

**PHOTOLUMINESCENCE IN CZOCHRALSKI AND
HYDROTHERMALLY GROWN BISMUTH
SILICON OXIDE**

By

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Bachelor of Science

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1992

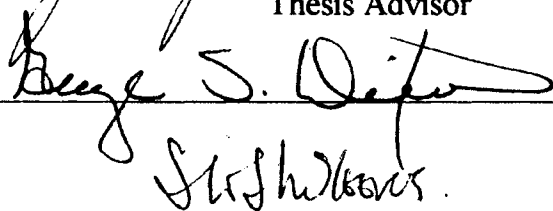
Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May, 1994

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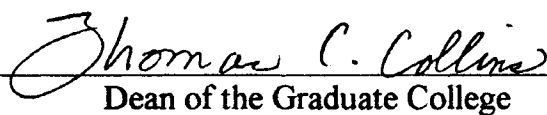
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Dean of the Graduate College

ACKNOWLEDGMENTS

Foremost, I wish to thank Dr. Joel Martin for his invaluable advisement and support during my graduate school venture. Without his assistance and constant reminder that "sometimes physics is like TV repair", my studies in the physics department would not have been as tolerable. His insights and expertise in solid state physics made this thesis a genuine learning experience. Additionally, the assistance of Dr. David Hart, programmer extraordinaire, is greatly appreciated. Dr. Hart's familiarity with experimental equipment and programming helped lessen the difficulty of data acquisition.

Thanks to Mr. Charles Hunt for the fine samples of OSU Czochralski-grown BSO. Thanks, also, to Mr. Meckie Harris and Dr. John Larkin of Rome Laboratory for the incredible samples of hydrothermally-grown BSO, without which, this thesis would have been impossible. Thanks, also, to Dr. Steven McKeever and Dr. George Dixon for donating part of their busy schedules to serve on my graduate committee.

I sincerely wish to thank my wife, E'vet, and my daughter, Elisha, for their patience during graduate school. They have tolerated much, from multiple relocations to my near manic-depressive mood swings, and have forfeited many hours of family time to my studies and homework. I greatly appreciate it.

This work was supported by the National Science Foundation and the State of Oklahoma.

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CHAPTER 1

INTRODUCTION

The crystalline compound bismuth silicon oxide, $\text{Bi}_{12}\text{SiO}_{20}$, hereafter referred to as BSO, is of considerable interest for a wide variety of advanced technology applications, ranging from beam steering to real-time interferometry [1]. The usefulness of BSO in these applications depends largely on the material's large photorefractive effect, or light-induced change in refractive index. Optimization of BSO for such applications requires a detailed understanding of the processes involved in the photorefractive effect.

BSO, along with the closely related compounds $\text{Bi}_{12}\text{GeO}_{20}$ (BGO) and $\text{Bi}_{12}\text{TiO}_{20}$ (BTO), forms a body-centered cubic structure known as sillenite, named after Sillen, the Swedish chemist who first studied the crystal [2]. The structure lacks inversion symmetry and has space group $I23$. The unit cell is complicated, consisting of two full chemical formula [3]. The corners and center of the body-centered frame contain silicon atoms, each surrounded by four oxygen atoms lying along the cube diagonals, forming perfect tetrahedra. Bismuth atoms within the cube are surrounded by seven oxygen atoms, forming distorted octahedra. BSO does not have inversion symmetry; consequently, it is piezoelectric and electro-optic and has been used as a surface acoustic wave device. Its electro-optic properties, when coupled with crystal defects, give rise to the photorefractive effect.

Defects

In BSO and a number of other noncentrosymmetric insulating materials, electrons or holes are trapped at impurities or other defects. These electrons or holes may be

optically excited to the conduction or valance bands, respectively, and migrate until recombining with shallower traps. If the illumination is nonuniform, the resulting charge distribution will also be nonuniform and will lead to a corresponding pattern in the index of refraction through the electro-optic effect. This is known as the photorefractive effect and was first observed in LiNbO_3 by Askin *et al.* [4].

Many different traps are present in BSO. Photoconductivity studies [5] have shown BSO to be p-type in the absence of illumination and n-type when illuminated. Two-wave mixing experiments with BSO by Attard and Brown [6] have found evidence for both hole and electron trapping and multiple shallow and deep traps. Optical excitation has been shown to induce absorption bands [7] likely associated with some of the traps. Hart *et al.* [8] used optical excitation at low temperatures followed by incremental annealing to study the stability of the traps responsible for the absorption bands. Their studies indicate many shallow traps of varying depth.

At room temperature, undoped BSO is pale yellow in coloration caused by to an absorption shoulder in the blue region of the visible spectrum. The absorption shoulder is due to a deep electron donor [5]. The addition of column III dopants, such as aluminum, gallium, or boron, will remove, or bleach, the absorption shoulder [2,5]. These dopants, when replacing the tetrahedrally coordinated silicon, act as acceptors and electronically compensate the deep donor. The use of column V dopants, such as phosphorus or nitrogen, also bleaches the absorption shoulder [2,21]. These dopants are believed to change to nature of the deep donor, making it unable to absorb light [3,5]. Interestingly, the addition of gallium and phosphorous simultaneously as dopants partially restores the absorption shoulder [2,21].

The exact nature of the deep electron donor is not understood. It appears to be related to deviations in stoichiometry. X-ray studies indicate only 87% of the silicon sites are occupied [9]. Hou *et al.* [5] suggest that the deep donor is due to a silicon vacancy complex occupied by an electron. Oberschmidt [10] has compared the silicon vacancy

model to that of an impurity occupying the silicon site and has concluded, on the basis of thermodynamic arguments, that an anti-site bismuth is the most likely cause of the deep donor. The anti-site bismuth would behave as a donor in the silicon site. The work of Craig and Stephenson [11] supports this possibility. They found that the compound $\text{Bi}_{25}\text{FeO}_{40}$ has the same structure as BSO, with iron at one silicon site and bismuth at the other in the body-centered cubic unit cell.

Crystal Growth

Single crystals of BSO can be obtained by using either the Czochralski or hydrothermal growth method. In Czochralski growth, a well mixed powder of bismuth oxide (Bi_2O_3) and silicon oxide (SiO_2) of 6:1 molar ratio is heated to 900°C in a crucible, typically platinum. Once the mixture melts, an oriented seed crystal is dipped into the melt and slowly withdrawn. The seed is usually rotated to prevent the formation of a core [12]. After grown, the crystal is slowly cooled to prevent cracking due to thermal stress.

In hydrothermal growth, BSO is prepared in a solution of NaOH by using moderate temperatures and high pressures [13]. Czochralski-grown samples of BSO are used as nutrient and are placed in the bottom of an autoclave. A seed is suspended near the top of the autoclave and is separated from the nutrient by a baffle. During growth, a temperature gradient between the top and bottom of the autoclave sets up convection currents which transport nutrient to the seed, allowing crystal formation.

Luminescence

Many insulating and semiconducting crystals exhibit some form of luminescence, or the production of light by a non-thermal process. Luminescence has many different

forms, such as electroluminescence, the luminescence induced by an electric field or current, triboluminescence, the luminescence caused by mechanical distortion, and photoluminescence, the luminescence induced by visible or UV light. Our interest lies primarily with photoluminescence.

Photoluminescence can be attributed to several different mechanisms. Ions, such as the Bi^{3+} occupying the distorted octahedral site in sillenites, can be optically excited. Transitions from excited to ground states may produce an emission. Shining light with energy greater than the bandgap energy can produce electron-hole pairs, called excitons. Bound together by the coulomb force, these electron-hole pairs may move freely through the lattice or be trapped by a lattice defect until recombination. The energy of the emission produced upon recombination is the difference between the coulomb binding energy and the bandgap energy.

Shining above-bandgap light on the sample can also move a valance band electron into the conduction band. Once in the conduction band, the electron makes radiative or non-radiative transitions to the valance band either directly or through intermediate steps. The electron may become trapped at an intermediate step and will remain there until it has sufficient energy, thermal or optical, to escape.

Statement of Purpose

BSO exhibits photoluminescence at low temperatures when excited with band-edge light. In the following experiment, a systematic study of the low temperature photoluminescence of undoped hydrothermally- and Czochralski-grown BSO is presented. The low-defect, hydrothermally-grown BSO allows the study of optical processes inherent to BSO. Comparison of hydrothermally-grown BSO to Czochralski-grown BSO helps to determine the nature of the defects introduced during the growth process.

CHAPTER 2

EXPERIMENTAL PROCEDURE

Samples

Samples studied in these experiments were single crystals of the compound bismuth silicon oxide, $\text{Bi}_{12}\text{SiO}_{20}$, hereafter referred to as BSO. Both Czochralski- and hydrothermally-grown BSO crystals were studied. Identification number, origin, and growth method of each sample is listed in Table I.

Undoped Czochralski BSO crystals were grown at both Rome Laboratories and Oklahoma State University. The chemicals were Johnson-Matthey Grade-1 bismuth oxide (Bi_2O_3) and silicon oxide (SiO_2). Materials were mixed in a 6:1 molar ratio and mixed in a tumbler for several days. The mixture was then heat treated at 800°C in a flowing oxygen atmosphere for 48 hours. The mixture was heated to 900°C in a platinum crucible by a 20 kW 450 kHz RF induction furnace and an [100] oriented seed crystal was partially immersed in the melt. The seed was pulled from the melt at 2.5 to 3 mm per hour and rotated at 30 to 86 revolutions per minute to suppress the core commonly observed when these crystals are grown [12].

At the end of the growth run, the crystals were cooled to room temperature over a period of 48 hours. Samples of either [100] or [110] orientation were cut from the boule. Samples were typically 1.0 to 2.0 mm thick and were polished to optical quality. Figure 1 compares the absorption spectra of undoped Czochralski-grown and hydrothermally grown BSO samples. The absorption shoulder present in the undoped Czochralski-grown

TABLE I
INVENTORY OF BSO SAMPLES

<u>Identification Number</u>	<u>Laboratory Origin</u>	<u>Growth Method</u>
BSO50	Rome	Hydrothermal
BSO40T2	Rome	Hydrothermal
060391	OSU	Czochralski
BSO102	Rome	Czochralski
BSO92	Rome	Czochralski from Hydrothermal

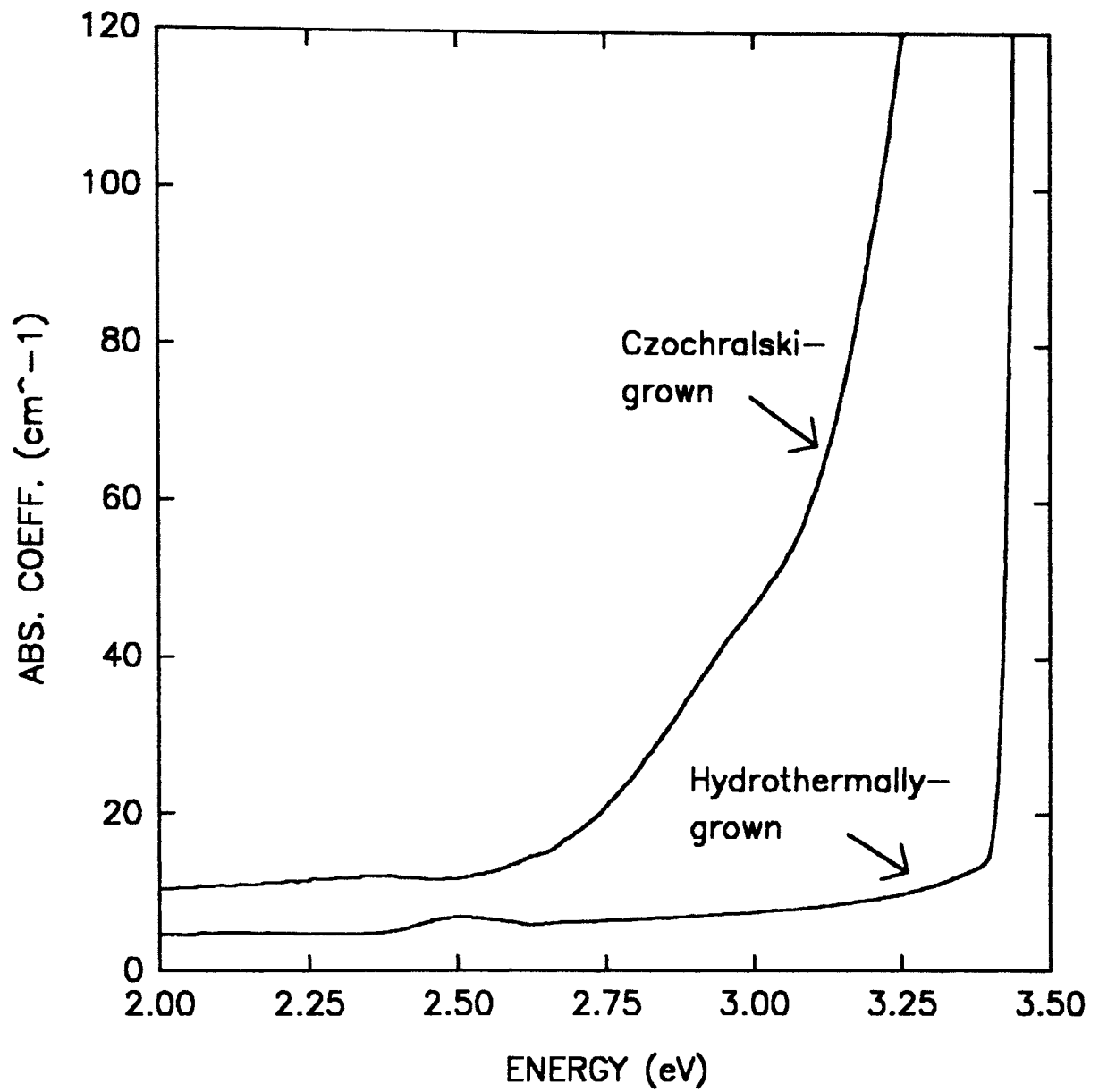


Figure 1. The absorption spectrum of Czochralski-grown BSO shows an absorption shoulder in the blue region of the visible spectrum, giving samples a pale yellow coloration. The shoulder is absent in hydrothermally-grown BSO samples.

samples causes their characteristic yellow coloration. This absorption shoulder is missing in the hydrothermally-grown samples giving them a nearly colorless appearance.

