RELIABILITY IMPROVEMENTS IN TUNABLE $Pb_{1-x}Sn_xSe$ DIODE LASERS OPERATING IN THE 8.5-30 MICROMETER SPECTRAL REGION*

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SUMMARY

This paper describes recent developments in the technology of Pb-salt diode lasers which have led to significant improvements in reliability and lifetime, and to improved operation at very long wavelengths. A combination of packaging and contacting-metallurgy improvements has led to diode lasers that are stable both in terms of temperature cycling and shelf-storage time. Lasers cycled over 500 times between 77K and 300K have exhibited no measurable changes in either electrical contact resistance or threshold current. Utilizing a newly developed metallurgical contacting process, both lasers and experimental n-type and p-type bulk materials have been shown to have electrical contact resistance values that are stable for shelf storage periods well in excess of one year. This paper summarizes some of the previously encountered problems and reviews several experiments which have led to devices with improved performance stability. Such stable device configurations have been achieved for material compositions yielding lasers which operate continuously at wavelengths as long as 30.3 µm.

INTRODUCTION

A number of different failure mechanisms have been observed in Pb-salt diode lasers. Some of these, such as failures due to power supply transients, accidental back-biasing or excessive forward-bias currents are operator or equipment related and can be avoided by the user if manufacturer's instructions are followed. Other failures observed appear to have been related to either temperature cycling (ref. 1) or shelf storage of the lasers (ref. 2). It is such failures and the successful efforts to overcome them that are described in this paper. In contrast to observations made on some of the III-V compound diode lasers, laser degradation under operating conditions has not been a problem with the Pb-salt lasers.

Stability in the operating characteristics of diode lasers requires stability in all parameters affecting these characteristics. Such parameters include the device mechanical characteristics (i.e., temperature-dependent

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stress effects which are usually package related), electrical characteristics (i.e., the stability of the electrical contact resistance) and thermal characteristics (i.e., the stability of the device thermal resistance). This paper describes the successful stabilization of the first two parameters. The problem of thermal resistance stability has been studied as part of a special research effort under Army contract DAAK21-79-C-0041, portions of which are reported here.

Following a description of present laser packaging techniques, the thermal cycling stability of some typical $Pb_{1-x}Sn_xSe$ diode lasers is described in the section entitled "Thermal Cycling Stability". The section entitled "Previously Observed Contact Resistance Degradation" discusses some typical contact resistance degradation problems observed in both p-type and n-type $Pb_{1-x}Sn_xSe$ materials as well as in p-n junction lasers. The section entitled "Diagnostic Measurements and Stability Results on Lasers Fabricated by Newly Developed Techniques" describes experiments aimed at investigating sources of such degradation and presents results on the stability of bulk n-type and p-type devices and of lasers fabricated by newly developed techniques. Some special results obtained for long-wavelength lasers of $Pb_{1-x}Sn_xSe$ are presented in the section entitled "Long Wavelength Laser Performance and Stability". Finally, an effort aimed at separating the effects of electrical and thermal resistance has led to some interesting observations, as described in the section entitled "Thermal Resistance Stability Measurements".

SYMBOLS

R_f forward bias resistance of diode lasers (ohms)

I_{th} laser threshold current (mA)

ΔP relative quantum efficiency of laser (no units)

P_{max} relative maximum output power of laser (no units)

RA resistance - active area product of diode laser

λ free space wavelength (μm)

W power (mW or μW as indicated)

CW continuous wave

I laser current (mA)

n refractive index of laser material

L length of optical cavity of the diode laser (μm)

m order of longitudinal mode (an integer)

T temperature (K)

THERMAL CYCLING STABILITY

The temperature extremes to which Pb-salt lasers are subjected are among the most severe in the semiconductor industry. Ranging from liquid helium (4.2K) to room temperature (300K), such temperature extremes require careful choice of crystal mounting techniques, package materials and physical configurations. The choice of materials is determined by such factors as thermal conductivity, thermal expansion coefficient and electrical properties at cryogenic temperatures.

The presently used package for Pb-salt diode lasers is shown in the scanning electron microscope (SEM) photograph of figure 1. This package provides easy access to the laser face and utilizes a pressure-free design in which the laser crystal is welded between an indium-plated stud and a flexible top contact strap.

