A Firmly Localized Hole Center in the Mineral Brazilianite $NaAl_3(PO_4)_2(OH)_4$

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Z. Naturforsch. **37a**, 280–286 (1982); received February 5, 1982

A hole center on an oxygen adjacent to one aluminum and one phosphorous was detected and analyzed in natural and X-ray irradiated brazilianite. The slightly anisotropic ^{27}Al shfs splitting is larger than in many other hole centers in which the Al is a lower valency impurity ion with only a coordinative bond to an oxygen lone pair. The hole is trapped at an oxygen with particularly long bond distances to one P and two Al. Thus one structural Al must be substituted by a presumably divalent cation of yet unknown nature. No optical absorption is associated with this center, therefore the large distortion of the coordination polyhedra must be responsible for absence of a light-induced hole transfer between different oxygen ions. Comparison with other systems suggests that the energy differences for other configurations of the hole center are also too high to allow thermal hopping of the hole at or below room temperature. Possible mechanisms for formation and destruction of this center are deduced from experimental results.

Introduction

By far the most frequent hole center in oxides is an O^- ion adjacent to an impurity cation X of lower valency. This type of radiation defect is often associated with an intense and broad absorption band in the visible region which can consistently be ascribed to a light-induced transfer of the hole between at least approximately equivalent oxygen ions [1, 2]. In some cases, namely the extensively studied smoky quartz centers with X=Al [3] and the $O^- \cdots$ Li centers in BeO and ZnO [4], the energy differences between slightly inequivalent configurations (localization of the hole on crystallographic nonequivalent oxygens) were determined from the equilibrium concentrations of these ground and excited state centers. The oxygen with the longest distance to the impurity ion X is the energetically favored position of the hole [4, 5]. In the $P{-}O^- \cdots Al$ center in natural rose-colored quartz [6] the longer $Al \cdots O$ distance made possible by the smaller P^{5+} impurity ion (relative to Si^{4+}) evidently localizes the hole on the oxygen bridging between P and Al in contradiction to electrostatic considerations which predict a repulsion between the effective positive charges of O^- and P^{5+} in the lattice.

For small or vanishing energy differences thermal hopping of the hole can cause broadening of the EPR spectra of such paramagnetic defects at higher temperatures, and indeed in many cases including smoky quartz [3] and feldspars [7] such O^- centers are observable by EPR at low temperatures only. On the other hand, for largely different oxygen bond lengths a firm localization of the hole on the energetically preferred oxygen over the whole stability range of these centers can be expected. Such a large inequivalence should also lead to a low probability for light-induced hole transfer, and with the low concentrations of these defects no optical absorption in the visible region should be observable from such localized centers. The citrine centers in quartz [8] are examples of such firmly localized centers, but unfortunately the defects causing the nonequivalence of one oxygen are not yet known. Another example is the hole center described here, and comparison with the crystal structure data [9] allows a more reliable assessment of the differences in bond lengths required for both localization of the hole and absence of strong visible absorption.

Experimental

The EPR measurements were performed with a commercial Bruker 420 Q Q-band spectrometer at room temperature, and details of the experimental procedures have been described elsewhere [10]. Some preliminary results were obtained with a Bruker 418s X-band spectrometer. Two crystals of brazilianite from Galilea Mine near Governador,

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Table 1. Impurity contents of the brazilianite crystals.

	Crystal 1		Crystal 2	
Element	10^{-4} wt.%	Atoms/10^6 Al	10^{-4} wt.%	Atoms/10^6 Al
Mg	42	219	19	100
Zn	198	385	15	30
Fe	1150	2610	369	840

Minas Geraes, Brazil, both of a light-green coloration, were examined. The results for both were identical, they differed, however, in the concentration of Mg, Zn and Fe impurities as shown in Table 1.

