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Polarization of the x-ray-induced blue luminescence in quartz

K. Tanimura* and L. E. Halliburton

Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74078

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The polarization of the x-ray-induced blue luminescence from synthetic quartz has been measured between 80 and 225 K. Two overlapping bands having different polarizations are observed; one peaks at 2.48 eV and is almost completely polarized perpendicular to the *c* axis, while the other peaks at 2.74 eV and is polarized parallel to the *c* axis with $(I_\parallel - I_\perp)/(I_\parallel + I_\perp) = 0.48 \pm 0.02$. This latter band corresponds to emission from a triplet state of the luminescence center. These results are discussed in terms of a previously proposed model.

I. INTRODUCTION

The response of quartz to ionizing radiation is a topic of considerable current interest. Its fundamental importance arises from the opportunity to explore new defect production mechanisms that occur in this unique "semicovalent" material,[1] and its practical importance comes from the applications of quartz in precision frequency-control devices.[2]

The "blue" luminescence that occurs during excitation with x rays at low temperature[3-5] is one of the least understood of the radiation-related phenomena in quartz. Previous studies have shown that this luminescence consists of at least three overlapping bands which are characterized by different peak energies, thermal quenching temperatures,[6,7] and decay times.[8] Even though it has been demonstrated that one of the components arises from electron-hole recombination at aluminum impurities compensated by alkali-metal ions,[7] the origin of the major portion of this blue luminescence has remained an open question. Several experimental studies[8-12] have suggested the intrinsic nature of the luminescence.

Recently, Tanimura, Tanaka, and Itoh[11] showed that a portion of the blue emission originates from the same radiation-induced transient defect that gives rise to optical absorption at 5.4 eV and a significant volume change. The long decay time of this defect, approximately 1 ms at 78 K, implies a triplet nature for its electronic structure. This expectation was elegantly verified by Hayes *et al.*[12] when they used optically detected magnetic resonance (ODMR) to demonstrate that a triplet state with a large fine-structure splitting contributes to the blue emission. Proposed configurations of the luminescence center in quartz are highly anisotropic, and this suggests that the blue luminescence should be polarized. The observation of polarization effects in the x-ray-induced luminescence has been reported by Trukhin and Plaudis,[8] but more detailed information which takes into account the overlapping structure of the emission is needed.

In the present Brief Report, we describe experimental results obtained from a polarization study of the blue luminescence in α quartz. Of two major bands monitored, one peaks at 2.48 eV, thermally quenches near 130 K, and is polarized almost completely perpendicular to the *c* axis, while the other peaks at 2.74 eV, thermally quenches above 160 K, and is polarized parallel to the *c* axis with a degree of polarization of 0.48. These results for the 2.74-eV band cannot be simply explained in terms of a proposed model[12] of an exciton localized primarily in a molecular oxygen configuration of the form $O_2{}^{2-}$.

II. EXPERIMENTAL PROCEDURE

The data presented in this paper were obtained from a quartz crystal cut from the *Z*-growth region of a premium-Q grade bar. This material, chosen because of its high purity, was purchased from Sawyer Research Products, Eastlake, Ohio. For comparison, we also examined a sample of natural Arkansas quartz but found no differences in the x-ray-induced luminescence spectra. This latter result supports the assignment of the blue emission to an intrinsic phenomenon since the point-defect concentrations in the natural sample were one to two orders of magnitude greater than in the synthetic sample.

Prior to taking the luminescence data, the samples were irradiated at 300 K with 1.7-MeV electrons from a van de Graaff accelerator. This eliminated the aluminum-related emission band and left only two contributions to the blue luminescence.[7] During our measurements, the samples were attached to the copper cold finger of a closed-cycle helium cryogenerator (Air Products model No. CS-202) and were excited with x rays from a Machlett OEG-60 tube operating typically at 45 kV and 5 mA. Temperatures were controlled to within ± 1 K over the range from 80 to 225 K. Light emitted along the *y* axis of the crystal (i.e., a direction perpendicular to both the threefold and one of the twofold axes of symmetry) was passed through a Glan-Thompson polarizer and then was detected by the combination of a Spex 0.25-m Minimate monochromator, an RCA C31034 photomultiplier tube, a Keithley 427 current amplifier, a Hewlett-Packard (HP) 3478A voltmeter, and an HP-85 computer. The spectral response of our optical system was corrected by using a quartz-iodine lamp traceable to the National Bureau of Standards.

III. RESULTS

Polarized emission spectra obtained from the synthetic quartz sample at 81 and at 168 K are shown in Fig. 1.