In an experiment to investigate the temperature cycling stability of this package, 3 $Pb_{1-x}Sn_xSe$ diode lasers were cycled between room temperature and 77K a total of 500 times. Each cycle consisted of a 10 minute dip in liquid nitrogen followed by a 20 minute blower-driven warm-up, with the lasers mounted in an evacuated "dip-stick". The dip-stick was designed to facilitate electrical testing by dipping into a liquid helium tank. Both the electrical contact resistance and threshold current were periodically measured. The results are summarized in table I. The variations in threshold current are commonly observed in Pb-salt diode lasers and are believed due to changes in surface leakage current. The contact resistance is essentially the same over the entire test period, since a variation of ± .0005 ohms is well within the expected experimental error. It is thus apparent that 500 temperature cycles have had no significant effect on the laser contact resistance. Subsequent room temperature storage lifetime data on these lasers are presented in the section entitled "Diagnostic Measurements and Stability Results on Lasers Fabricated by Newly Developed Techniques".

PREVIOUSLY OBSERVED CONTACT RESISTANCE DEGRADATION

The electrical contact resistance to diode lasers is a major factor in laser heating and therefore current tuning rate during operation. A common source of shelf storage degradation of Pb-salt diode lasers has been a progressing increase in this parameter. This phenomenon was even found to occur on the bulk n-type and p-type $Pb_{1-x}Sn_xSe$ samples. The contact resistance to n-type and p-type samples of $Pb_{0.926}Sn_{0.074}Se$, measured over a period of several months, is shown in figure 2. The sample areas were approximately 8×10^{-4} cm^2 and the storage conditions were at room temperature, under ambient conditions.

The progressive contact resistance degradation illustrated here was somewhat erratic in that not all lasers degraded this rapidly. Lasers can, in general, operate under CW conditions with contact resistance values as high as approximately 0.1 ohms. Thus lasers with initial resistance values of 0.005 ohms may continue operating for long periods before the resistance increases to the point where CW laser action ceases. During this time, however, the progressive resistance increases would cause continual changes in the laser tuning rates and operating frequencies at given temperature-current combinations.

The diagnostic measurements carried out to investigate the sources of this contact resistance degradation and the results of these measurements are discussed in the following section.

DIAGNOSTIC MEASUREMENTS AND STABILITY RESULTS ON LASERS

FABRICATED BY NEWLY DEVELOPED TECHNIQUES

The existence of progressive increases in electrical contact resistance of both bulk and p-n junction devices suggested metallurgical interactions either between the contact metal layers or between the semiconductor and the metal layers as possible sources of this problem. These possibilities were investigated by use of Auger electron spectroscopy (AES) of the semiconductor and metal interface surfaces. Several $Pb_{1-x}Sn_xSe$ wafers were analyzed by removing the metallization layer by a tape-pulling technique and probing the semiconductor surfaces. The results are summarized in Table II. These results suggest that failing devices were characterized by the presence of In on the p-type semiconductor surface extending at most 150Å below the crystal surface (such a distance being the resolution limit of these AES measurements). Since In is a critical part of the bond used in mounting the laser crystals into the laser packages, the elimination of this material was not considered. To prevent the apparent migration of In through the Au and, in some cases, barrier metal layer, the use of new metallic barrier layers was investigated. The proper use of such layers can be expected to prevent In migration to the crystal surface. A process utilizing multiple metallization layers deposited by electron beam evaporation techniques was developed, and a number of experimental bulk n-type and p-type devices were fabricated and evaluated for shelf storage stability. These devices have exhibited excellent contact resistance stability to date. As of 2/20/80, the p-type samples have an accumulated shelf storage time of 17 months, while the n-type samples have been shelf-stored for almost 15 months. The retest data for these junctionless devices are summarized in figure 3. As the device areas were approximately 8×10^{-4} cm^2, the RA products of the n-type samples are approximately 4×10^{-7} ohm cm^2 per side while those of the p-side are approximately 1.6×10^{-6} ohm cm^2. The n-contact values are among the lowest ever reported to any semiconductor material.