Results

A signal group with a characteristic hyperfine pattern of nearly equidistant lines with twelve components resolved in favorable orientations was observed in addition to strongly anisotropic signals due to Fe^{3+} and weaker signals from electron centers. The linewidths of individual components varied between 0.4 and 0.48 mT. This center was stable to about 190 °C. After thermal bleaching it was again formed by X-ray irradiation, and in addition the signals due to atomic hydrogen appeared [11]. Measurement of rotational diagrams around the three mutually perpendicular b, c and a' axes of the brazilianite showed the hyperfine pattern to consist of two equal sextets with an additional doublet splitting between 4.3 and 6 mT, the splitting within the sextets ranged from 0.83 to 0.97 mT. In Fig. 1 an example of these spectra for a preferred orientation is shown, Fig. 2 presents the angular variations of the centers of gravity of these multiplets. As required by the symmetry of the crystal two centers of this kind (1 and 2 in Fig. 2) are observed for general orientations which coincide for $H_0 \parallel b$ and $H_0 \perp b$. Their concentrations differed significantly. Matrix diagonalisation yielded the principal values and principal axes directions of the g-tensor shown in Table 2. Selected directions between atoms in brazilianite are also included in this table for comparison. The direction of g_3 very nearly coincides with the O(6)—P(1) bond direction, but is also close to the O(7)—P(2) direction. These are the longest P—O bonds within each PO_4 unit with distances of 156.5 and 155.8 pm resp. [9]. O(6) is also bound to Al(2) and Al(3) with the longest bond distances within these AlO_6 units of 210.7 and 202.1 pm resp. while O(7) has bond distances to

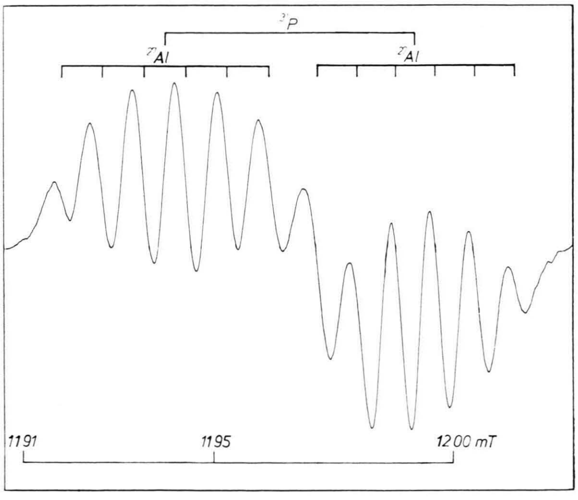


Fig. 1. EPR spectrum of the hole center in brazilianite for $H_0 \parallel c$ axis at 33.67 GHz and room temperature.

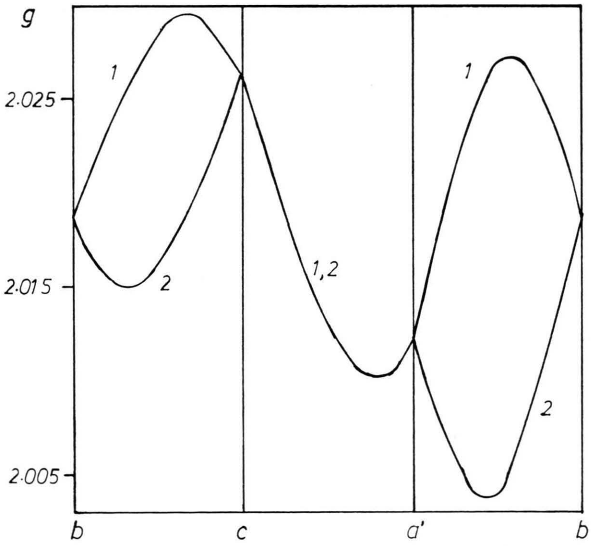


Fig. 2. Angular variation of the center of gravity of the EPR spectrum from the hole center in brazilianite for rotations around the a', b and c axes.

Table 2. Principal values g_k and principal directions of the g-tensor of the hole center and selected directions in brazilianite.

k	g	$\vartheta/°$ [a]	$\varphi/°$ [a]
1	2.0296 ± 0.0007	123.8 ± 2.0	5.4 ± 2.0
2	2.0266	126.1	124.6
3	2.0009	54.1	66.4
	P(1)—O(6)	54.2	70.6
	Al(2)—Al(3)	50.9	110.5
	Na—O(6)	53.9	−4.9
	P(2)—O(7)	41.8	67.9
	Al(1)—Al(2)	58.6	105.8
	Na—O(7)	73.6	−10.4

[a] ϑ and φ are the angles to the crystal b and c axes resp. Note that the principal directions $180° \pm \vartheta$, $360 - \vartheta$ and $180 + \varphi$ are also possible.