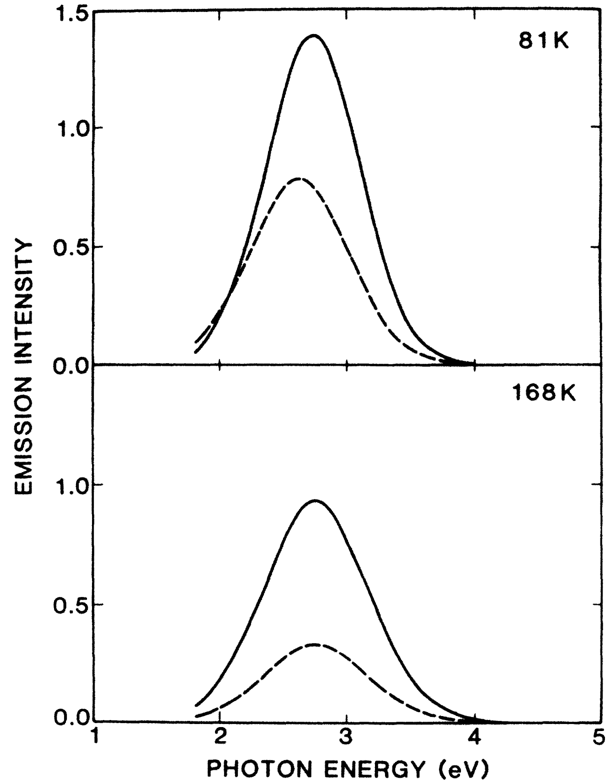

FIG. 1. The polarized emission spectra taken at 81 and at 168 K from synthetic quartz. Solid and dashed curves correspond to spectra with the electric vectors parallel to the z and x axes, respectively.

These two temperatures were chosen because they occur just before the quenching steps associated with each band. Thus, we expected contributions from both bands at 81 K and from one band at 168 K. The solid and dashed curves in Fig. 1 correspond to the electric field vector parallel to the z and x axes of the crystal, respectively. The $\mathbf{E}\parallel\hat{\mathbf{z}}$ spectra have the emission peaking at 2.74 eV at both temperatures, whereas the $\mathbf{E}\parallel\hat{\mathbf{x}}$ spectra show a shift in the peak energy from 2.62 to 2.74 eV with increasing temperature. At 168 K, band shapes for the two polarizations were identical within experimental error (see the lower portion of Fig. 1).

Figure 2 shows the temperature dependence of the total emission (i.e., the area under the spectrum) corresponding to the $\mathbf{E}\parallel\hat{\mathbf{z}}$ and the $\mathbf{E}\parallel\hat{\mathbf{x}}$ polarizations. These two sets of data are represented by the open circles and the open squares, respectively, in Fig. 2. The integrated intensity of the $\mathbf{E}\parallel\hat{\mathbf{x}}$ spectrum thermally quenches in two stages, one near 130 K and another above 160 K. On the other hand, there is no observable quenching stage at 130 K for the $\mathbf{E}\parallel\hat{\mathbf{z}}$ spectrum; instead, the entire integrated intensity of the $\mathbf{E}\parallel\hat{\mathbf{z}}$ spectrum thermally quenches in the single stage above 160 K. As the two polarized components of the emission decrease in the temperature range from 160 to 225 K, the ratio of their intensities remains constant and their band shapes remain identical. These results suggest that the two separately polarized components of the emission which are shown in the lower portion of Fig. 1 originate from the same optical transition within the emitting defect. Thus, we can determine the polarization of the 2.74-eV band unambiguously from the data taken above 160 K. The degree of polarization P for this band is found to be 0.48 ± 0.02. In our case, P is defined as $(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ represent the emission intensities measured with the electric field vector parallel and perpendicular to the c axis.

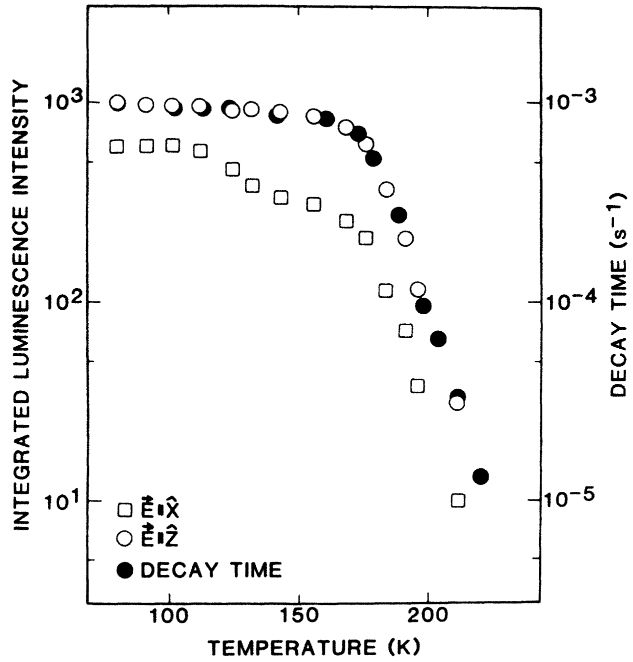

FIG. 2. Temperature dependence of the integrated intensities of the $\mathbf{E}\parallel\hat{\mathbf{z}}$ and the $\mathbf{E}\parallel\hat{\mathbf{x}}$ components of the luminescence. Also, the temperature dependence of the decay time of the 2.8-eV emission induced by pulsed electron excitation, as described in Ref. 11, is shown for comparison.