The stability of a number of CID-type (ref. 3) $Pb_{1-x}Sn_xSe$ lasers fabricated by the improved metallization techniques was tracked for a period of over a year. Some of these results are shown in figure 4 which tabulates the contact resistance, threshold current and relative quantum efficiency as a function of time for a group of 4 $Pb_{1-x}Sn_xSe$ lasers. A total time period of 15 months is covered by these data (the latest points corresponding to measurements made on 2/20/80). The relative quantum efficiency parameter was obtained by measuring the relative rate at which the output power increased with laser current just above threshold. In absolute terms, the external quantum efficiencies corresponding to these values are of the order of 0.5% per laser end. The comparative data are presented here to show that the output power from these lasers was relatively stable over the 15 month shelf storage time period. All data points presented in figure 4 were obtained at liquid helium temperature. The emission spectra for one of these lasers (8292-2) as measured under identical test conditions at time periods approximately 1 year apart are shown in figure 5. While there appears to be a spectral shift towards higher energy by about 6 cm^{-1}, the relative longitudinal mode distribution appears quite stable, and the total output power somewhat higher. Some of this discrepancy may be due to a change of power meters during this time interval.

A second group of lasers stored and retested over a 15 month period are the 3 devices which comprised the group described in the section entitled "Thermal Cycling Stability". After being temperature recycled 500 times the devices were periodically retested for contact resistance, threshold current, relative quantum efficiency (ΔP) and relative maximum output power (P_m). As in the case of relative quantum efficiency, the relative maximum output power corresponded to the current through a Ge:Cu photodetector mounted adjacent to the laser and is shown for comparative purposes only. The actual maximum output power for these lasers was of the order of a mW per end. The value of these test parameters at various retest intervals are shown in table III. All parameters are seen to be relatively stable and show no tendency for degradation over this time period. Unit 8324-10 apparently had an initially high threshold current (which could have been an instrument error) but thereafter appears to have settled down. The period in time at which these devices were temperature cycled is indicated in the table.

A third group of lasers consisted of 2 units which were fabricated from $Pb_{.928}Sn_{.072}Se$ (corresponding to 16 μm emission at 15K). These units were periodically retested over an 11 month shelf storage period and then delivered under NASA-Langley contract NAS1-15190. The results of these measurements, shown in table IV, indicate excellent stability.

The metallization process used in fabricating the devices described here was shown to be capable of withstanding air-ambient bake temperatures of 65°C for periods of 63 hours. In an experiment involving 9 lasers from several different $Pb_{1-x}Sn_xSe$ wafers, 8 of them (89%) survived this bake. Of these survivors, 6 (or 75%) remained stable thereafter. While it is not standard practice to subject Pb-salt lasers to such high temperatures, the experiment demonstrated the relative thermal stability of the presently used metallization process.

LONG WAVELENGTH LASER PERFORMANCE AND STABILITY

Long wavelength lasers (λ>25μm) have been fabricated from $Pb_{1-x}Sn_xSe$ material with compositions on both side of the zero-gap crossover point (ref. 4). The temperature dependence of the bandgap (hence, emission frequency) on opposite sides of the crossover at $x \simeq 0.14$ differ markedly. For $x < 0.14$ the band gap (emission frequency) increases with increasing temperature while for $x > 0.14$ the band gap decreases with increasing temperature. We report the operational results obtained from some $Pb_{0.90}Sn_{0.10}Se$ lasers in the 29-30 μm spectral region. This composition region has the advantage of yielding the most power at the long wavelength region of operation, since this occurs at the lowest temperatures. The emission spectrum of a $Pb_{0.90}Sn_{0.10}Se$ laser operating CW at 10K and 2000 mA is shown in figure 6. With a total measured output power of 141 μW, the mode which occurs at 338.5 cm^{-1} (29.5 μm) has a CW power of approximately 30 μW. When operated just above threshold, the laser emits at 330 cm^{-1} (30.3 μm) in a single mode. This spectrum is shown in figure 7.

The stability of four such lasers was monitored over a 10 1/2 month time period (as of 2/22/80). A plot of contact resistance, threshold current and relative quantum efficiency is shown in figure 8. All operating parameters are reasonably stable over this time period, although two of the lasers do exhibit some increase in contact resistance. As in the measurements described previously, some of the differences in the relative quantum efficiency are due to the fact that these measurements were made in different sample test fixtures with different detector sensitivity values.