The hydrothermal growth of BSO crystals was done exclusively at Rome Laboratories [13]. Growth took place within a sealed noble metal liner inside a research-size autoclave. Oriented [100] Czochralski-grown BSO crystals were used as seeds and centimeter size pieces of Czochralski-grown BSO were used as nutrient. A baffle was used to separate the crystal growth and nutrient regions. The liner was filled with 4N NaOH and the external void of the autoclave was filled with a pressure-balancing sodium-silicate solution. The entire apparatus was then sealed and the upper end of the autoclave was maintained at 385° C and the lower at 390° C. Pressures were in the range of 6000 to 12000 psi. Growth rates were 0.1 to 0.3 mm per day for the entire run of 30 to 40 days. Hydrothermally-grown samples lacked the yellow coloration found in the Czochralski-grown samples (see Fig. 1).

To test the nature of the yellow coloration found in the Czochralski-grown samples, a Czochralski crystal was pulled from a melt made of crushed samples of colorless, hydrothermally-grown BSO crystals. The final crystal showed the yellow coloration typical of Czochralski-grown crystals starting from raw material.

Experimental Setup

Samples studied in these experiments were mounted on the cold finger of a CTI closed cycle cryogenic refrigerator. Temperature was controlled through the use of a diode thermometer, heater, and programmable temperature controller. The excitation and emission light paths were at right angles to each other to reduce excitation energy from entering the detection equipment, as shown in Fig. 2. Samples were mounted at a 45 degree angle to permit backside illumination. The windows of the cold head were UV-grade silica to minimize the absorption of the UV excitation source.

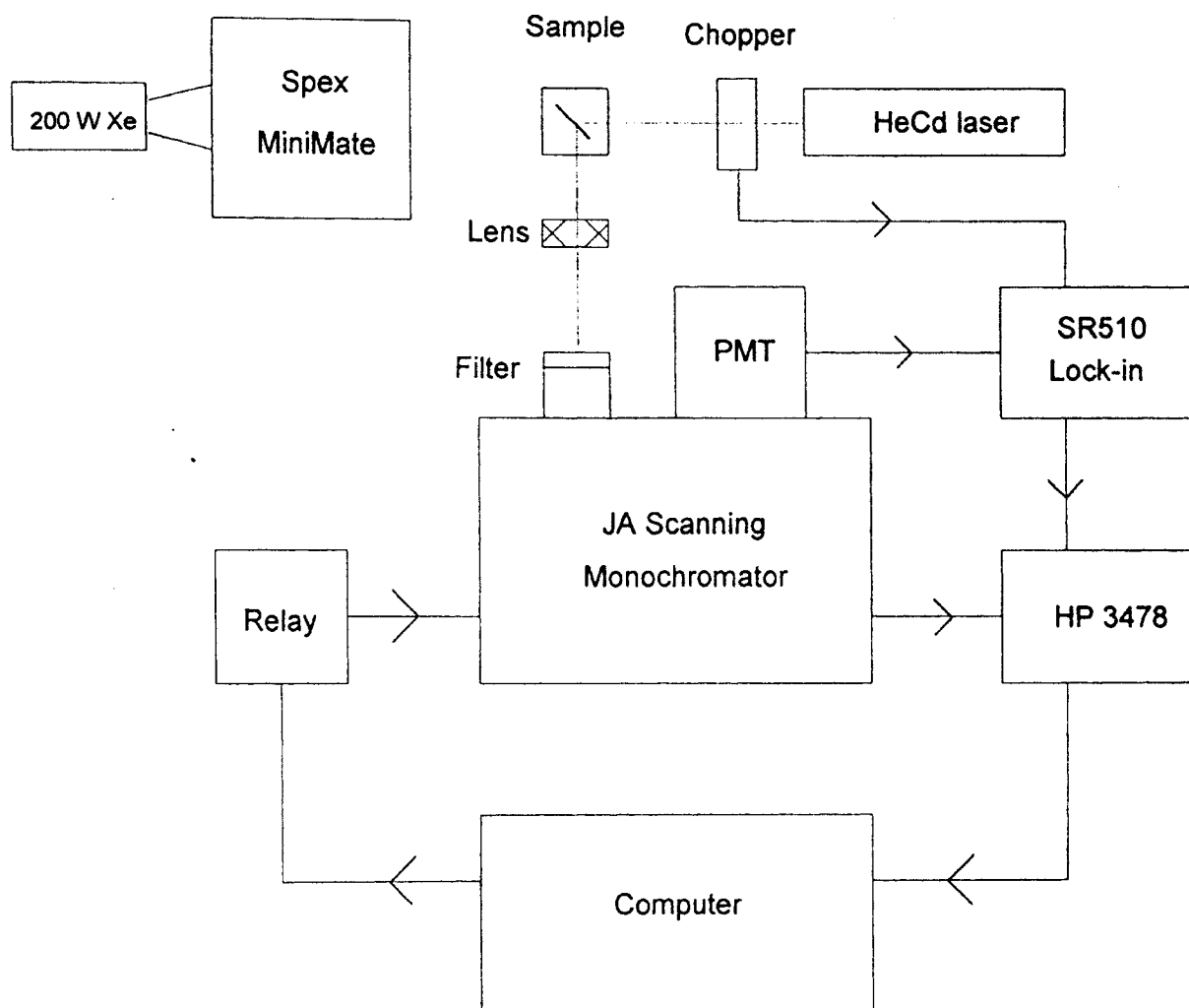


Figure 2. The experimental setup of the characterization study allowed the sample to be adjusted 90 degrees, permitting backside-illumination from either excitation source.

Two chopped light sources were used for exciting the sample. The laser source was a Liconix Helium-Cadmium laser operated at 325 nm. The laser power was adjusted through various combinations of neutral density filters. The other excitation source was an Oriel 200 watt mercury-free xenon arc lamp, sent through a Spex MiniMate monochromator. A stepper motor driving the selection knob of the monochromator was used to scan the excitation wavelength.

The emission from the sample was focused onto the slits of the detection monochromator to maximize signal. Detection was accomplished by a monochromator coupled to a photomultiplier tube. The monochromator was a $\frac{3}{4}$ m Jarrel-Ash high-resolution scanning model, blazed at 5000 Å, with curved, adjustable slits and a slot for inserting a two inch square filter. An internal circuit, incorporating several integrated circuits and a rotary encoder connected to the scanning drive shaft, provided a TTL pulse out at user selectable intervals of 0.2, 0.5, 1, or 5 Å. The circuit schematic is included in Appendix A. The PMT was a water and thermo-electrically cooled RCA 31034 operated at 1400 V. This particular PMT has a relatively flat, broad spectral response from 300 to 850 nm.

A computer was used to acquire data and control equipment during the experiments. During a typical data acquisition run, the sample was mounted and illuminated with the appropriate excitation source. The scanning monochromator was set to the proper starting wavelength, the shutter to the PMT opened, and the computer program started. The computer powered the monochromator motor by switching a HP 59306 relay actuator, and monitored the internal encoder circuit for a pulse. The pulse triggered a HP 3478 multimeter to read the emission signal value present on a Stanford Research Systems SR 510 lock-in amplifier. This value, along with the current temperature and wavelength values, were plotted on the computer screen and stored on a floppy disk for later analysis with various spreadsheet programs. The data acquisition program is included in Appendix B.

System Calibration

The entire detection system was calibrated using a 1000 W quartz-iodine bulb traceable to the National Bureau of Standards. A 3161 K blackbody curve was fit to the spectral information supplied with the bulb. The bulb was held at precisely 7.9 amps and a data scan of its spectral output was made. A transfer function was constructed by dividing the intensity measured with the PMT by the value generated by the blackbody curve at the appropriate wavelength. The resulting data, shown in Fig. 3, was suitably scaled and used to correct the scan data prior to storing to floppy disk.

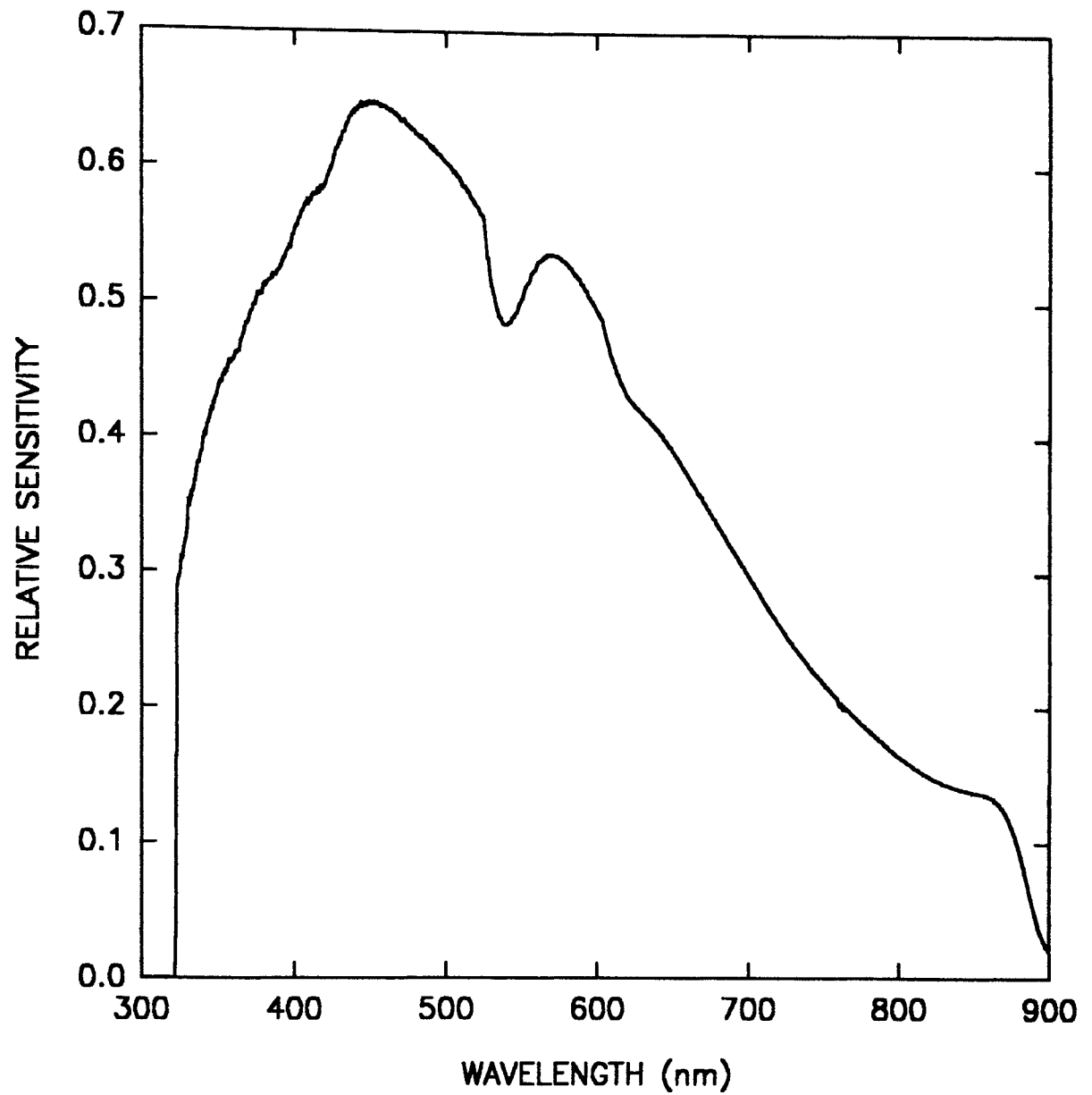


Figure 3. Calibration of the complete experimental setup with a standard lamp generated a transfer function for adjustment of spectral data. The transfer function closely resembled the efficiency curve of a reflection grating.

