decay of the afterglow at 80°K.

At temperatures above 150°K the temperature was raised continuously by 0.5°K/sec. A thermoluminescence peak with a maximum at ~290°K was observed, corresponding to a trap depth of ~0.6 eV. The presence of even deeper traps is indicated by the fact that in crystals which had previously been irradiated in the intrinsic absorption band at 5°K the uv emission could be stimulated with radiation with energies between 3.10 and 1.70 eV.

4. Discussion

4.1. The Blue Emission

The blue emission occurs in blue colored as-grown Zr-, or Si-doped, or undoped crystals. The higher electronic conductivity of these crystals compared with the electronic conductivity of the equilibrated crystals, as well as the ir absorption indicate the presence of free charge carriers (*4*). We have argued before that, on cooling these crystals from the growth temperature to room temperature, the incorporation of oxygen into the lattice according to

$$\tfrac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e' \rightarrow O_O^{\times}$$

or

$$2Ga_i^{\cdot\cdot\cdot} + \tfrac{3}{2}O_2 + 6e' \rightarrow 2Ga_{Ga}^{\times} + 3O_O^{\times}$$

(depending on the existence of a Schottky or Frenkel disorder, respectively) is not complete, resulting in frozen-in $V_O^{\times}$ or $Ga_i^{\times}$ centers. If the crystals are heat treated at 1200°C equilibrium is rapidly reached, which causes both a lower electronic conductivity and a lower absorption in the infrared. The blue emission in the doped crystals cannot be due to the presence of Si or Zr alone, since in annealed crystals only the intrinsic uv emission is observed. Charged defects ($V_O^{\cdot}$, $V_O^{\cdot\cdot}$, $Ga_i^{\cdot}$, $Ga_i^{\cdot\cdot}$, or $Ga_i^{\cdot\cdot\cdot}$) cannot cause the blue emission either, because Mg-doped crystals which contain high concentrations of either charged oxygen vacancies or charged gallium interstitials as a charge compensation for Mg^{2+} ions on Ga^{3+} positions do not show the blue emission. Therefore we assume that $V_O^{\times}$ or $Ga_i^{\times}$ centers that are already present in the samples or have been formed from the charged centers by capturing electrons created during the excitation, are involved in the luminescence process. It is improbable, however, that the emission is an F center ($V_O^{\times}$) emission as is encountered in alkaline earth oxides (*15–17*). Measurements by Lorenz *et al.* (*2*) have revealed that the first ionization of the donor centers in blue-colored crystals takes place below room temperature; this means that the distance between the relevant donor levels and the conduction band is of the order of 30 meV. A similar energy difference between donor levels created by oxygen deficiency and the conduction band is found in other *n*-type semiconducting oxides (*18*, *19*). An excited state of these donor centers 4.7 eV above the ground state would have an energy corresponding with conduction band levels, which makes localization of the energy highly improbable.

In conclusion we assume that the blue emission occurs when an electron from a $\mathrm{V}_{\mathrm{O}}^{\times}$ or $\mathrm{Ga}_{\mathrm{i}}^{\times}$ center recombines either with a trapped hole or with a hole in the valence band. The latter possibility is excluded because at 5°K in blue luminescent crystals (which should contain neutral donor centers, as was mentioned above) the blue emission can be excited in a band different from the intrinsic excitation band. Since a self-trapped hole cannot be excited directly, the possibility of recombination between an electron from $\mathrm{V}_{\mathrm{O}}^{\times}$ (or $\mathrm{Ga}_{\mathrm{i}}^{\times}$) and a self-trapped hole can be eliminated as well. Gallium ion vacancies that will act as charge compensators for Zr or Si in gallium positions are the most likely hole traps to play a part in the recombination process that causes the blue emission. This suggestion that the blue emission occurs when an electron on a $\mathrm{V}_{\mathrm{O}}^{\times}$ (or $\mathrm{Ga}_{\mathrm{i}}^{\times}$) center recombines with a trapped hole is in accordance with the conclusion drawn from the hyperbolical decay curve that the recombination mechanism is bimolecular. From the fact that the decay curve does not change in the temperature region 200–300°K we conclude that the quenching of the luminescence above 250°K is due to ionization of the donor centers involved. The conductivity measurements of Lorenz led us to expect ionization at this temperature.

Powders and crystals show an extremely different behavior with respect to the occurrence of the blue emission. Polycrystalline material that is deposited on the pedestal and the single crystals during the Verneuil process frequently shows a strong blue luminescence when the single crystals are nonluminescent. This indicates that the blue emission in powders is a surface property and that it is not caused by some undefined impurity in the 6*n* material. This view is substantiated by the observation that even in powders that show a bright blue luminescence at room temperature this blue emission cannot be excited at 5°K in the defect excitation band. Radiation with energies below the energy of the band–band transition penetrates far into the sample and excites the green emission, indicating that the blue centers are present only in the surface layer. Apparently the concentration of $\mathrm{V}_{\mathrm{O}}^{\times}$ or $\mathrm{Ga}_{\mathrm{i}}^{\times}$ centers is higher in the surface layers than in the bulk. Large differences between the defect concentrations in the bulk and at the surface have been noted before, for example by Hoyen in silver halides (*20*). The role of Si, Sn, and Ge in the powder samples is not yet understood.

4.2. *The Green Emission*

The green emission is obtained only after doping the samples with specific elements. The different behavior of Be on the one hand and, e.g., Ca and Mg on the other hand shows that the green emission cannot be due to the introduction of charge compensating point defects (e.g., $\mathrm{V}_{\mathrm{O}}^{\cdot\cdot}$) alone. Possibly $\mathrm{Be}'_{\mathrm{Ga}}$, $\mathrm{Sn}'_{\mathrm{Ga}}$ and $\mathrm{Ge}'_{\mathrm{Ga}}$ act as acceptors and $\mathrm{Ge}_{\mathrm{Ga}}^{\cdot}$ and $\mathrm{Sn}_{\mathrm{Ga}}^{\cdot}$ as donors in a donor–acceptor pair recombination. This might account for the different influence exerted on the luminescent properties by Sn and Ge and by cations that show only one valence. However, no direct evidence for such a donor–acceptor pair recombination is available at present.

4.3. *Energy Migration*

Energy migration was observed above 120°K, irrespective of the nature of the defect center. When specimens doped with Dy^{3+} or Eu^{3+} were excited in the interband transition, the emission that is characteristic of the dopant appeared above 120°K as well. Therefore we conclude that the mechanism for energy migration is the same in all cases studied. Energy migration can occur either by diffusion of free holes or by diffusion of the self-trapped hole. A distinction between these possibilities cannot be made on the basis of the present results. The self-trapped hole may become mobile and transfer its energy to the other centers, as is the case with KI–Tl (*21*) and CsBr–In (*22*). It is also possible that the capture cross section of the self-trapped hole decreases with temperature, so that holes remain in the valence band and can therefore migrate to the other defect centers.

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