THERMAL RESISTANCE STABILITY MEASUREMENTS

In an effort to determine the thermal resistance stability of Pb-salt diode lasers, several units known to have stable electrical contact resistance values were checked for single mode tuning rate. This parameter was periodically remeasured. The results indicated that while some devices are stable, some can also show a slight tendency towards increasing thermal resistance with time.

The single mode tuning rate $\frac{\partial\left(\frac{1}{\lambda}\right)}{\partial I}$ is given by

$$\frac{\partial\left(\frac{1}{\lambda}\right)}{\partial I} = \frac{m}{2nL}\left(\frac{1}{n}\frac{\partial n}{\partial T} + \frac{1}{L}\frac{\partial L}{\partial T}\right)\frac{\partial T}{\partial I} \qquad (1)$$

where m is the order of the longitudinal laser mode, typically 550 for a 1/2 mm cavity length, L, at 10 μm. The refractive index, n, is temperature dependent and the $\frac{1}{n}\frac{\partial n}{\partial T}$ term is larger than the thermal expansion term $\frac{1}{L}\frac{\partial L}{\partial T}$ (which is known to be approximately 20 x 10^{-6} K^{-1} for PbSe). The

$\frac{\partial T}{\partial I}$ term is proportional to the thermal resistance of the laser. Thus, the single mode tuning rate provides a qualitative measure of the thermal resistance. Preliminary measurements indicate that small thermal resistance increases can occur on devices that are electrically stable. This technique provides a useful tool for analyzing the thermal stability of various laser mounting techniques.

An experiment was performed to measure the temperature differential across a laser crystal under operating conditions. By use of a precalibrated miniature Si diode sensor which was mounted directly to the top contact strap of a laser, it was possible to measure the temperature at that point, while the temperature on the other side (in contact with the large heat sink of the mounting stud) was measured with a second calibrated sensor. It was found that temperature differentials of 2-5K were typical at the full laser operating current values of 2 amps. To the best of our knowledge, this represents the first reported measurement of this parameter.

CONCLUDING REMARKS

Package design modifications and contact technology developments have led to significant improvements in the reliability and stability of $Pb_{1-x}Sn_xSe$ diode lasers operating in the 8-30 μm spectral region. Representative lasers subjected to over 500 temperature cycles between 77K and 300K have exhibited no significant changes in their operating parameters. Lasers stored under ambient temperature conditions have exhibited excellent stability in electrical contact resistance, threshold current and relative output power over test periods of 15 months. These improvements have been successful even for long wavelength material compositions with the demonstration of laser performance stability for periods in excess of 10 months to date. Such lasers have emitted up to 30 μW of CW power at 29.5 μm. Recently fabricated lasers have been shown capable of withstanding 65°C bake temperatures with high survival and good subsequent stability yields.

Indirect measurements of thermal resistance have indicated that it is, in some cases, possible to measure small increases in thermal resistance on devices whose electrical contact resistance is stable. Such findings indicate the diverse nature of the problems associated with diode laser failure mechanisms.

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TABLE I.-STABILITY DATA ON LASERS CYCLED 500 TIMES BETWEEN 300K AND 77K.

	Original Data		After 135 temp cycles		After 500 temp cycles	
Laser No.	R_f (ohms)	I_{th} (mA)	R_f (ohms)	I_{th} (mA)	R_f (ohms)	I_{th} (mA)
8324-11	.005	1410	.006	1360	.005	1320
8324-12	.006	1270	.005	1200	.005	1200
8324-10* (control)	.005	> 2000	.005	1380	.005	1350

*Laser 8324-10 was a control sample from the same lot. This laser was not temperature cycled.

TABLE II.-SUMMARY OF AES FINDINGS ON $Pb_{1-x}Sn_xSe$ LASER WAFERS.