CHAPTER 3

RESULTS AND DISCUSSION

Emission Spectra

Figures 4 and 5 show the low temperature emission spectra of hydrothermally-grown BSO50 and BSO40T2, respectively. Samples were held at the indicated temperatures and excited with 1.0 mW, 325 nm (3.8 eV) light from a Liconix HeCd laser. An emission centered at 2.8 eV and of constant full-width-at-half-maximum of 0.4 eV is present in both samples at temperatures of 10 K to 60 K. No other emission is present in the scan range of 1.5 eV to 3.5 eV.

Setting the detection monochromator at 2.8 eV and varying the energy of the xenon source from 3.0 eV to 5.0 eV allowed the determination of the excitation spectrum of hydrothermally-grown BSO. The blue emission rises rapidly near an excitation energy of 3.4 eV and gradually weakens at higher excitation energies. Overlaying the excitation spectrum with the absorption spectrum, as shown in Fig. 6, shows that the blue emission is caused by exciting across the bandgap of BSO.

Figures 7-9 show the emission spectra of Czochalski-grown samples 060391, BSO102, and BSO92, respectively, at several temperatures and identical illumination as with the hydrothermally-grown samples. The Czochralski-grown samples show the same 2.8 eV emission found in the hydrothermally-grown samples, but with a factor of 100 decrease in intensity. An additional broad emission centered at 1.9 eV (red) is present, with constant full-width-at-half-maximum of 0.6 eV. No other emissions are observed in the 1.5 to 3.5 eV scan range. The low temperature spectra are similar to that reported by Grabmaier and Oberschmidt [2] for undoped Czochalski-grown BSO. The red emission

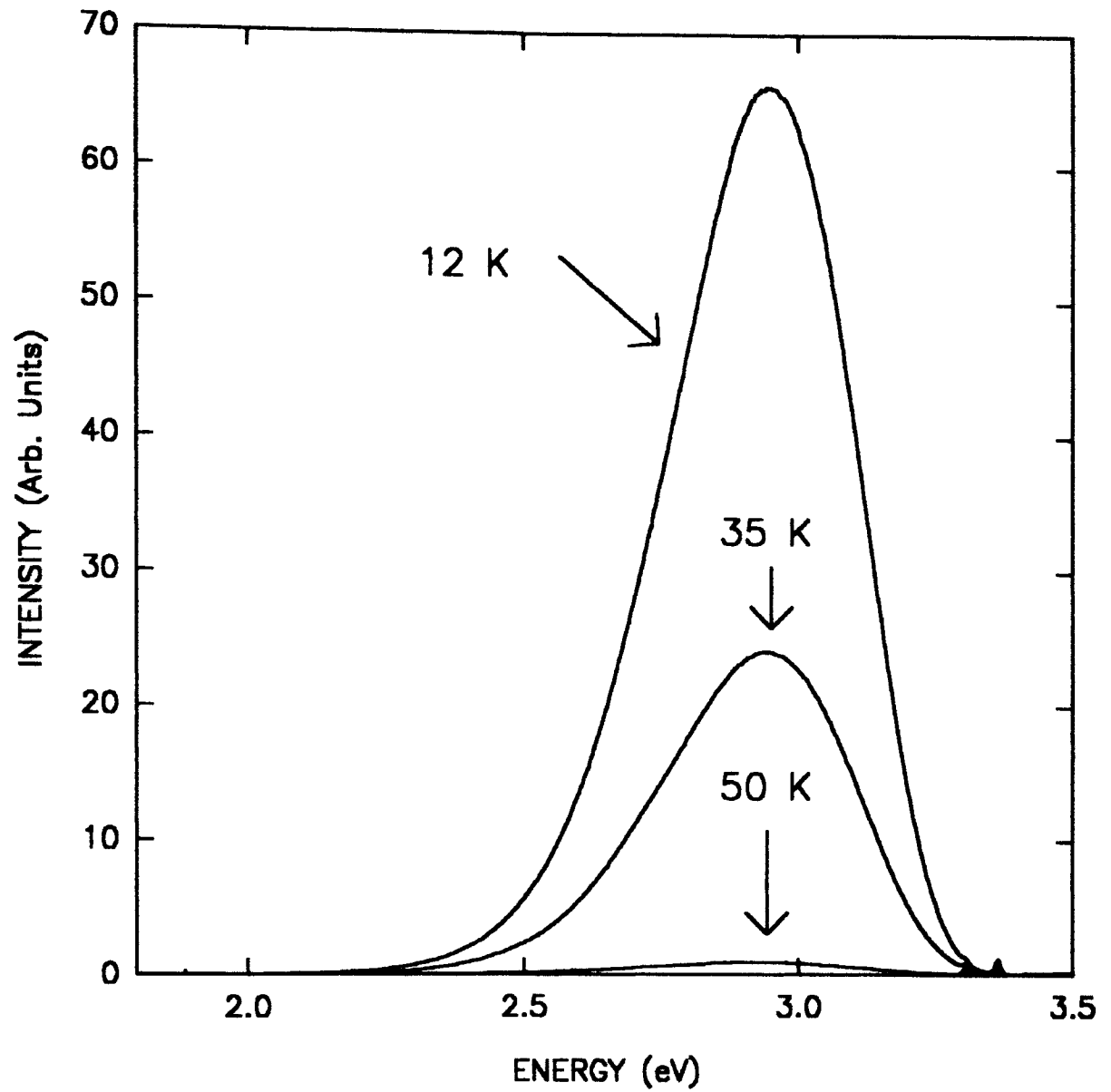


Figure 4. Emission spectra of hydrothermally-grown BSO50 at 12 K, 35 K, and 50 K. A single 2.8 eV (blue) emission is observed.

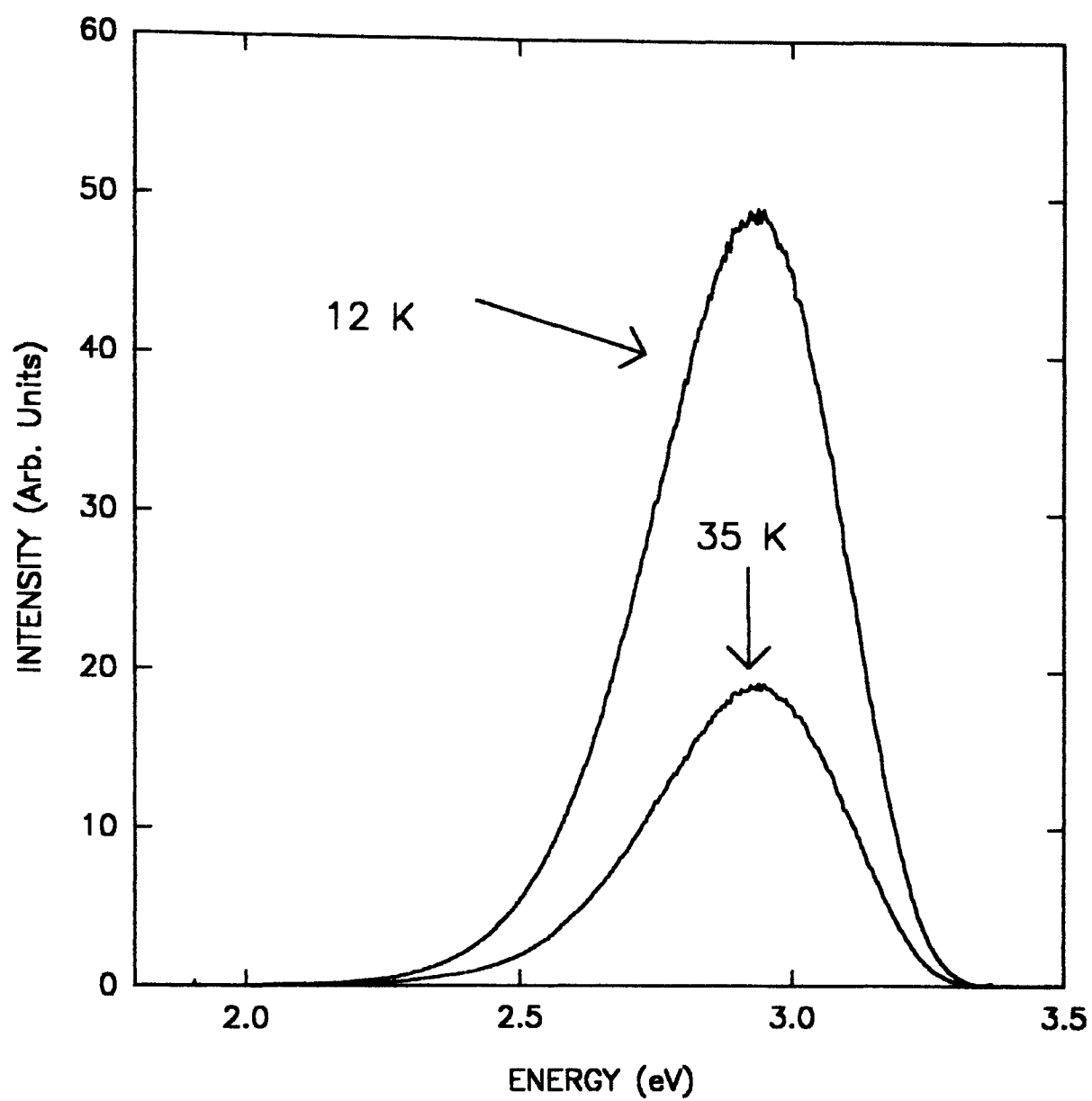


Figure 5. Emission spectra of hydrothermally-grown BSO40T2 at 12 K and 35 K. A single 2.8 eV (blue) emission is observed.

