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HIGH EFFICIENCY GaP POWER CONVERSION FOR BETAVOLTAIC APPLICATIONS[1]

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SUMMARY

AstroPower is developing a gallium phosphide (GaP) based energy converter optimized for radio luminescent light-based power supplies. A "two-step" or "indirect" process is used where a phosphor is excited by radioactive decay products to produce light that is then converted to electricity by a photovoltaic energy converter. This indirect conversion of β-radiation to electrical energy can be realized by applying recent developments in tritium based radio luminescent (RL) light sources in combination with the high conversion efficiencies that can be achieved under low illumination with low leakage, gallium phosphide based devices. This tritium to light approach is inherently safer than battery designs that incorporate high activity radionuclides because the beta particles emitted by tritium are of low average energy and are easily stopped by a thin layer of glass. GaP layers were grown by liquid phase epitaxy and p/n junction devices were fabricated and characterized for low light intensity power conversion. AstroPower has demonstrated the feasibility of the GaP based energy converter with the following key results: 23.54% conversion efficiency under 968 $\mu W/cm^2$ 440 nm blue light, 14.59% conversion efficiency for 2.85 $\mu W/cm^2$ 440 nm blue light, and fabrication of a working 5 V array. We have also determined that at least 20 $\mu W/cm^2$ optical power is available for betavoltaic power systems. Successful development of this device is an enabling technology for low volume, safe, high voltage, milliwatt power supplies with service lifetimes in excess of 12 years. One potential application for the RL-power supply system concept is illustrated in Figure 1.

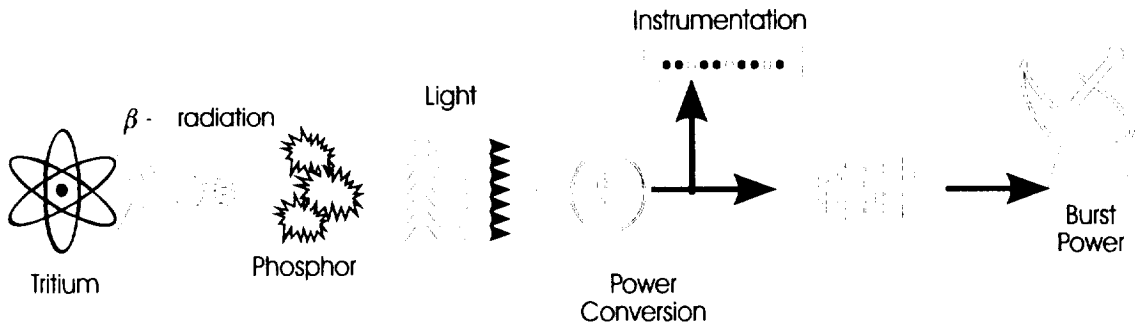

Figure 1. Two step betavoltaic conversion.

There are three major product sectors that the development of betavoltaic technology enables: 1) 10 to 20 year milliwatt power sources for medical implants, remote instrument packages, deep space probes, or security devices 2) 10 to 20 year nanowatt "static" voltage sources for on circuit board (or on chip) illumination and power cogeneration, and 3) integrated illumination and power generation for portable computers and embedded roadside/road sensors for the Intelligent Vehicle Highway System.

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INTRODUCTION

The approach of this research is to utilize the tritium fueled two step method to develop cost effective betavoltaic-batteries (β-batteries). The betavoltaic effect was discovered by Rappaport in 1953 (ref. 1). Soon after, the Elgin-Kidde (ref. 2) two-step, 5 year atomic battery was developed. This was based on ^{147}Pm/ZnS/Si. Conversion efficiencies were low, and the subsequent development of Li based batteries quickly made the Elgin-Kidde cell obsolete. Olsen (ref. 3, ref. 4) has reported on the conversion efficiency of direct betavoltaic power supplies. A review of this technology reveals that there are three major limitations to the direct conversion approach.

Direct Conversion

- the activity and range of the beta emitter must be coupled to the diffusion length of the semiconductor material
- the power flux produced by a beta emitter cannot be concentrated
- the effective ionization energy of the converter material limits the efficiency of the device

Indirect Conversion

- the activity and range of the beta source is coupled to a phosphor which is chosen so that the light emitted is optimal for conversion by the semiconductor material.
- the use of down converting phosphors allows for a volumetric concentration of the beta energy in the form of light flux.
- energy loss is transferred to the phosphor which has experimentally demonstrated radioluminescent conversion efficiencies from 10 to 30%, depending on phosphor type and material quality.