Wafer No.	Description	AES Findings
D700 p-side	P-diffused, striped wafer of $Pb_{.93}Sn_{.07}Se$. Lasers exhibited contact resistance increases after a few months.	Surface: Trace of Au (~.1%). Strong In signal (~few %). More In in stripe than on insulator. Below Surface: 50 Å of material removed gave same results as above. 150 Å of material removed, and the In signal was gone.
D1002 p-side	N-diffused, non-striped wafer of $Pb_{.989}Sn_{.011}Se$. Lasers degraded in a few days.	Surface: Au approximately 2% In approximately 2%
n-side		Surface: Approximately 5% In
D448 p-side	N-diffused, striped wafer of $Pb_{.935}Sn_{.065}Se$. Lasers were stable for over one year.	Surface: Approximately 5% Au, no trace of In found.

TABLE III.-COMPARATIVE STABILITY DATA FOR THREE $Pb_{1-x}Sn_xSe$ LASERS STORED FOR OVER ONE YEAR AT ROOM TEMPERATURE.

Laser	Test Date	R_f (ohms)	I_{th} (mA)	ΔP	P_{max}	Laser History*
8324-10	11-20-78	.007	>2000	--	--	Control sample -
	12-07-78	.006	1380	43	78	No special
	12-18-78	.006	1350	71	109	cycling.
	1-08-79	.006	1280	58	93	
	2-08-79	.005	1330	59	102	
	2-24-79	.006	1350	69	104	
	5-25-79	.006	1500	54	90	
	11-06-79	.006	1330	49	97	
	2-20-80	.006	1400	40	90	
8324-11	11-20-78	.005	1490	50	84	
	11-27-78	.005	1410	49	88	
	11-30-78	.006	1360	52	90	Cycled 135 times
	12-07-78	.005	1320	53	95	Cycled 365 times
	12-18-78	.006	1300	50	90	77-300K
	1-08-79	.006	1260	59	103	
	2-08-79	.005	1250	52	95	
	2-24-79	.006	1220	52	96	
	5-25-79	.005	1160	50	98	
	7-26-79	.006	1250	48	98	
	11-06-79	.006	1210	46	96	
	2-20-80	.006	1180	52	100	
8324-12	11-20-78	.006	1350	48	82	
	11-28-78	.005	1270	43	85	
	11-30-78	.006	1200	51	96	Cycled 135 times
	12-07-78	.006	1200	52	95	Cycled 365 times
	12-18-78	.005	1250	51	91	77-300K
	1-08-79	.006	1220	50	96	
	2-08-79	.006	1230	48	90	
	2-24-79	.006	1260	42	86	
	5-25-79	.006	1160	43	94	
	7-27-79	.006	1360	35	76	
	11-06-79	.006	1400	23	65	
	2-20-80	.006	1310	30	70	

*All lasers stored in air at room temperature between tests.

TABLE IV.-STABILITY TEST DATA FOR LASERS 9093-21 AND 9110-3

Laser No.	Test Date	Electrical Contact Resistance (ohms)	Threshold Current (mA)
9093-21	4-04-79	0.007	+330
	4-09-79	0.008	+310
	4-23-79	0.008	+320
	7-13-79	0.007	+315
	1-11-80	0.004	+300
	2-12-80	0.005	+305
9110-3	4-20-79	0.007	-430
	7-30-79	0.007	-395
	8-31-79	0.006	-400
	2-12-80	0.005	-430

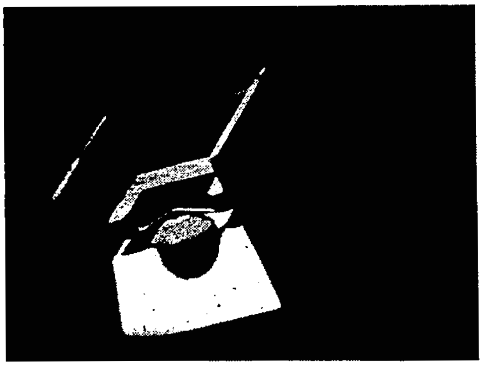

Figure 1.- SEM photograph of a Pb-salt diode laser package. This design minimizes crystal stress by eliminating pressure.