Al(1) and Al(3) of 212.0 and 200.2 pm resp. In addition both are coordinated to the Na^+ ion in the structure. The other two principal directions can also be correlated with directions involving these two oxygens: The direction of g_2 is close to the Al(2)—Al(3) direction, but also not far from the Al(1)—Al(2) direction, and g_1 points close to the O(6)—Na direction, a somewhat larger deviation is again obtained for the O(7)—Na direction.

Due to partly incomplete resolution resulting from the large linewidths the shfs-tensors for the sextet and doublet splittings could not be determined, but approximate values of 26 and 145 MHz resp. can be estimated for their isotropic parts, the anisotropic parts are of the orders of 1 and 10 MHz resp.

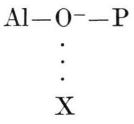
Discussion

The discussion will be concentrated on some static properties of the center, the relative stability and possible formation of excited state configurations and on pecularities of the photochemical formation and thermal destruction of these defects.

Basic Structure of the Center

According to the g-tensor orientation the hole is evidently localized on either O(6) or O(7). A precise coincidence with bond directions cannot be expected since distortions due to the presence of the hole and a lower valency impurity ion (see below) must occur. In any case the ordering of the g-tensor components is in agreement with that found in many other O^- centers, and in particular the localization of the hole on an oxygen with long bond distances is in accord with observations in other systems. With the first order approximation $\Delta g_i = -2\lambda/\Delta E_i$ $(i = x, y)$ the positions of the filled p_x and p_y levels relative to the half-filled p_z orbital along g_3 can be estimated. Taking the spin-orbit coupling parameter λ for O^- as $-120\ cm^{-1}$, $\Delta E = 8800$ and $9900\ cm^{-1}$ are obtained. The symmetry appears to be very nearly axial with a rather small overall splitting of the $2p$ level, possibly as a result of the high coordination number of oxygen.

The observed shf splittings must arise from nuclei with 100% abundance and $I = 5/2$ and $I = 1/2$ resp. Only ^{27}Al and either ^{31}P or ^{1}H as stoichiometric constituents of the crystal fulfil these requirements, but a proton can be excluded since a hole on a hydroxyl group would not be stable in the presence of oxide ions due to the higher electron affinity of the former. Since hyperfine splitting from only one aluminum is observed, the second one must be substituted by a presumably divalent ion X. This would also explain the fairly high thermal stability of this center. According to the trace analyses both Mg and Zn are present in sufficient amounts. However, unless these impurities occupy one Al site preferentially, the Zn content in crystal 2 is somewhat low since the concentration of the centers must be in the range of $100/10^6$ sites. Since all three AlO_6 units have the same average bond lengths within the limits of error, no obvious reason for such a site preference of the larger divalent ions exists, and thus Mg seems more likely. In any case the center can be described as an



$$\begin{array}{c} \mathrm{Al{-}O^{-}{-}P} \\ \vdots \\ \mathrm{X} \end{array}$$

unit where the dashes indicate true bonds between the structural atoms and the points represent a coordinative bond between the impurity ion X and an oxygen lone pair*. In principle, shfs satellites should be observable from isotopes of lower abun-

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* There is no universally accepted notation for centers of this kind, $[X]°$, $[XO_6]°$, $[AlO_6]^+$ or $[PO_4]^{2-}$ are other notations which are in use. The one chosen here has (in our view) the advantage of giving information about both environment and bonding of the O^-. It violates, however, the principle of taking the normal constituents of a lattice as being neutral.

Table 3. ^{27}Al shfs splitting constants for hole centers in oxides.