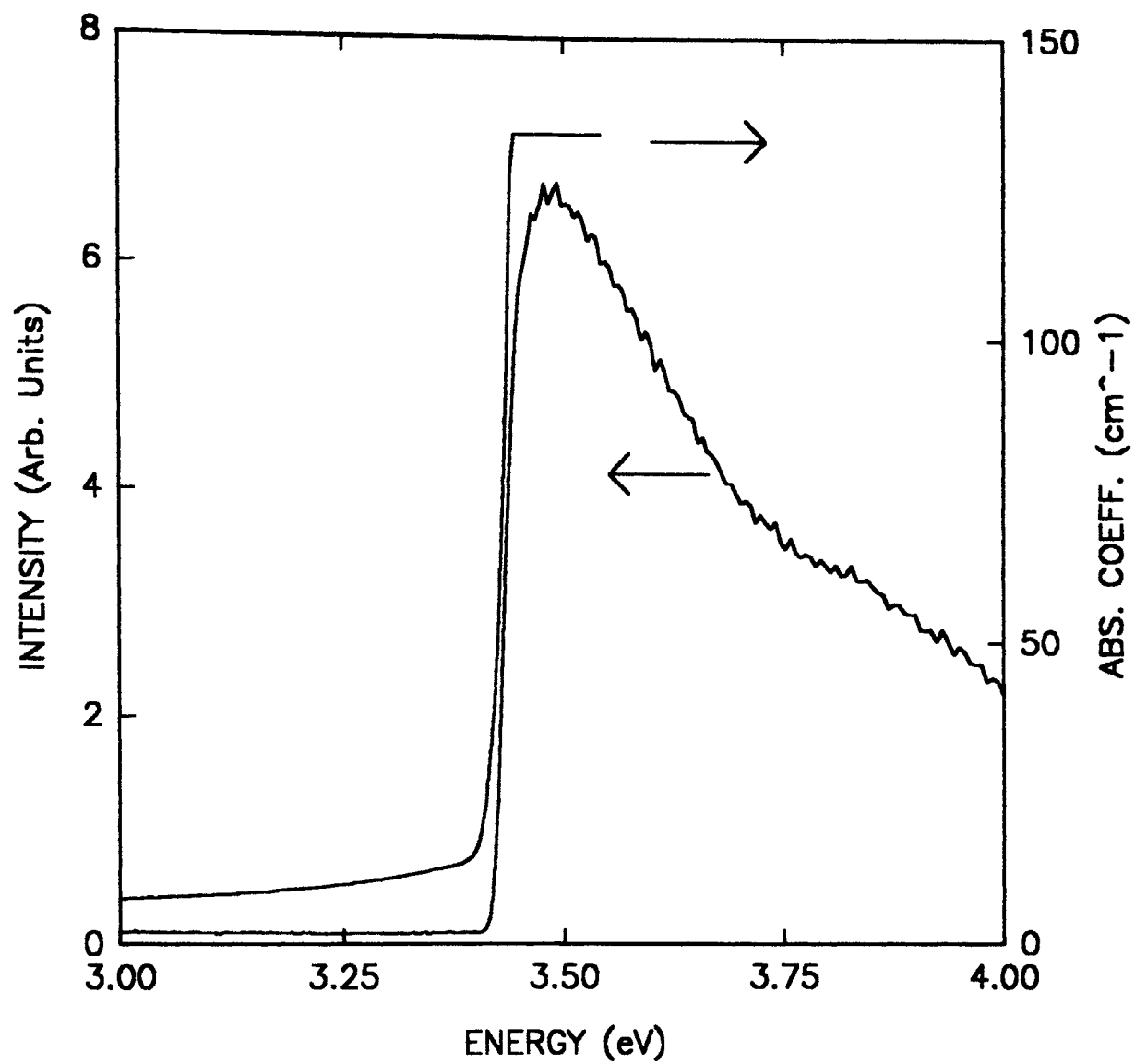


Figure 6. Comparison of hydrothermally-grown BSO absorption and excitation spectra shows the 2.8 eV emission is due to excitation across the bandgap.

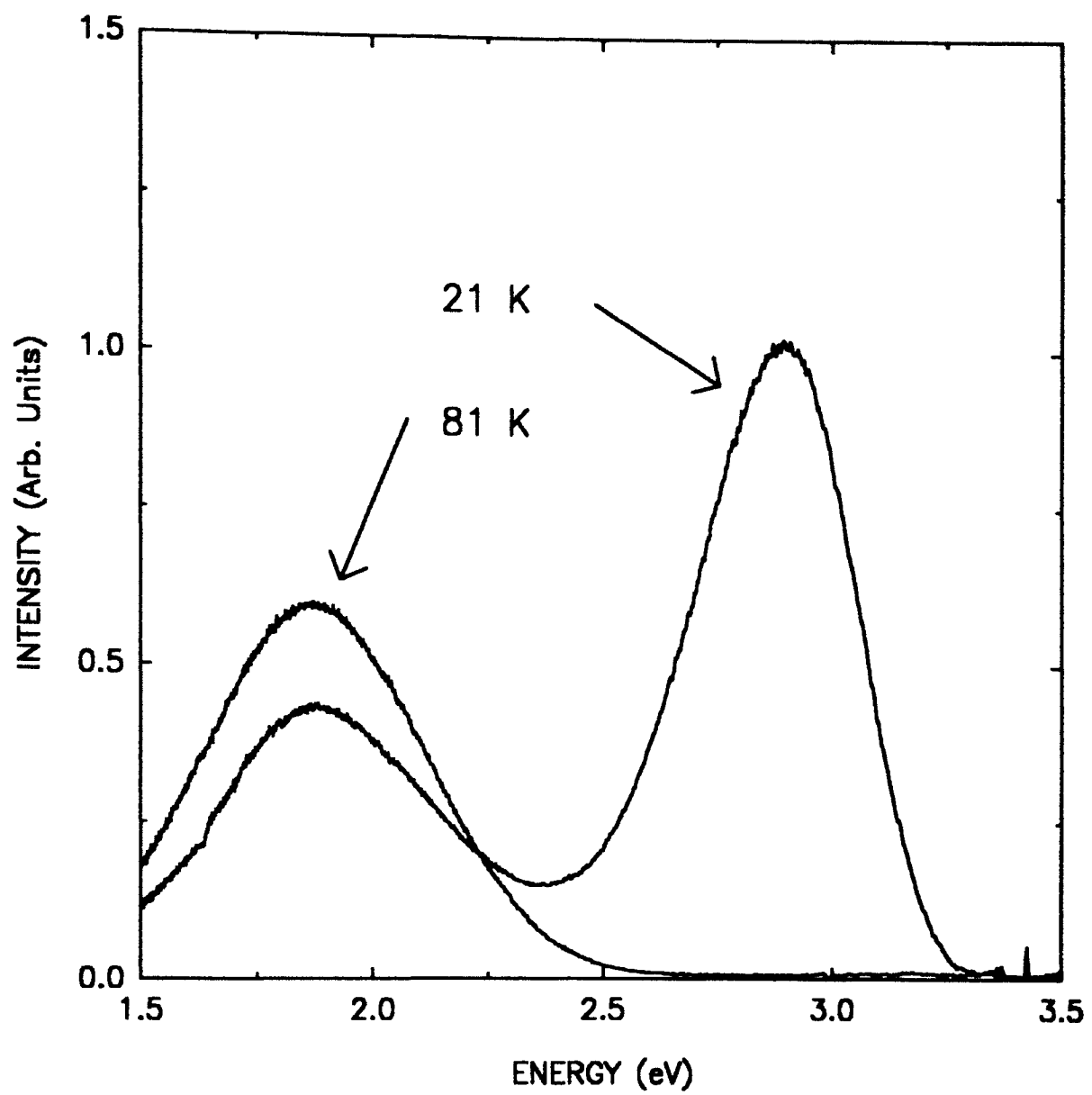


Figure 7. Emission spectra of Czochralski-grown 060391 at 21 K and 81 K. Both 2.8 eV and 1.9 eV emissions are observed.

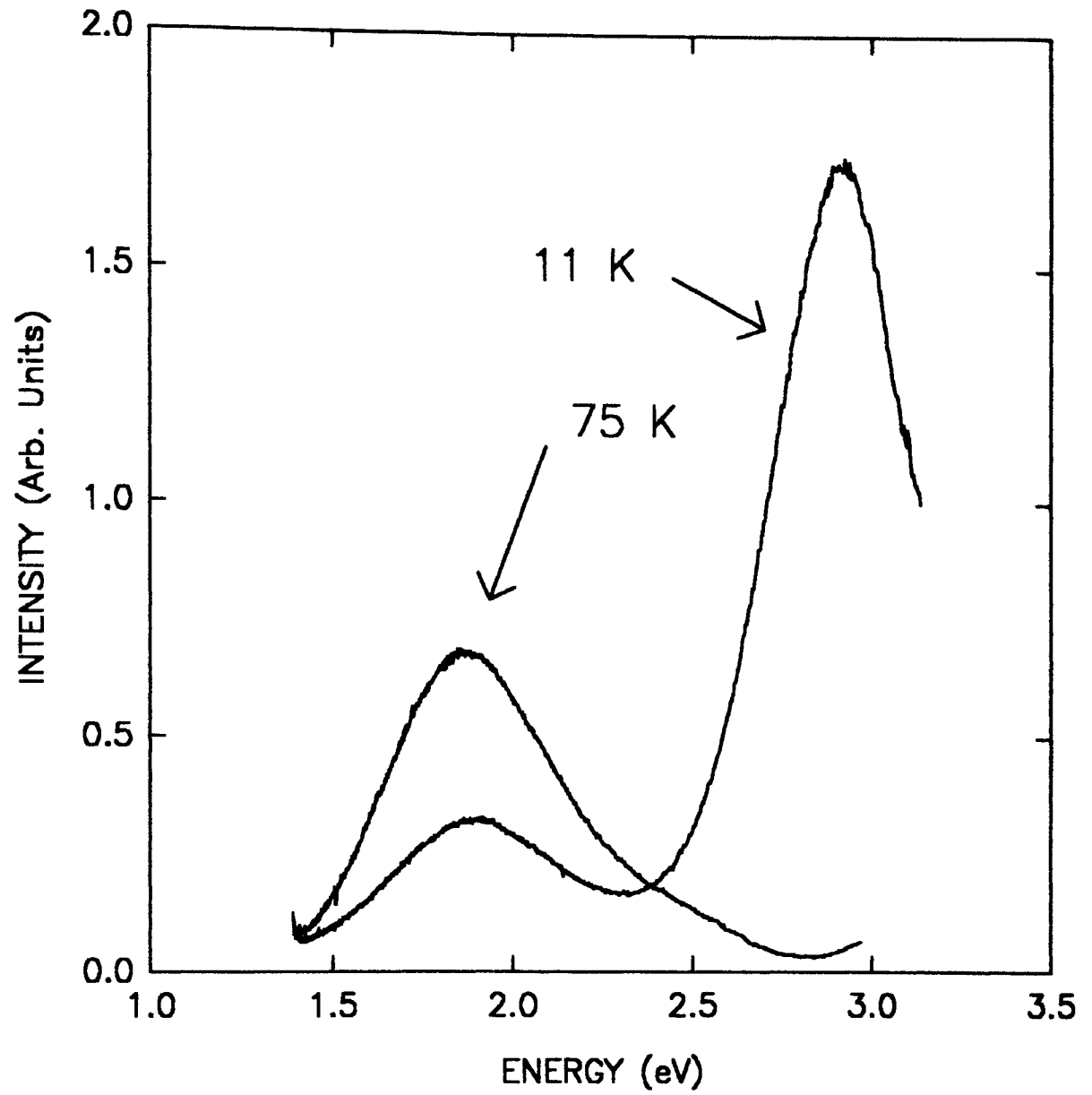


Figure 8. Emission spectra of Czochralski-grown BSO102 at 11 K and 75 K. Both 2.8 eV and 1.9 eV emissions are observed.

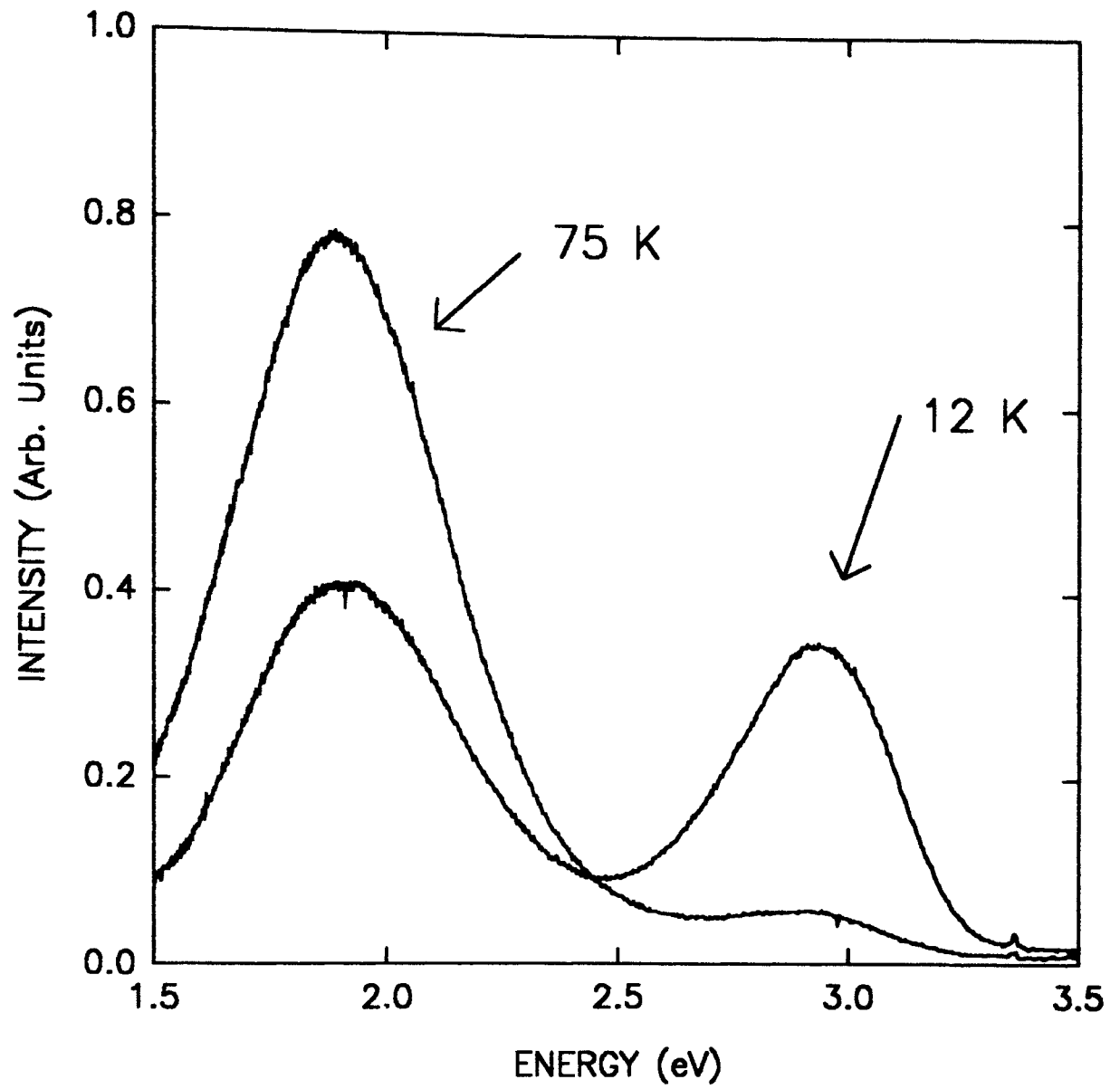


Figure 9. Emission spectra of Czochralski-grown BSO92 at 12 K and 75 K. Both 2.8 eV and 1.9 eV emissions are observed.

is in good agreement with earlier work at liquid nitrogen temperatures (80 K) by Lauer [14].