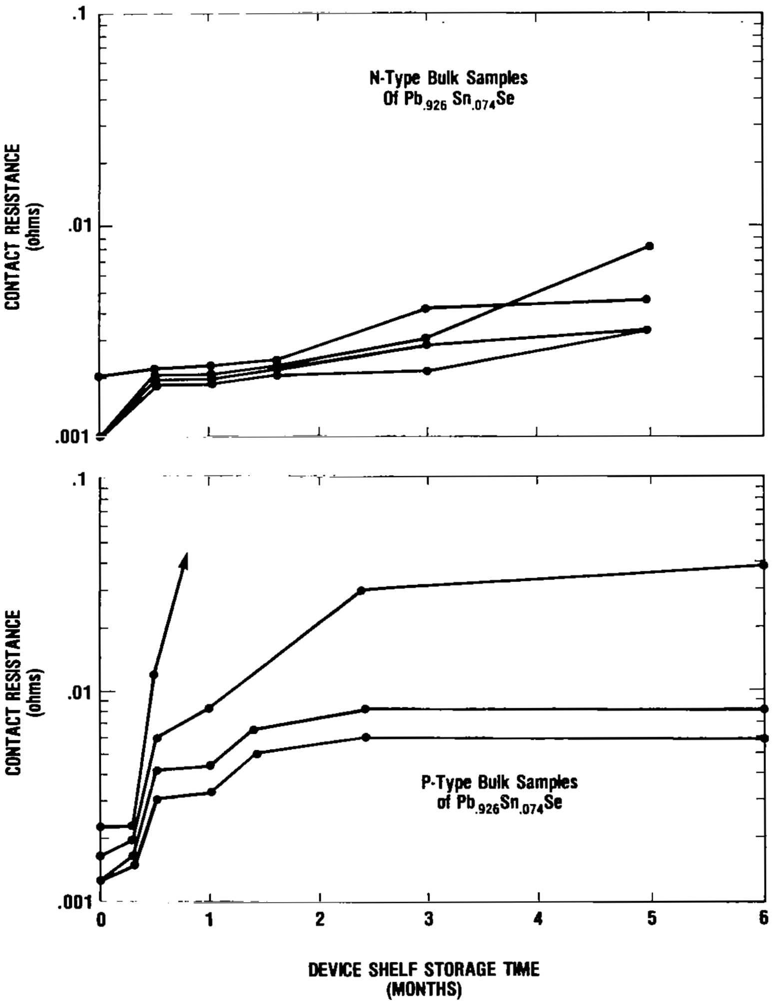

Figure 2.- Contact resistance to n-type and p-type $Pb_{.924}Sn_{.076}Se$ material with etched surfaces and standard contacts showing severe degradation.

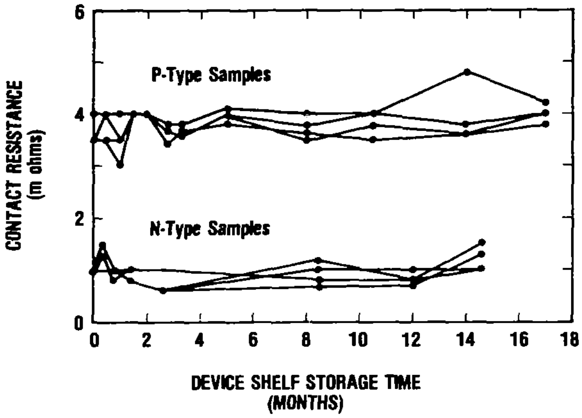

Figure 3.- Contact resistance to n-type and p-type $Pb_{.924}Sn_{.076}Se$ with improved contacts.