Crystal	R_{M-O}/pm	Center	$\|A\|$/MHz	% *s*	*B*/MHz	% *p*	Source
GeO_2	188.2	$O^- \cdots Al$	11.8	0.3	0.87	1.0	[12], [13]
TiO_2	195.9	$O^- \cdots Al$ I	15.9	0.4	0.96	1.2	[12], [14]
(rutile)		$O^- \cdots Al$ II	15.2	0.4	0.45	0.5	
SnO_2	205.4	$O^- \cdots Al$	9.1	0.2	0.89	1.1	[12], [15]
$SrTiO_3$	195.2	$O^- \cdots Al$	15.6	0.4	0.6	0.7	[16], [17]
$YAlO_3$	191	$O^- - Al$? I	11.8	0.3	0.85	1.0	
		$O^- - Al$? II	14.1	0.4	1.1	1.4	[18]
brazilianite	190.7	$Al - \underset{\underset{X}{\cdot}}{O^-} - P$	26	0.7	1.0	1.2	[9], this work
SiO_2	160.9	$O^- \cdots Al$	16.4	0.4	0.81	1.0	[5]
(α-quartz)		$O^- \cdots Al/H$	25.6	0.7	1.1	1.4	[20]
		$O^- \cdots Al/Li$	21.9	0.6	1.2	1.4	[19], [20]
		$O^- \cdots Al/Na$	22.7	0.6	1.5	1.8	[21]
		$O^- \overline{\cdots} Al \overline{\cdots} O^{-a}$	23.5	0.6	0.63	0.7	[22]
		$Al \cdots O^- - P$	4.2	0.1	0.81	1.0	[6]
feldspars	167	$Al \overline{\cdots} O^- \overline{\cdots} Al$	25	0.6	?		[7]

[a] Double hole center, designated $[AlO_4]^+$ by the authors.

dance for both ^{25}Mg and ^{67}Zn, but their relative intensities must be below 2% and are thus too low for our signal/noise ratios. For X=Be, on the other hand, a small shf splitting might be observable like in phenacite [29] and in BeO [4], but the low abundance of this element makes it less likely.

As apparent from the Tables 3 and 4, the isotropic ^{27}Al and ^{31}P shf splitting constants are on the upper range of those observed in related centers. Unpaired electron densities, calculated from atomic data reported by Morton and Preston [23], are also included in these tables. Since effects of core polarization were neglected, the absolute values are less meaningful than their variations. Concentrating on the ^{27}Al splittings first, we see that there is a noticeable, but not decisive influence of the bond lengths (for the pure host lattice), but no clear effect of the coordination number of the metal ion (six in the upper and four in the lower part of Table 3). In most cases the Al is a lower valency impurity ion, and for an unperturbed center of this kind an upper value of 0.4% s-electron density evidently holds like in TiO_2 [14] and the smoky quartz center [5] with some variation possibly due to the different electronegativities of the host cations. The exceptionally low value for the $Al \cdots O^- - P$ center in quartz [6] evidently results from the effective positive charge of the pentavalent phosphorous opposite to Al. On the other hand, values in the same range as in brazilianite are observed for the overall positively charged centers in quartz with additional cations [20, 21] and in the feldspars [7]. In the latter case one of the two approximately equivalent Al atoms substitutes for Si, and thus on the average the situation is intermediate between a true and a coordinative bond. In the double hole center with a similarly high splitting [22], finally, two unpaired electrons adjacent to one Al are present. The variations of the anisotropic splittings are somewhat smaller, and their trends are less obvious.

Table 4. Isotropic ^{31}P shf splitting constants for $X \cdots O^-P$ centers in oxides.

Crystal		*A*/MHz	% *s*	Source
KH_2PO_4	I	140	1.1	[24]
	II	90	0.7	[25]
various phosphates		77.3 to 100.1	0.6 to 0.8	[26]
$CaWO_4$		77.8	0.6	[26]
calcite		53.6	0.4	[27]
α-quartz (X=Al)		126	0.9	[6]
$AlPO_4$	I	103.5	0.8	[28]
	II	92.9	0.7	
brazilianite		146	1.1	this work

Turning now to the isotropic ^{31}P shf splitting constants in Table 4, we see that here a variation of less than a factor of 3 has been observed so far. All these centers can be described as $[PO_4]^{2-}$ ions where either the P itself is the lower valency ion like in

$CaWO_4$ [26] or a metal ion adjacent to one of the oxygens plays this role like in quartz [6], $AlPO_4$ [28] and brazilianite. There is again a clear trend, but no obvious borderline for these two cases. In $CaCO_3$ with the lowest isotropic splitting the excess negative charge of the whole $[PO_4]^{3-}$ group substituting for $[CO_3]^{2-}$ seems to be responsible for hole formation. An excess positive charge in the neighborhood, initially incorporated for charge compensation, would explain the unusually low value of A.

The anisotropic parts are usually very small (up to 1 MHz in solid phosphates and 2.8 MHz in aqueous phosphoric acid [26]). The considerably higher B near 10 MHz observed in brazilianite may be due to the large distortions.