Temperature Dependence

Figure 10 shows the blue emission temperature dependence of hydrothermally-grown BSO50, showing rapid decay from 10 K to 60 K. BSO40T2 shows an identical decay. Weber and Monchamp [15] have attributed a similar, broad emission centered at 2.6 eV in the closely related compound bismuth germanate ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) to Bi^{3+} transitions. Bismuth atoms in both bismuth germanate and BSO occupy an octahedral site, with one of the corners in heptacoordinated BSO containing two oxygen atoms [3]. It seems likely that the 2.8 eV emission observed in BSO has the same origin as the 2.6 eV emission in bismuth germanate. More recently, the 2.6 eV emission in bismuth germanate has been attributed to a self-trapped exciton [16,17].

Figure 11 shows the temperature dependence of both the blue and red emissions present in Czochralski-grown 060391. The temperature dependence of BSO102 and BSO92 are very similar. The blue emission decays exactly as in hydrothermally-grown BSO, dropping rapidly to zero near 60 K. The red emission grows rapidly as the blue decays, reaching a relatively flat, broad peak extending from 50 K to 100 K, and gradually decaying to 225 K. The coincidence of the red emission growing as the blue decays suggests that the red emission serves as part of a thermally-activated radiative decay path.

In Fig. 12, an energy level diagram demonstrates several possible decay paths. In part (a) of Fig. 12, the electron is moved from the valence band to the conduction band by illuminating the sample with light of photon energy greater than the 3.4 eV bandgap. Once in the conduction band, the electron may fall into and escape from traps formed by defects and impurities. In part (b), the electron falls into a trap possibly caused by the binding energy of the exciton prior to the 2.8 eV emission.

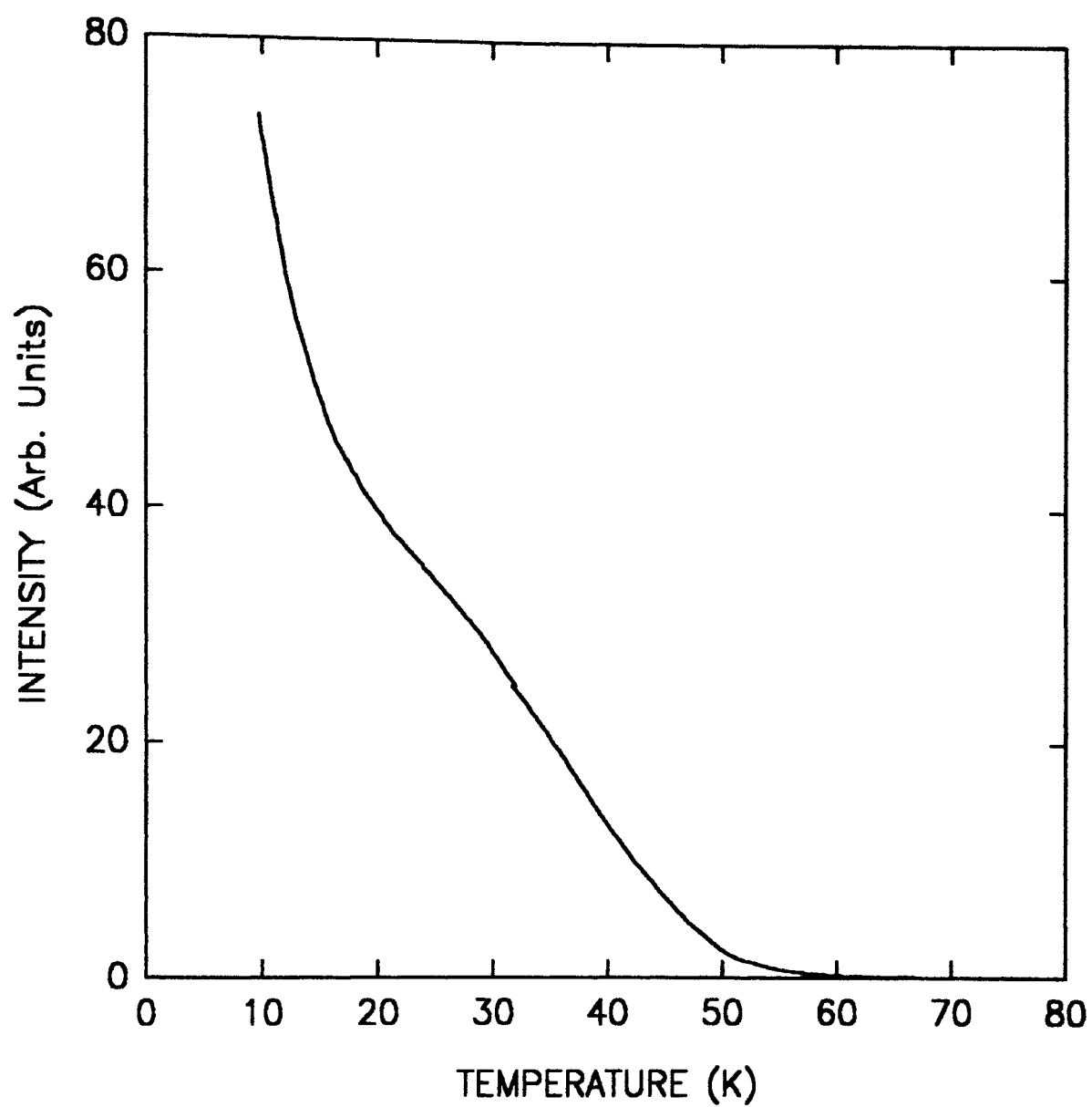


Figure 10. Temperature dependence of 2.8 eV emission of hydrothermally-grown BSO50.

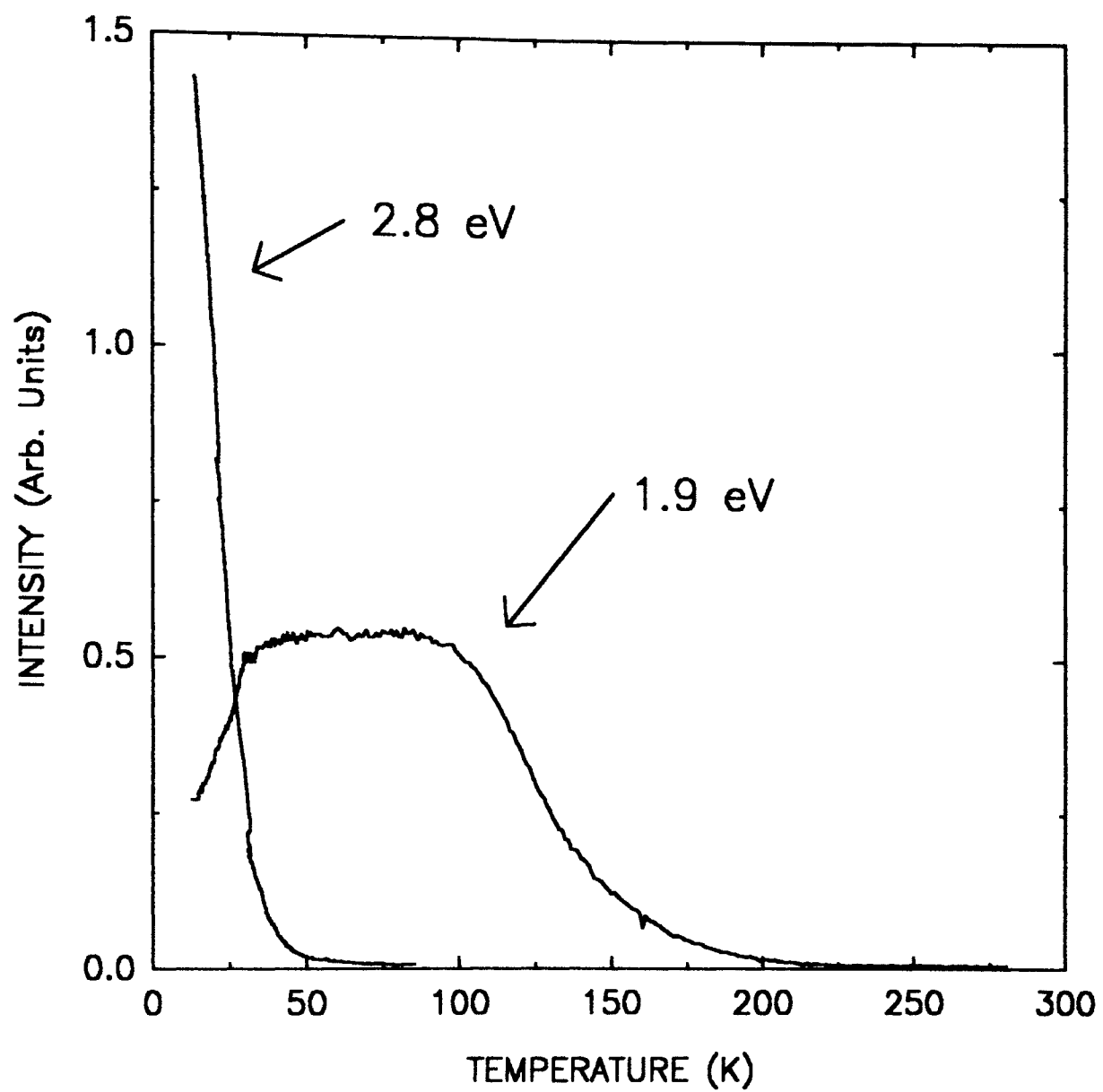


Figure 11. Temperature dependence of both the 2.8 eV and 1.9 eV emissions of Czochralski-grown 060391 BSO.