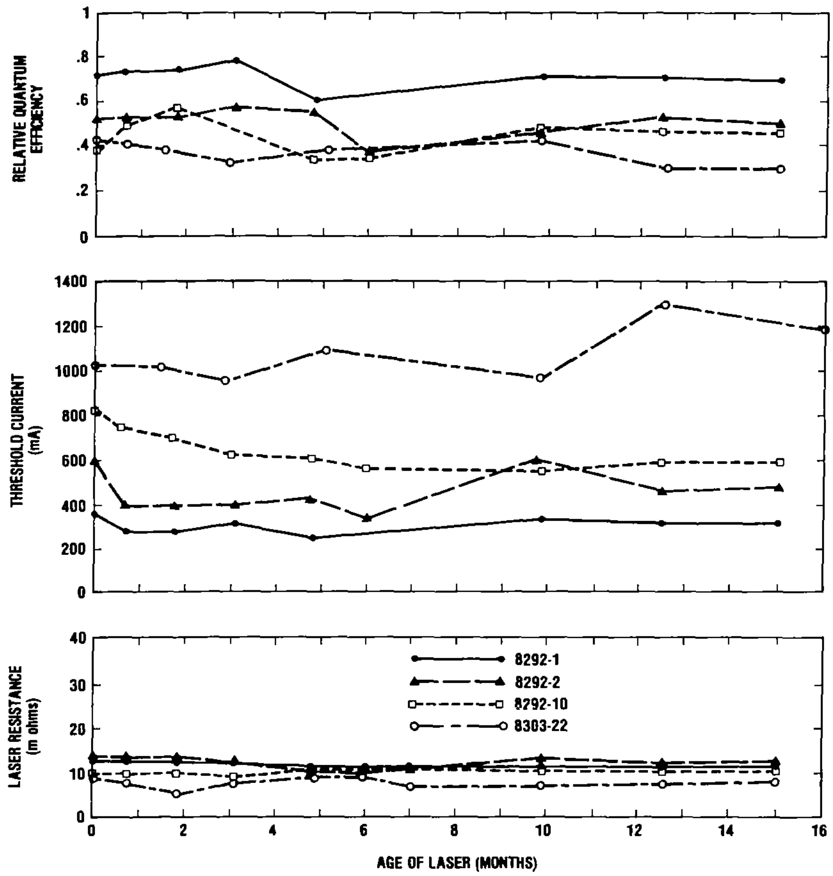

Figure 4.- Plots of relative quantum efficiency, threshold current and laser contact resistance as functions of shelf storage time covering a period of over one year. Lasers 8292-1 and 2 were fabricated from $Pb_{.966}Sn_{.034}Se$ and lasers 8292-10 and 8303-22 were fabricated from $Pb_{.927}Sn_{.073}Se$ corresponding to the 11.5 and 17.2 μm spectral regions, respectively.

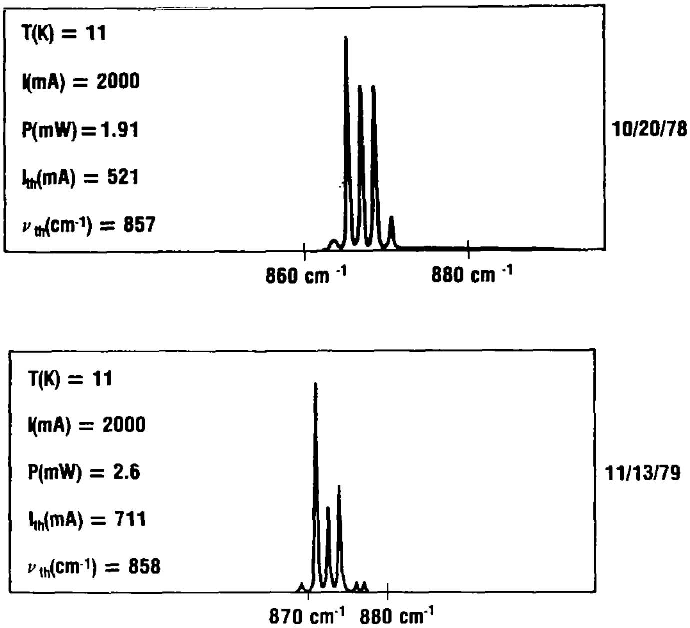

Figure 5.- Comparison of emission spectra from laser 8292-2 taken on October 20, 1978 and again on November 13, 1979. Differences in power reading could, in part, be due to different power meters. Shift of 6 cm^{-1} towards higher wave number is possibly due to slight thermal resistance increase.