No shf splitting is observed from ^{23}Na as a further neighbor of both O(6) and O(7). Thus this ion must either be absent or the splitting is too low to be observable. The halfwidths of the EPR signals place an upper limit near 0.5% s electron density on this ion which is slightly lower than those calculated for both Al and P. Judging from the O ··· Li centers in ZnO, BeO [4] and MgO [30], a sufficiently large splitting may appear likely. However, the high and irregular coordination of the Na^+ tends to shield this ion, and ENDOR measurements would be required to resolve this ambiguity.

Thermal and Optical Properties of the Center

The equilibrium ratios N_e/N_g of excited and ground state configurations (hole on oxygen with short or long bond distance resp.) have been determined for the smoky quartz [3] as well as the $O^- \cdots Li$ centers in ZnO and BeO [4] as a function of temperature. The energy differences ΔE obtained from these measurements can be correlated with the differences in bond lengths [19, 31, 32] for the nonequivalent oxygens involved. In Fig. 3 they are correlated using the approximation

$$\Delta E = a \, \Delta R \cdot \bar{R}^t .$$

As seen in Fig. 3, a value of $t = -3.3$ was obtained for the $O^- \cdots Li$ centers*, but the data for the

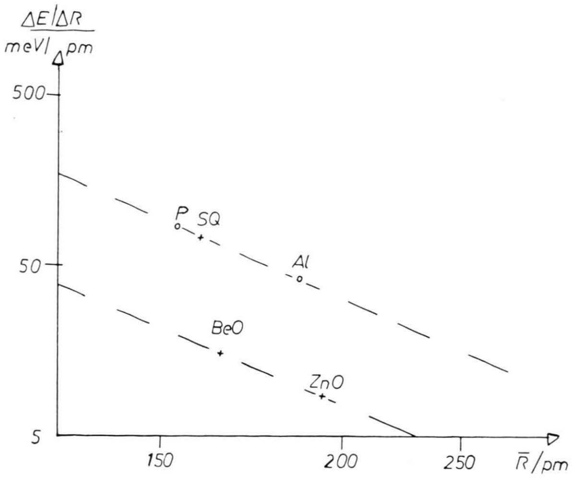

Fig. 3. Correlation of the energy differences between ground and excited state configurations of O^- hole centers with the differences in bond lengths of the ideal lattices. SQ — smoky quartz center, P, Al — PO_4 and AlO_6 units resp. in brazilianite.

smoky quartz centers are far above the line joining these two systems, perhaps as a result of the higher valencies of Si and Al. With the same exponent of $t = -3.3$ we then obtained estimates for the thermal hopping rates at room temperature (relative to the $O^- \cdots Li$ center in BeO) and for the equilibrium ratios N_e/N_g for the hole center in brazilianite from the average bond length $\bar{R}$ and the minimum differences ΔR (upper line in Figure 3). Since both sets of data accidentally almost agreed, only the former are shown in Table 5. Hopping within each AlO_6 unit must be considered since one of them must be the location of the divalent ion X, but hopping within the PO_4 units also cannot be excluded. For the hole on O(7) the divalent ion X cannot occupy an Al(2) site since its bond to O(7) is considerably shorter than that to O(6).

Table 5. Estimated energy differences of excited state configurations and thermal hopping rates (relative to $O^- \cdots Li$ in BeO) at 300 K for the hole center in brazilianite.

Cation	Oxygens	ΔR/pm	ΔE/meV	s_{th}/s_{th} (BeO)
Al(2)	O(6)—O(7)	10.5	448	$2 \cdot 10^{-8}$
Al(3)	O(6)—O(3)[a]	9.0	384	$3 \cdot 10^{-7}$
P(1)	O(6)—O(9)	2.1	243	$6 \cdot 10^{-5}$
Al(1)	O(7)—O(4)[a]	16.6	708	10^{-12}
P(2)	O(7)—O(10) or O(12)	1.8	208	$5 \cdot 10^{-4}$

[a] These are oxygens of OH groups. The next oxygens have 13.6 and 24.8 pm resp. shorter bond lengths.