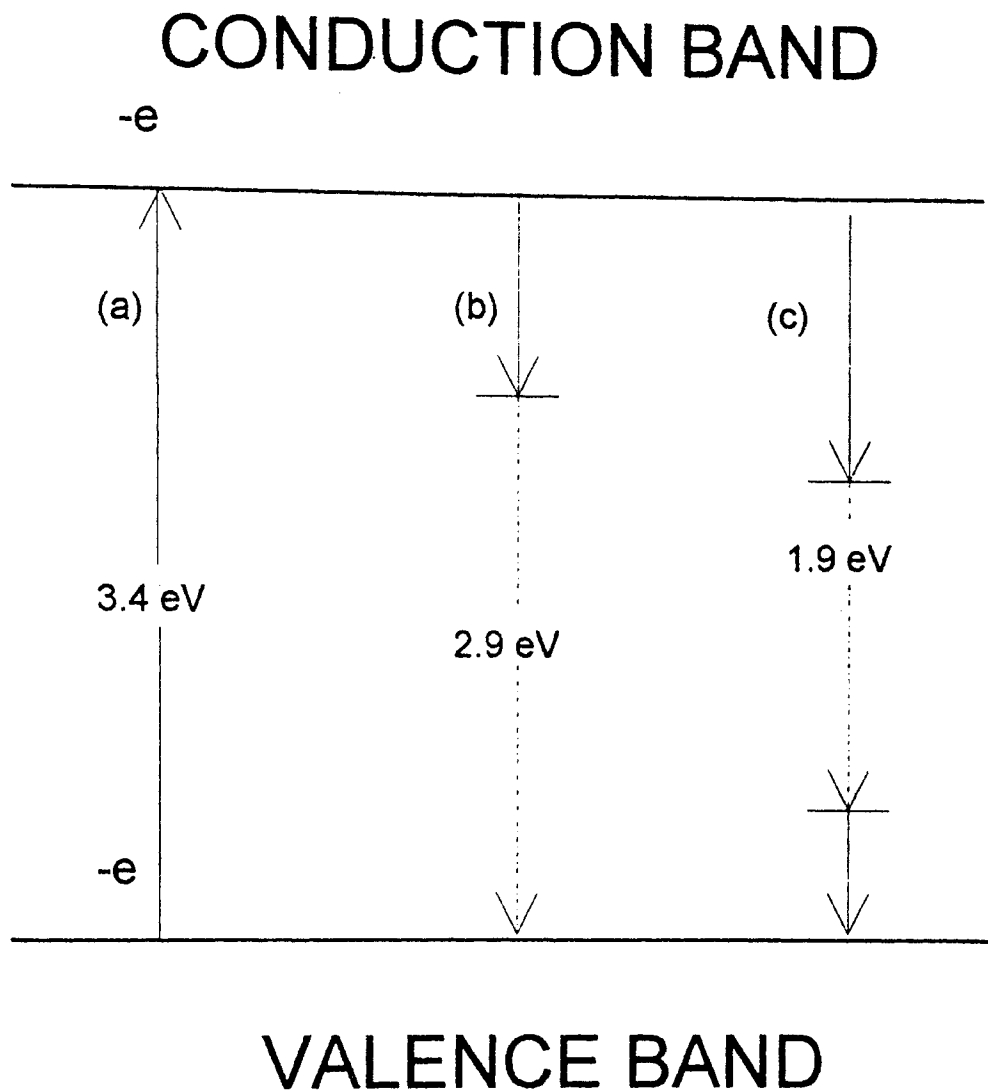


Figure 12. Energy level diagram showing the suggested transitions responsible for emissions present in both hydrothermally- and Czochralski- grown BSO.

The likelihood of an electron escaping from a trap to the conduction band is given by a Boltzman factor [18]. As the temperature increases, the electron more easily escapes to other traps that provide alternative radiative and non-radiative paths to the valance band. In the case of the 2.8 eV emission, these extra paths reduce the intensity of the emission. The 2.8 eV emission has an effective thermal deactivation energy, given by

$$I_{\text{emission}} \approx \exp(E_{\text{thermal}} / kT), \quad (1)$$

where I_{emission} is the 2.8 eV emission intensity and E_{thermal} is the thermal deactivation energy of the 2.8 eV emission. The deactivation energy of the blue emission in both hydrothermally- and Czochralski-grown BSO is found to be 63 meV (Fig. 13).

In Czochralski-grown BSO, the reduced intensity of the blue emission and the presence of the red emission may be due to defects introduced during the growth process that provide additional traps at low temperatures. The red emission may be bismuth transitions arising from the anti-site bismuth defect [19], where a bismuth atom becomes tetrahedrally coordinated by replacing a silicon atom in the lattice. In this arrangement, bismuth becomes $\text{Bi}^{3+} + \text{h}^+$, with the hole localized on one of the adjacent oxygen atoms [10]. The emission path may be as in part (c) of Fig. 12, with the trap being from the hole. The decay of the red emission at 100 K to 150 K coincides with the decay of the photochromic absorption bands during annealing of Czochalski-grown BSO as reported by Hart *et al.* [8], which the authors attribute to recombination of various defect-introduced traps.

Power Dependence

The dependence of the blue emission on the power of the 325 nm laser excitation source in hydrothermally-grown BSO50 is shown in Fig. 14. The data was obtained at 15K and over a range of power from 0.001 mW to 1.0 mW. The data for hydrothermally-grown BSO40T2 is similar. Figure 15 shows the power dependence of the red and blue

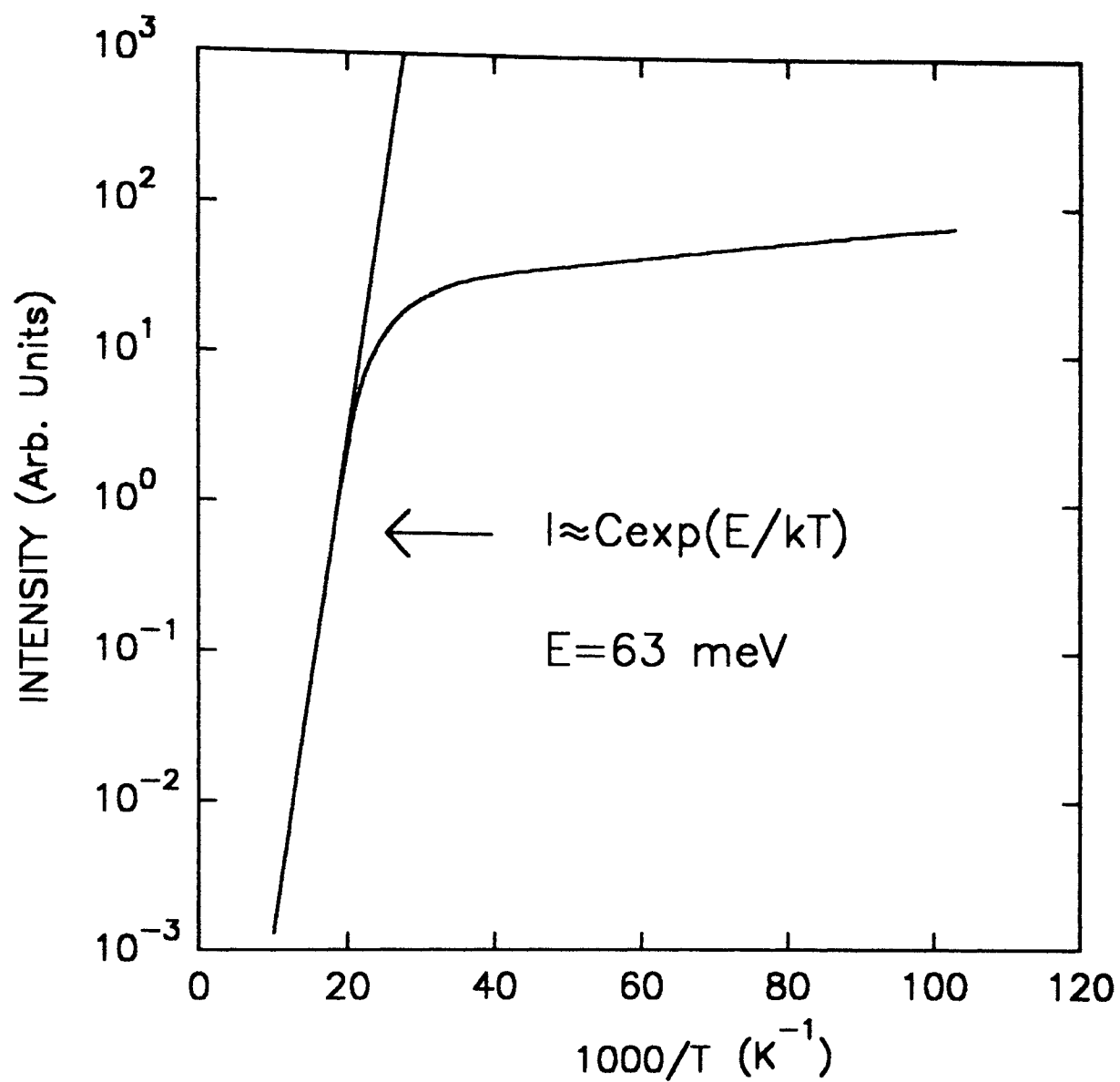


Figure 13. The thermal deactivation energy for the 2.8 eV emission in Czoehral ski- and hydrothermally-grown BSO is found to be 63 meV.

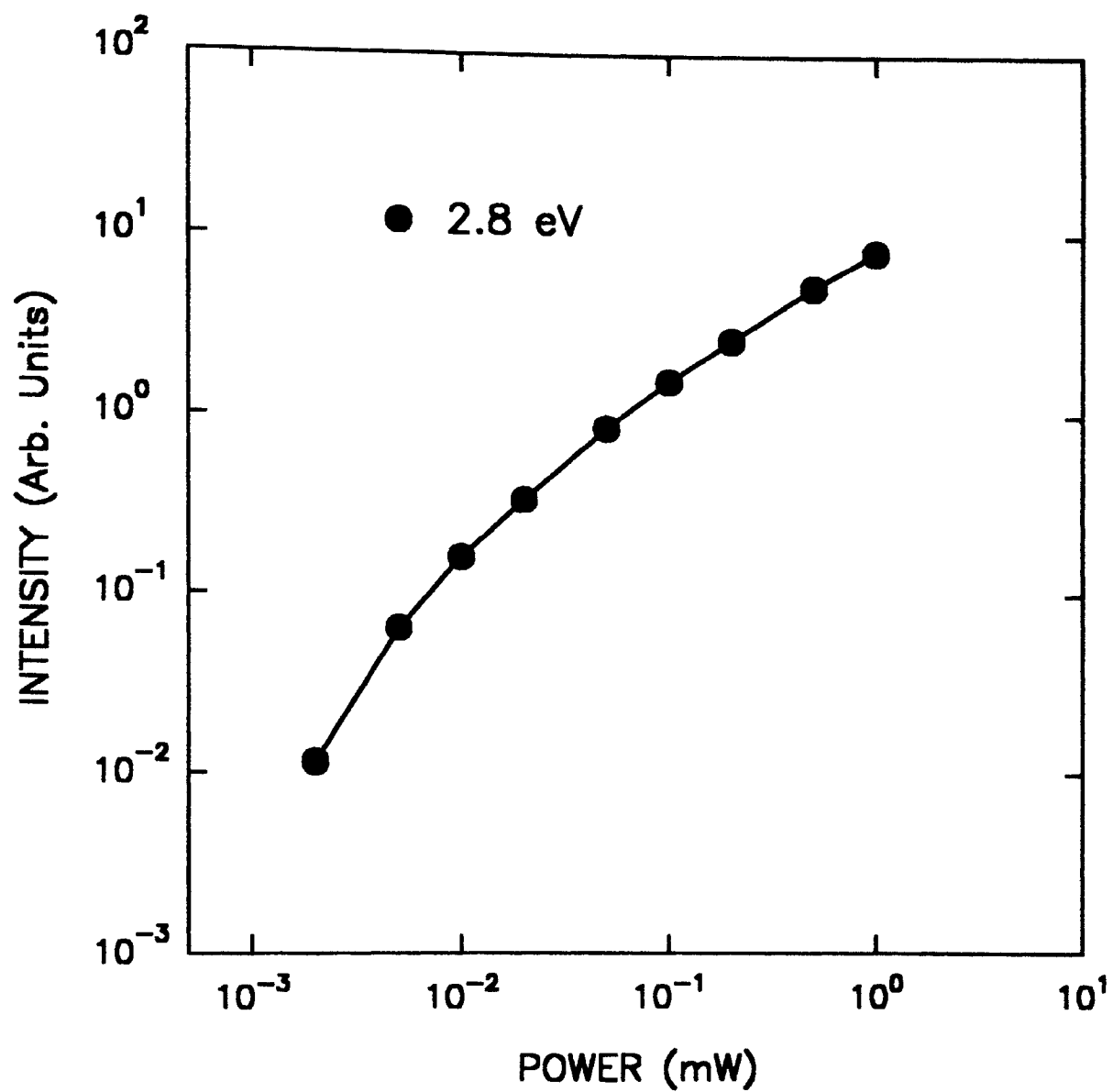


Figure 14. Power dependence of the blue emission observed in hydrothermally-grown BSO50.