Light emission has been accomplished with an areal power flux greater than that which has been considered to be the maximum possible for tritium gas (ref. 5). The available power density from the tritium/phosphor light is at least 23 μW/cm^2. Device modeling results indicate that the light to electricity converter of a β-battery system can have a 20 to 30% conversion efficiency. The modeled efficiency for identical devices with indirect and direct conversion configurations are displayed in Figure 2. The efficiency of the direct conversion configuration is much less than the conversion efficiency of the "indirect" process.

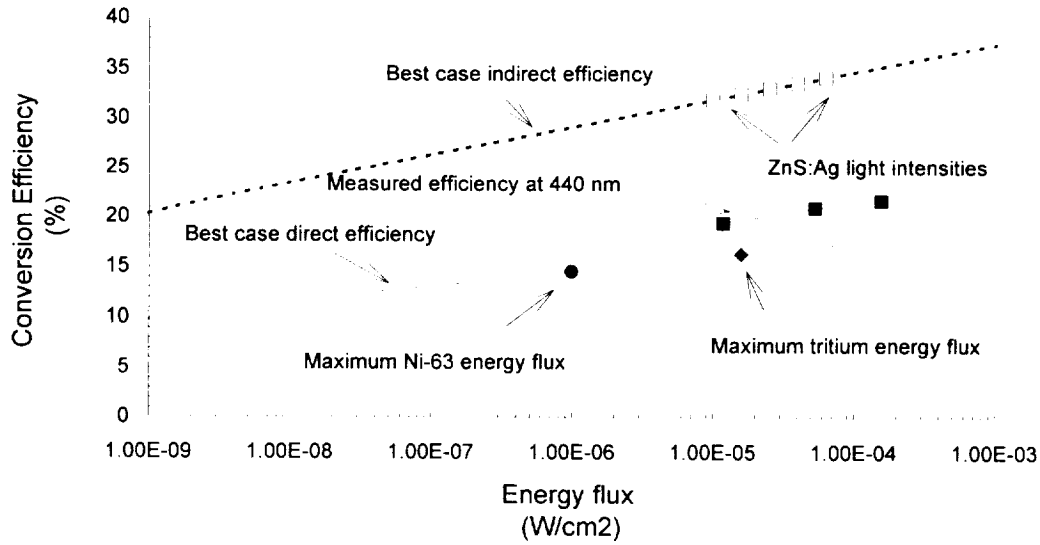

Figure 2. Best case conversion efficiency of GaP.

EXPERIMENTAL RESULTS

Blue Phosphors

The absorption edge for gallium phosphide extends from 549 nm to 520 nm, consequently only the higher photon energy blue and UV phosphors are of interest. Blue phosphors consist of a high bandgap semiconducting or semi-insulating material doped with mid-bandgap luminescent center impurities. These impurities provide midband energy levels for the radiative recombination of a carrier that has been excited by impact ionization to an energy state within the conduction band. In principle, phosphors can be highly efficient because the light is emitted within a non-absorbing lattice. In practice, phosphor efficiencies are lower, mainly due to non-radiative recombination mechanisms dependent on the material quality and material processing. It is important to note that phosphor generated light cannot be intensified by simply increasing the thickness of the phosphor layer. Optical effects such as scattering, absorption, and light trapping will determine the optimum thickness for maximum brightness of a phosphor at a given level of excitation.

For this application, power generation efficiency depends on beta-to-optical and optical-to-electrical conversion efficiencies, therefore, a literature search for phosphor conversion efficiency was conducted. The most comprehensive source of this type of data has been found in Bril (ref. 5). Table 1 gives a summary of the available phosphors.

Table 1. Blue Phosphors

Phosphor	Emission (nm)	Bandwidth (fwhm)	e^--beam Quantum Efficiency*		UV Quantum Efficiency**	
$Ca_3(PO_4)_2$:Tl	300	40 nm	η_R=0.2%		η_R = 49%, QE = 56%	
$BaSi_2O_5$:Pb	351	90 nm	η_R=4%		η_R = 55%, QE = 75%	
SrB_4O_7:Eu	371					
$Sr_2P_2O_7$:Eu	420					
$CaWO_4$:Pb	446	120 nm	η_R= 3%	η_L= 5 lm/W	η_R = 42%, QE = 75%	η_L= 65 lm/W
$Sr_5Cl(PO_4)_3$:Eu	447					
$BaMg_2Al_{16}O_{27}$:Eu	450					
ZnS:Ag	450	55 nm	η_R = 21%	η_L = 22 lm/W		
$Sr_2P_2O_7$:Sn	460					
$MgWO_4$	473	160 nm	η_R = 2.5%	η_L = 7 lm/W		
ZnS:Tm	477	10 nm				
$Ca_5F(PO_4)_3$:Sb	482					

* e^--beam efficiency is determined at 20 keV.
** UV efficiency is determined at 260 nm.
η_R = radiant efficiency
η_L = luminous efficiency

From these data, it appears that silver doped zinc sulfide is a superior phosphor for this application. The majority, 99%, of the light emission from ZnS:Ag is above the bandgap of gallium phosphide (2.26 eV) and 75% of the light emission is in the spectral region where GaP has a high spectral response. Silver doped zinc sulfide also has demonstrated a high radiative conversion efficiency when excited by 20 keV mono-energetic electrons (ref. 6) and the highest conversion efficiency (20.1%) of the phosphors found in the literature search. Since the phosphor must be stable for 10 to 20 years under betavoltaic irradiation, lifetime studies under high energy electron irradiation need to be performed for the appropriate phosphors.