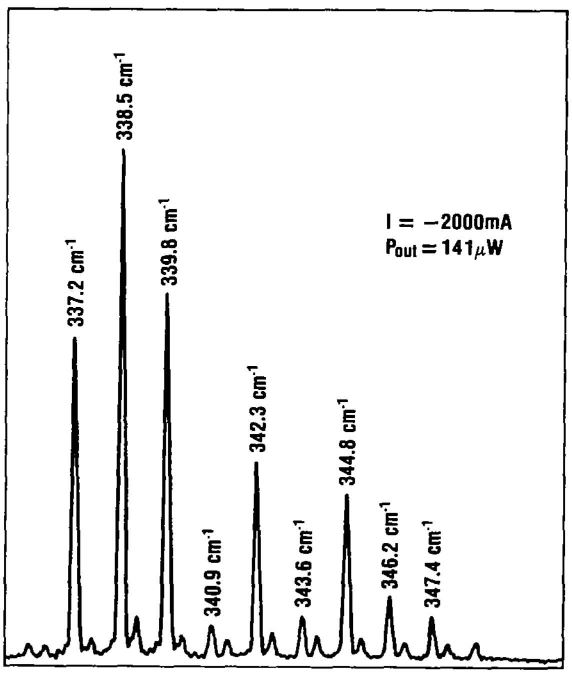

Figure 6.- Emission spectrum of laser 9096-10 operating CW at a 2 Amp current at 10 K. The 338.5 cm^{-1} mode has approximately 30 μW of power.

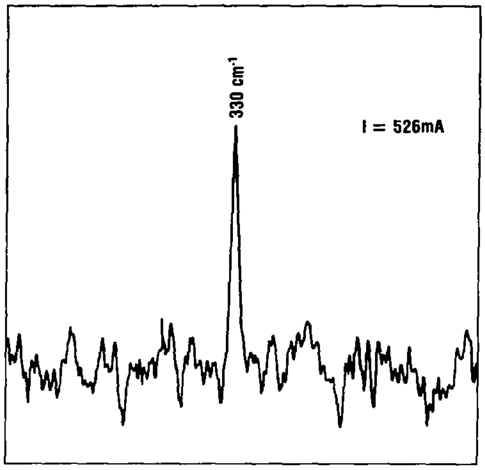

Figure 7.- Emission spectrum of laser 9096-10 operating slightly above threshold at 10 K showing single mode emission at 330 cm^{-1} (30.30 μm).

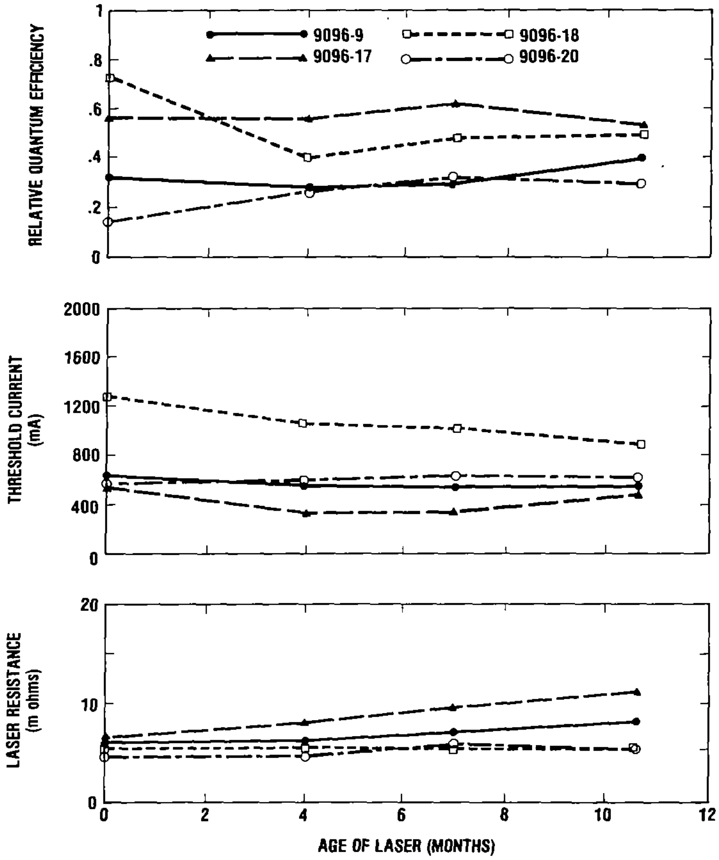

Figure 8.- Stability data for long wavelength (28 μm region) $Pb_{0.90}Sn_{0.10}Se$ lasers stored under ambient conditions for a 10½ month period.