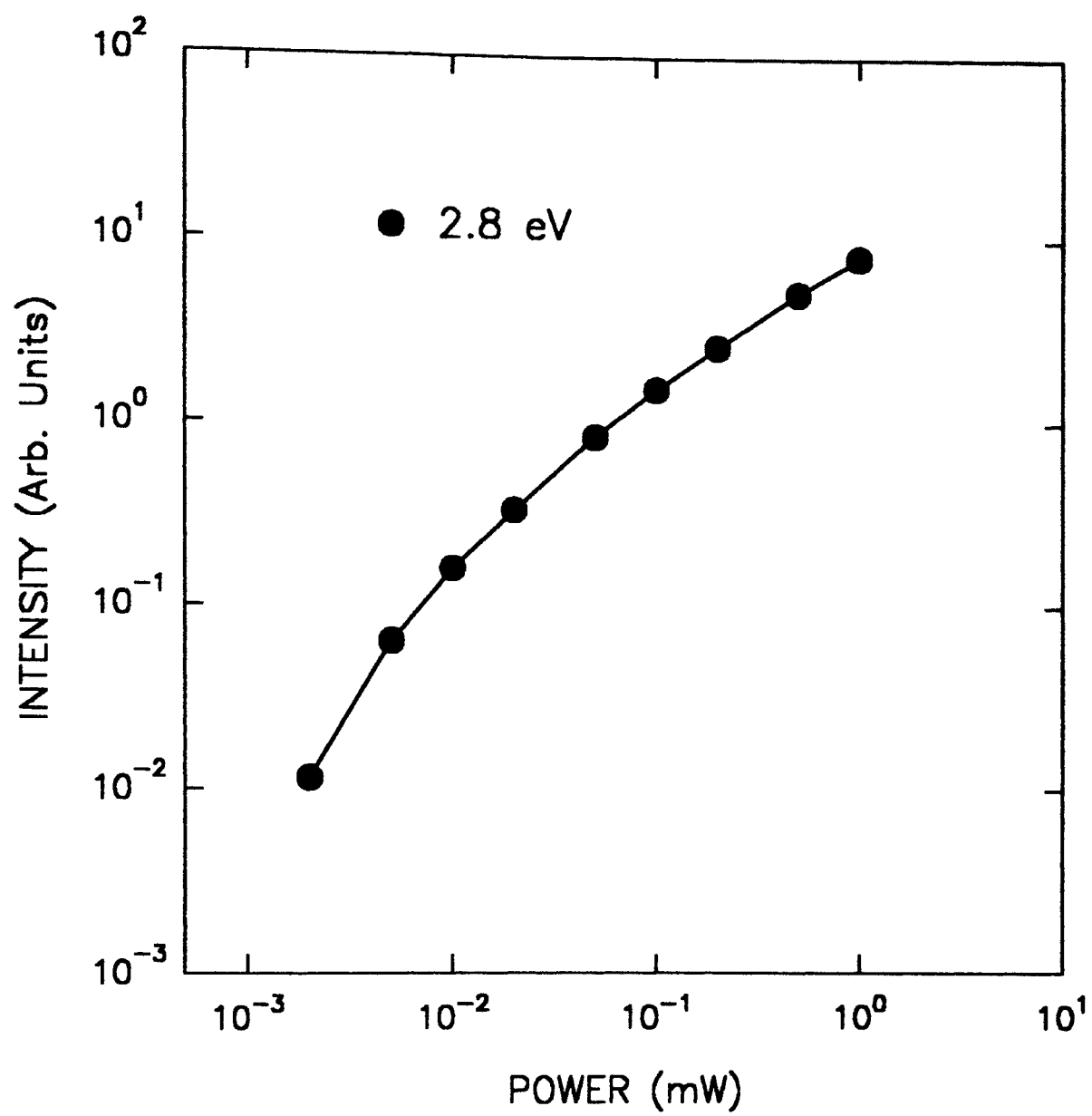


Figure 15. Power dependence of the blue and red emission observed in Czochralski-grown BSO102.

emissions observed in Czochralski-grown BSO102, with the blue emission data taken at 15 K and the red emission data taken at 80 K and a range of 0.003 mW to 1.0 mW. The data for Czochralski-grown 060391 and BSO92 were similar.

Light with photon energy greater than the band-gap can produce bound electron-hole pairs called excitons. The exciton is bound by coulomb forces and may either move freely, be self-trapped, or be trapped by a defect in the lattice. Through solutions to the set of rate equations, Schmidt, Daniel, and Lischka [20] have shown that the range of values of the exponent in the relationship

$$I = L^K, \quad (2)$$

where I is emission intensity and L is excitation power, can be attributed to different excitonic processes. Provided the excitation power does not change by more than two orders of magnitude, values of $K = 1$ are attributed to free excitons and $K > 1$ to donor- and acceptor-bound excitons.

The blue emission observed in both hydrothermally- and Czochralski-grown BSO increased faster than the first power of the laser intensity and slowed at higher outputs so that the emission increased at a rate slightly less than the first power. Thus, either form of exciton may apply. A recent explanation to the 2.6 eV emission in bismuth germanate has been given by Baltramiejunas *et al.* [16] and Moncourage, Jacquier, and Boulon [17] as arising from self-trapped excitons. The red emission observed in Czochralski-grown BSO increased at a nearly constant power of 1.5 throughout the range of laser power. The red emission may also be a bound exciton trapped by the additional defects present due to the growth method.

Lifetime of Emission

A pulsed nitrogen laser, with pulse width of 5 nsec and wavelength of 337 nm, was used to measure the lifetime of the blue and red emissions in BSO. The PMT signal was

sent through an amplifier and monitored on a 100 MHz oscilloscope. Both the blue and red emissions had a width of 10 nsec, the limit of the equipment. Both emissions, therefore, appear to have lifetimes less than 10 nsec.

CHAPTER 4

CONCLUSION

At low temperatures, undoped samples of hydrothermally- and Czochralski-grown BSO exhibit photoluminescence when excited with light of photon energy greater than the 3.4 eV bandgap energy. A 2.8 eV (blue) emission is present in both hydrothermally- and Czochralski-grown samples and an additional 1.9 eV (red) emission is present only in Czochralski-grown samples. The blue emission is a factor of 100 less intense in Czochralski-grown samples and decays to zero intensity at 60 K in both samples. The red emission grows to a broad maximum at 50 K to 100 K and gradually decays to zero intensity at 150 K.

Although the exact origin of the blue and red emissions is not certain, several mechanisms are possible. The blue emission may be due to Bi^{3+} transitions or a self-trapped exciton. The red emission may be due to a bound exciton, bismuth transitions, or the recombination of the traps that participate in the photorefractive effect in BSO. The reduced intensity of the blue emission in the Czochralski-grown samples is likely due to non-radiative decay paths caused by additional defects introduced during the growth of the crystal.

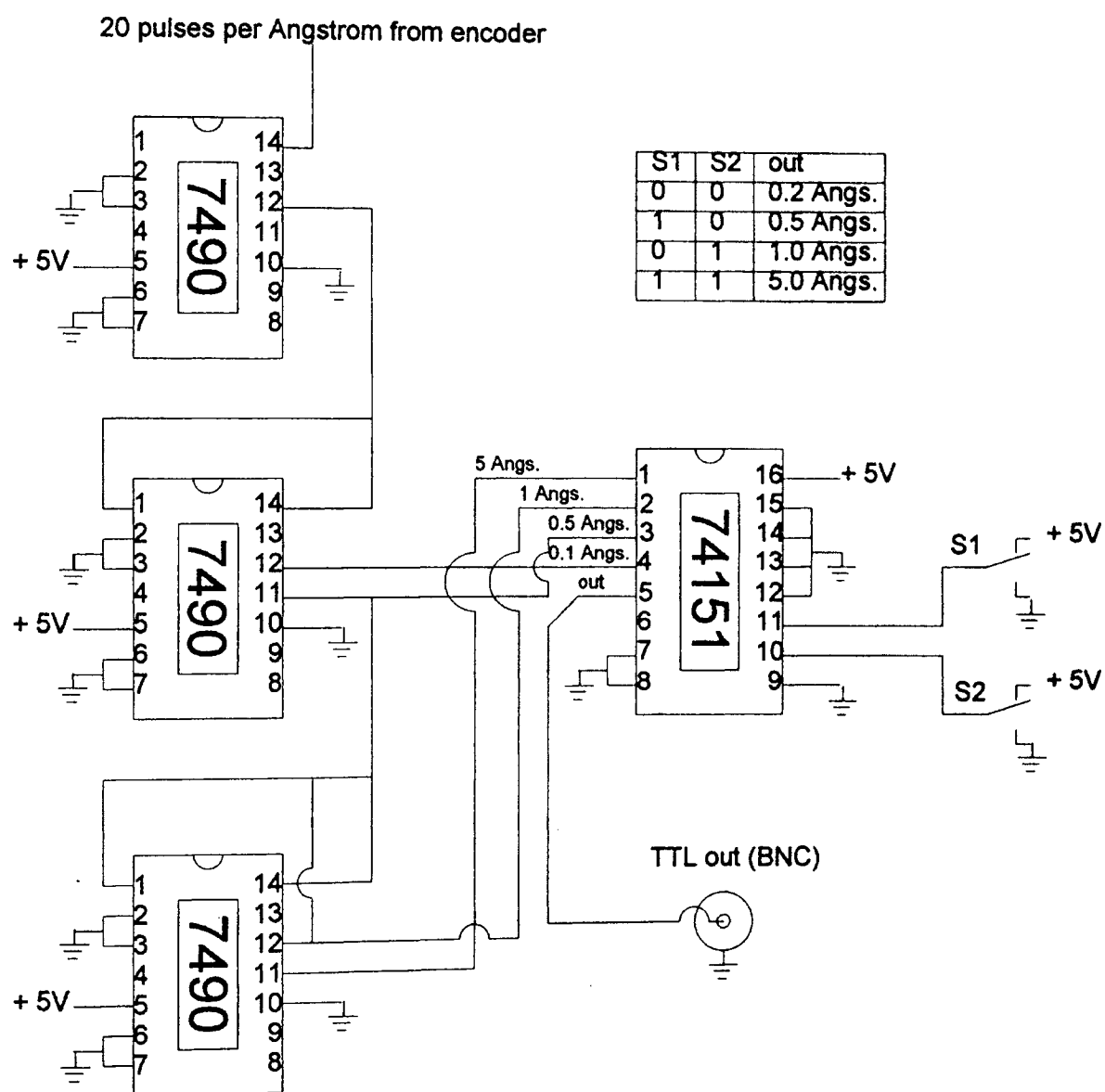
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APPENDIX A

SCHEMATIC DIAGRAM OF COUNTER CIRCUIT.




```

1100 INPUT Incr
1110 ! NPTS IS THE ACTUAL NUMBER OF DATA POINTS
1120 Npts=(We-Ws)/Incr+1
1130 IF Npts<=Dpts THEN 1220
1140 CLEAR SCREEN
1150 PRINT "Total number of allowed data points is",Dpts
1160 PRINT
1170 PRINT "YOU HAVE CHOSEN ("We,"-",Ws,")",Incr,"=",Npts," DATA POINTS"
1180 PRINT
1190 PRINT
1200 PRINT "Please re-enter scan parameters"
1210 GOTO 1000
1220 CLEAR SCREEN
1230 ! READING XFER DATA FILE-----
1240 PRINT "READING XFER DATA FILE"
1250 Xfer$="WG360.PRN" ! NAMES TRANSFER FILE
1260 Xpts=1121 ! NUMBER OF DATA POINTS IS XFER FILE
1270 Xbegin=3400 ! STARTING WAVELENGTH OF XFER FILE
1280 IF Ws>=6500 THEN
1290     Xfer$="RG640.PRN" ! NAMES TRANSFER FILE
1300     Xpts=601 ! NUMBER OF DATA PTS IN XFER FILE
1310     Xbegin=6000 ! STARTING WAVELENGTH OF XFER FILE
1320     END IF
1330     ALLOCATE Wx(Xpts),Xfer(Xpts)
1340     ASSIGN @File TO "C:\XFER\"&Xfer$;FORMAT ON
1350     FOR I=1 TO Xpts
1360         ENTER @File;Wx(I),Xfer(I)
1370     NEXT I
1380     ASSIGN @File TO *
1390     Nstart=(Ws-Xbegin)/5+1 ! DETERMINES STARTING POINT FOR XFER
1400     CLEAR SCREEN
1410     GOTO 10000 ! MAKES PLOT
2000 ! TAKES DATA*****
2030     LINPUT "Enter FILE NAME (F$) for the data.",F$
2040     LINPUT "INPUT PEN NUMBER FOR PLOT",Pn$
2050     PEN VAL(Pn$)
2060     GOSUB 20000! PRINTS SCAN PARAMETERS
2070     W=Ws
2080     MOVE Ws/10,0
2090     MAT V=(0)
2100 ! CLEARS THE HP3478
2110     CLEAR 725
2120     DISP "Set dial to",Ws,". Press CONTINUE."
2130     PAUSE
2140 ! SETS UP THE HP3478
2150     DISP "SETTING UP THE HP3478"
2160     OUTPUT 725;"F1R1T2"! DC VOLTS, 30V RANGE, EXTERNAL TRIGGER
2170     OUTPUT 725;"D3DATA"! TURNS OFF DISPLAY UPDATE-DISPLAYS "DATA"
2180     WAIT 1
2190 !
2200 ! STARTS SCAN
2210     OUTPUT 702;"B1"
2220     FOR I=1 TO Npts
2230         ENTER 725;V1! WAITS FOR EXTERNAL TRIGGER AND ENTERS VOLTS