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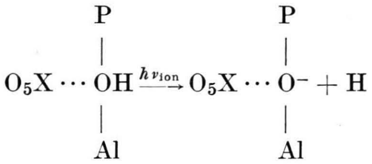
* For BeO a value of $\Delta E = 21$ meV (instead of the quoted 34 meV) was obtained taking the high temperature limiting ratio $N_e/N_g = 3$ as required by the ratio of oxygen ions (and realized in the original data for ZnO). Without this correction the exponent is higher leading to slightly lower ratios for the PO_4 and higher ratios for the AlO_4 polyhedra.

In BeO the $O^- \cdots Li$ center can be observed by EPR up to temperatures above 420 K, the effects of thermal hopping are visible only in a decreasing anisotropy of the g-tensor between 77 and 420 K [4]. It is therefore very unlikely that any thermal effects are present in the hole center in brazilianite at or below room temperature, the large linewidth of its EPR spectra must arise from unresolved shf structure since all cation nuclei in the structure have $I > 0$.

The optical transfer of the hole still occurs despite rather large differences in bond lengths. This is clearly demonstrated by the results for the $O^- \cdots Li$ center in ZnO [4] where the optical absorption due to this light-induced transfer changes only slightly between 6 and 300 K although at low temperatures practically no excited state centers are present and thus the transfer must occur to the equatorial oxygens with 1.8 pm shorter bond lengths [4]. No optical absorption in the visible region is associated with the hole center in brazilianite, the green color of natural crystals must have a different origin since it is less stable than the hole center and is not restored after thermal bleaching and subsequent X-ray irradiation. The differences in bond lengths within the AlO_6 units are much larger than in any other system for which hole centers with intense visible absorption are known to exist, and for them a low probability for this light-induced hole transfer seems plausible. However, the differences in bond lengths within the PO_4 units in brazilianite are in the same range as for ZnO : Li, and in the $Al \cdots O^- - P$ centers in rose-colered quartz this light-induced hole transfer occurs within the PO_4, not the AlO_4 units [6]. Thus either a very abrupt decrease of intensity must occur for differences in bond lengths near 2 pm or the different surroundings of the oxygens create an additional unfavorable inequivalence which either suppresses this optical excitation or shifts it into the ultraviolet region. A precise determination of the oscillator strengths for this absorption as a function of the distortion would be desirable, and investigation of other systems with similar distortions might help to gain more insight.

Possible Mechanisms of Color Center Formation and Destruction

The simultaneous formation of atomic hydrogen and hole centers suggests a primary photochemical process



$$\begin{array}{ccc} \mathrm{P} & & \mathrm{P} \\ | & & | \\ O_5X \cdots OH & \xrightarrow{h\nu_{\mathrm{ion}}} & O_5X \cdots O^- + H \\ | & & | \\ \mathrm{Al} & & \mathrm{Al} \end{array}$$

(where the proton is an impurity charge compensating for X^{2+}). Formation of several configurations of this atomic hydrogen can consistently be explained by the assumption of initial presence of crystallographically inequivalent OH groups which nevertheless would lead to only one type of hole center. The atomic hydrogen has a lower thermal stability than the hole center [28]. After intense X-ray irradiation hydrogen concentrations in the range of 100 ppm per formula unit are present which favor thermal destruction via an irreversible second order reaction like

$$H + H \xrightarrow{kT} H_2 .$$

With slow radioactive irradiation in nature low stationary concentrations of atomic hydrogen are formed for which a destruction via a first order reaction like

$$H + O - Fe(III) \xrightarrow{kT} HO \cdots Fe(II)$$

should dominate. The green color of natural brazilianite with a broad absorption band near 13000 cm^{-1} is believed to arise from this divalent iron formed by a secondary thermal process. The increase of ultraviolet absorption near 39000 cm^{-1} with destruction of the green color above 140 °C suggests reoxidation to Fe(III), but a direct proof of this postulated increase of the concentration of trivalent iron would be desirable. With the high concentration of iron present in brazilianites (see Table 1) careful quantitative measurements, e.g. by EPR, would be required.

Absence of thermoluminescence during thermal destruction of the different radiation defects in brazilianite suggests that more complex and most likely irreversible reactions are involved, not just electron-hole recombination which prevails in most other systems.

Acknowledgements

This work was supported by grants from the Deutsche Forschungsgemeinschaft and the Forschungsministerium des Landes Nordrhein-Westfalen.

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