Furthermore, the lack of any measurable first-stage quenching in the $\mathbf{E}\parallel\hat{\mathbf{z}}$ component of emission (i.e., the open circles in Fig. 2), clearly shows that the electric vector of the luminescence band which is quenched at 130 K is almost completely oriented perpendicular to the c axis. This latter observation allowed us to determine the band shape and peak position of the band which is quenched at 130 K. Specifically, we assumed the band quenching at 130 K is 100% polarized (i.e., it makes no contribution to the $\mathbf{E}\parallel\hat{\mathbf{z}}$ spectrum at 81 K). Then we determined the contribution of the 2.74-eV band to the $\mathbf{E}\parallel\hat{\mathbf{x}}$ spectrum at 81 K by using the ratio of its two polarized intensities at 168 K. Finally, subtracting the contribution of the 2.74-eV band from the total $\mathbf{E}\parallel\hat{\mathbf{x}}$ spectrum at 81 K gave a band which peaks at 2.48 eV.

Although our results are in direct agreement with all of the general conclusions of Alonso, Halliburton, Kohnke, and Bossoli,[7] specific values for the peak positions of the two contributing components reported here are measurably different from those found in the earlier paper. The peak position of the band quenching near 130 K is now 2.48 eV, instead of the earlier value of 2.82 eV, and the peak position of the band quenching above 160 K is now 2.78 eV, instead of the earlier value of 2.92 eV. We believe the primary reason for these differences in peak positions is the corrections for spectral response of the optical system that were used in the present investigation but not in the previous work. Thus, we suggest that the present values are more accurate.

Finally, in Fig. 2, the temperature dependence of the decay time of the 2.8-eV emission, as determined earlier by Tanimura *et al.*,[11] is plotted for comparison with our present data. This decay time and our intensity of the 2.74-eV band have identical thermal quenching characteristics over the range from 80 to 225 K. This correlation strongly suggests that the 2.74-eV emission band is the portion of the blue luminescence that directly relates to the transient defects giving rise to the large volume change and the uv absorption band.[11]

IV. DISCUSSION

We now consider the defect model which has been proposed for the transient effects in quartz, and evaluate whether it is consistent with the polarization data reported in the present paper. Attention is focused on the 2.74-eV band since it is now known to be directly related to the transient triplet-state defect. Hayes *et al.*[12] suggested that the triplet recombination center is a split oxygen interstitial with an adjacent neutral oxygen vacancy. Their ODMR results indicate that the unique principal axis of the oxygen molecule is perpendicular to the c axis and makes an 85° angle with the x axis (i.e., the twofold axis). In general, there are six distinguishable symmetry-equivalent oxygen sites in the quartz lattice; but, in the present case, these reduce to three because of the double degeneracy imposed by having the unique axis of the molecule oriented perpendicular to the threefold symmetry axis. These three distinguishable orientations of the oxygen molecules have their unique principal axes in the x-y plane of the crystal, and they make 120° angles with each other. From these symmetry considerations, we can calculate the degree of polarization for the triplet-state luminescence from the oxygen molecule.

Following the approach of earlier investigators, we describe the components of the defect in purely ionic terms. Thus, the split oxygen interstitial is described as an O_2^{2-} molecular ion. In terms of a molecular orbital scheme, O_2^{2-} molecular ions have the electronic configuration of

$$(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g)^4{:}\,^1\Sigma_g^+$$

for the ground state. The lowest triplet state then can be described as

$$(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g)^3(2p\sigma_u){:}\,^3\Pi_u\ .$$

A radiative transition from $^3\Pi_u$ to $^1\Sigma_g^+$ may occur because of spin-orbit coupling. The resultant transition dipoles are oriented parallel (σ_u) and perpendicular (π_u) to the molecular axis. When we assume that the radiative transitions induced by the dipoles are equally probable, the predicted degree of polarization is -0.20 for the sample geometry used in the present experiment. This result is not consistent with the observed value of $+0.48$. Therefore, the O_2^{2-} molecular ion model for the x-ray-induced blue luminescence center does not explain our polarization data. As a cautionary note, there might be a mechanism which suppresses the transitions due to dipoles lying in the x-y plane and enhances the transitions due to dipoles oriented along the c axis of the crystal. However, in such a case, the description of an O_2^{2-} molecular ion for the luminescence center may no longer be appropriate.

Recently, Skuja, Streletsky, and Pakovich[13] proposed a model consisting of a twofold coordinated silicon ion (i.e., a silicon with two neighboring oxygen vacancies) as the origin of the 2.65- and 4.3-eV photoluminescence bands in amorphous SiO_2. Their model is intriguing, but it remains to be seen whether it could be applied to the x-ray-induced blue luminescence in single-crystal quartz. In fact, we found no trace of the 4.3-eV luminescence in samples used in the present study.

Obviously, more sophisticated experiments are needed to determine the detailed atomic and electronic structures for the blue luminescence center. Also, theoretical studies are needed before a complete understanding is developed of this luminescence in quartz.

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[*] Permanent address: Department of Crystalline Materials Science, Nagoya University, Furo-cho, Chikusa, Nagoya 464, Japan.

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