```

```

2240      V(I)=INT(ABS(V1/Xfer(Nstart+I-1)*10000))/10000
2250      DRAW W/10,V(I)! PLOTS DATA POINT
2260      DISP W,V(I)! DISPLAYS DATA POINT
2270      W=W+Incr
2280      NEXT I
2290 ! STOPS THE SCAN
2300      OUTPUT 702;"A1"
2310      LOCAL 7
2320      BEEP 900,.1
2330      CLEAR 725
2340      LOCAL 722
9000 ! STORES DATA SEQUENTIALLY ON FLOPPY*****
9010 ! Only the actual nonzero data are stored.
9020      CREATE Dnd$&F$&".TXT",N+4
9030      ASSIGN @File TO Dnd$&F$&".TXT";FORMAT ON
9040      OUTPUT @File;F$
9050      OUTPUT @File;Ws
9060      OUTPUT @File;We
9070      OUTPUT @File;Incr
9080      OUTPUT @File;VAL$(T)&"K"
9090      OUTPUT @File;VAL$(Sensitivity)&Units$
9100      FOR I=1 TO Npts
9110          OUTPUT @File;V(I)
9120      NEXT I
9130      ASSIGN @File TO *
9140      DISP "DATA STORED AS ",Dnd$&F$&".TXT"
9150      PRINTER IS 10
9170      CONFIGURE DUMP TO "HP-PCL"
9180      DUMP DEVICE IS 10
9190      DUMP GRAPHICS #10
9200      PRINT CHR$(12)
9210      PRINTER IS 1
9220      BEEP 750,.1
9230      GOTO 900
10000 ! MAKES PLOT*****
10010 ! Depending on x-axis scale-labels are done in increments of 10 or 25 nm.
10020 !
10030      PRINTER IS 1
10031      Ws=Ws/10
10032      We=We/10
10033      Incr=Incr/10
10040      Fac=10
10050      Xshift=0
10060      IF We-Ws>200 THEN Fac=25
10070      Xmin=INT(Ws/100)*100+INT(((Ws-INT(Ws/100)*100)/Fac))*Fac
10080      Xmax=INT(We/100)*100+INT(((We-INT(We/100)*100)/Fac+1))*Fac
10090      IF INT(Ws/Fac)=Ws/Fac THEN Xmin=Ws
10100      IF INT(We/Fac)=We/Fac THEN Xmax=We
10110      Range=Xmax-Xmin
10120      IF Fac=10 THEN 10180
10130      Xstep=50
10140      Xtick=10
10150      IF FRACT(Xmin/50)>0 THEN Xtick=25
10160      IF FRACT(Xmin/50)>0 THEN Xshift=25

```

```

10170 IF Fac=25 THEN 10260
10180 Xtick=10
10190 Xstep=20
10200 IF Range>50 AND Range<=100 THEN Xstep=10
10210 IF Range>50 AND Range<=100 THEN Xtick=5
10220 IF Range<=50 THEN Xstep=5
10230 IF Range<=50 THEN Xtick=5
10240 IF FRACT(Xmin/20)>0 THEN Xshift=10
10260 Ymax=10
10280 Ytick=1
10300 Ystep=2
10310 Ymin=0
10320 GINIT
10330 CLEAR SCREEN
10340 DEG
10350 LDIR 0
10360 CSIZE 5,.5
10370 PEN 1
10380 VIEWPORT 0,100*RATIO,30,100
10390 Xbdr=.15*(Xmax-Xmin)! BORDER ON X DIMENSIONS
10400 WINDOW Xmin-.8*Xbdr,Xmax+.6*Xbdr,-.2*Ymax,1.05*Ymax! SCALES THE PLOT AREA
10410 CLIP Xmin,Xmax,0,Ymax
10420 AXES Xtick,Ytick,Xmin,0,2,4
10430 AXES Xtick,Ytick,Xmax,Ymax,2,4
10440 !LABEL AXES-----
10450 CLIP OFF
10460 LORG 6
10470 Y=-.02*Ymax
10480 FOR X=Xmin+Xshift TO Xmax STEP Xstep
10490 MOVE X,Y
10500 L1=X
10510 GOSUB 10740
10520 NEXT X
10530 LDIR 0
10540 LORG 6
10550 MOVE (Xmax+Xmin)/2,-.1*Ymax
10560 LABEL "WAVELENGTH (nm)"
10570 LORG 8
10580 X=Xmin-.1*Xbdr
10590 FOR Y=0 TO Ymax STEP Ystep
10600 MOVE X,Y
10610 L1=Y
10620 GOSUB 10740
10630 NEXT Y
10640 CSIZE 6,.6
10650 LDIR 90
10660 LORG 5
10670 MOVE Xmin-.6*Xbdr,Ymax/2
10680 LABEL "VOLTS"
10690 CSIZE 5,.6
10700 LORG 2
10701 Ws=Ws*10
10702 We=We*10
10703 Incr=Incr*10

```

```

10710     DISP "Press F4 DATA to start scan"
10720     GOTO 900
10730     REM
10740 !LABELS USING ZEROS WITHOUT SLASHES_____
10750     L$=VAL$(L1)
10760     N=LEN(L$)!NUMBER OF CHARACTERS IN LABEL
10770     L1$=""! NULL CHARACTER
10780     FOR I=1 TO N
10790         Lp$(I)=L$(L,I)
10800         IF Lp$(I)="00" THEN Lp$(I)="00"
10810         L1$=L1$&Lp$(I)
10820     NEXT I
10830     LABEL L1$
10840     RETURN
20000 ! PRINTS SCAN PARAMETERS*****
20010     OUTPUT 707;"01"
20011     ENTER 707;Stemp
20030     IMAGE "SAMPLE TEMPERATURE: ",3D.DD," K"
20031     IMAGE "SAMPLE TEMPERATURE (DT-470): ",3D.DD," K"
20032     REM OUTPUT 712;"SDAT?"
20034     REM ENTER 712;Stemp
20040     PRINTER IS 10
20050     READ LABEL Vlabel$ FROM "A:"
20060     PRINT Vlabel$;"\":Dnd$;F$;" ",DATE$(TIMEDATE),TIME$(TIMEDATE)
20070     PRINT
20080     PRINT USING 20030;T
20081     PRINT USING 20031;Stemp
20090     PRINT
20100     PRINT "      VOLTAGE DATA OBTAINED USING LOC-IN AMPLIFIER"
20110     PRINT
20120     IMAGE 10X,"STARTING WAVELENGTH:",4D," nm"
20130     IMAGE 10X," ENDING WAVELENGTH:",4D," nm"
20140     IMAGE 10X,"  DATA INCREMENT:",2D.D," nm"
20150     IMAGE 10X,"EXCITATION WAVELENGTH: 325 nm"
20160     PRINT USING 20120;Ws
20170     PRINT USING 20130;We
20180     PRINT USING 20140;Incr
20190     PRINT
20200     PRINT
20201     GOSUB 25000! GOES TO ROUTINE WHICH DETERMINES THE SENSITIVITY
20210     IMAGE 10X,"SENSITIVITY SETTING OF THE LOC-IN= ",3D,1X,AA
20220     PRINT USING 20210;Sensitivity,Units$
20230     PRINTER IS 1
20240     RETURN
25000 ! DETERMINES SENSITIVITY SETTING OF THE LOC-IN*****
25010     OUTPUT 730;"G"
25020     ENTER 730;Sens
25021     RESET 7
25030 ! DETERMINING THE UNITS OF THE SENSITIVITY mV, æV, OR nV
25040     Units$="mV"
25050     IF Sens<=15 THEN Units$="æV"
25060     IF Sens<=6 THEN Units$="nV"
25070 ! SENSITIVITY IS CALCULATED BY DIGIT * MULT
25080 ! DETERMINING DIGIT. THIS NUMBER IS EITHER 1, 2, OR 5.

```

```

25090      Digit=5
25100      IF INT(FRACT(Sens/3)*100)=33 THEN Digit=1
25110      IF INT(FRACT(Sens/3)*100)=66 THEN Digit=2
25120 ! DETERMINING THE MULTIPLIER (MULT) TO CALCULATE SENSITIVITY
25130      Gain=Sens
25140      IF Gain>6 THEN 25180
25150      Mult=10
25160      IF Gain>=4 THEN Mult=100
25170      GOTO 25230
25180      IF Gain>15 THEN Gain=Gain-9
25190      Mult=1
25200      IF Gain>=10 AND Gain<=12 THEN Mult=10
25210      IF Gain>=13 AND Gain<=15 THEN Mult=100
25220 ! CALCULATING AND PRINTING THE SENSITIVITY
25230      Sensitivity=Digit*Mult
25240      RETURN
30000 ! TRI TEMPERATURE CONTROLLER SETUP*****
30010      DISP "TSETUP--SETUPS UP TRI TEMP CONTROL ON THE HPIB"
30020      IMAGE "P",3D.DD
30030 !SENSOR #1
30040      OUTPUT 707;"S1"
30050 !SET GAIN TO 40
30060      OUTPUT 707;"G40"
30070      WAIT 1
30080 !SET INTEGRAL TO 20
30090      OUTPUT 707;"I20"
30100      WAIT 1
30110 !SET DERIVATIVE TO 0.2
30120      OUTPUT 707;"D.2"
30130      WAIT 1
30140 !SET INITIAL CONTROL TO TO 4K
30150      OUTPUT 707 USING 30020;4
30160 !START CONTROL LOOP
30170      OUTPUT 707;"R"
30180 !SET REFRIG CONTROL TO RUN--VHF RY TO B1
30200      DISP "TRI CONTROLLER HAS BEEN SET UP AND STARTED"
30210      RETURN
40000 ! ANNEALS SAMPLE*****
40010      DISP "ANNEAL --USES TRI CONTROLLER TO SET ANNEAL T"
40020      LINPUT "ENTER DESIRED ANNEAL TEMP",Tan1$
40030      Tan1=VAL(Tan1$)
40040      IMAGE "P",DDD.DD
40050      IMAGE "TEMPERATURE = ",3D.DD,"K"
40060      OUTPUT 707 USING 40040;Tan1
40070      WAIT 1
40080 !STOP REFRIG COLD HEAD--VHF RY TO B2
40090      OUTPUT 703;"B1"! STOPS COLD HEAD
40100      OUTPUT 707;"O1"! SIGNALS CONTROLLER READY FOR TEMP
40110      ENTER 707;Temp! ENTERS TEMPERATURE
40120      DISP USING 40050;Temp
40130      IF Temp<Tan1 THEN 40100
40140 !RETURN SETPOINT TO 4 K AND START COLD HEAD--VHF RY TO B1
40150      OUTPUT 703;"B4"! STARTS COLD HEAD
40160      OUTPUT 707 USING 40040;4

```

```
40170     FOR I=1 TO 100
40180         OUTPUT 707;"O1"! SIGNALS CONTROLLERS READY FOR TEMP
40190         ENTER 707;T(I)! ENTERS TEMPERATURE
40200         DISP USING 40050;T(I)
40210         WAIT 3
40220     NEXT I
40230     PRINTER IS 10
40240     IMAGE "ANNEAL TEMP= ",3D.DD," K"
40250     PRINT USING 40240;MAX(T(*))
40260     PRINTER IS 1
40270     DISP USING 40240;MAX(T(*))
40280 !CONNECT HEATER POWER
40290     OUTPUT 703;"B4"
40300     RETURN
50000 ! HOLDS TEMPERATURE*****
50010     DISP "HOLD T -USES TRI CONTROLLER TO HOLD TEMPERATURE AT SPECIFIED VALUE"
50020     LINPUT "ENTER DESIRED TEMP FOR HOLD",Thold$
50030     Thold=VAL(Thold$)
50040     IMAGE "P",DDD.DD
50050     IMAGE "TEMPERATURE = ",3D.DD,"K"
50060     OUTPUT 707 USING 50040;Thold
50070     WAIT 1
50080     PRINTER IS 1
50090     DISP "SET POINT= ",Thold," K FRONT PANEL ON TRI GIVES ACTUAL TEMPERATURE"
50110     RETURN
50120     END
```

VITA 2

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