Phosphor packaging

There are currently four options for packaging light generating phosphors for the β-battery. These are: the commercially available tritium/phosphor tube; microspheres; aerogels; and, tritirated polymers.

The standard commercial tritium/phosphor light is basically a fluorescent light bulb where the UV excitation by an ionized gas is replaced by beta excitation from tritium gas. This technology is compatible with all of the commercially available powdered phosphors. "The maximum light power flux from a standard tritium gas tube RL light has been experimentally shown to be limited to ~ 2·3 $\mu W/cm^2$ {1 Footlambert (fL) @ 520 nanometers} because of beta self-absorption in the gas"(ref. 5).

The second possible light source is "Self-Luminous Microspheres" (ref. 7). Microspheres consist of a phosphor and T_2 gas enclosed in a hollow glass sphere. This is similar to the standard commercial package with some important differences. The spheres are very small, 0.1 mm in diameter, and each contains less than 3.6×10^{-5} cm^3 of T_2 at STP. The possible light intensity is estimated at 1 to 10 ft.-lamberts. Since the glass sphere completely absorbs beta emission, no external shielding or high pressure containment is required for a battery assembly. The use of microspheres solves the design issues of safety and containment of the tritium gas, and is compatible with any phosphor. In principle, this type of light source can be concentrated by suspending the glass balls in a transparent matrix. However, there is currently no experimental evidence of the degree of concentration that can be achieved. Some of the items that must be considered are that the glass used to encapsulate the tritium and phosphor will have some absorption and that the scattering mechanisms that limit the brightness of commercial T_2/phosphor lights still applies.

The third possible light source is the use of aerogels. Phosphors may be suspended in a transparent matrix such as a silica aerogel. The advantage to this type of approach is that volumetric light concentration can be achieved since the aerogel is an open pore structure and tritium completely infiltrates the matrix. Preliminary experiments at Sandia National Laboratories (SNL) have determined that this type of light source can achieve an intensity of at least 23 $\mu W/cm^2$ (ref. 8). This technology is promising and seems to have the best potential for producing a high luminous flux.

The fourth possible technology is a completely organic, optically clear polymeric matrix demonstrated by Renschler et al. (ref. 9) at SNL in 1989, and Naumann (ref. 10) at E.F. Johnson in 1991. This technology is based on an all-organic, clear system where tritium is covalently bound within a transparent polymeric matrix containing a set of soluble organic scintillant dyes. All of the components are distributed on a molecular scale and reside within angstroms of each other for efficient conversion. However, research by Webb (ref. 7) indicates that there are inherent problems with this technology; exposure to its own radiation causes the tritirated polymer to lose gas. Therefore, the tritirated gas compounds readily diffuse through the polymer leading to radiation hazards and degradation of the transparency of the polymer. Walko (ref. 8) comments that the overall conversion efficiency of this technology is less than 5%. American Atomics, Inc., Self Powered Lighting, Inc., the Oak Ridge National Laboratories, and the 3M company have investigated self-luminous signs and self-lumination based on the tritirated polymer.

The only technology that is immediately available is the standard commercial package. The two more promising technologies, the microsphere concept and the aerogel concept, are both in developmental stages. The microsphere is being developed by Encapsulight, Inc. The aerogel concept has been evaluated by SNL and some preliminary investigations have been done at AstroPower using aerogel material supplied by CF-Technologies, Inc. The organic matrix approach does not seem to be interesting for this application at the current state of development.

Device Modeling

In order to develop a cost-effective β-battery system, a conversion efficiency of 30% at 20 μW/cm^2 is desired. The modeling results indicate that this is possible. A 30% efficient device imposes stringent requirements on both the device design and on the quality and reproducibility of the growth and fabrication process. The device must both collect the maximum amount of current and generate power with minimal losses. The pertinent factors are the shunt resistance of the diode (R_{sh}), the depletion region recombination reverse saturation current (J_{02}), the external quantum efficiency of the device (EQE), and the photodiode's fill factor (FF). Figure 3 displays the effects that each of these parameters has on the device conversion efficiency.

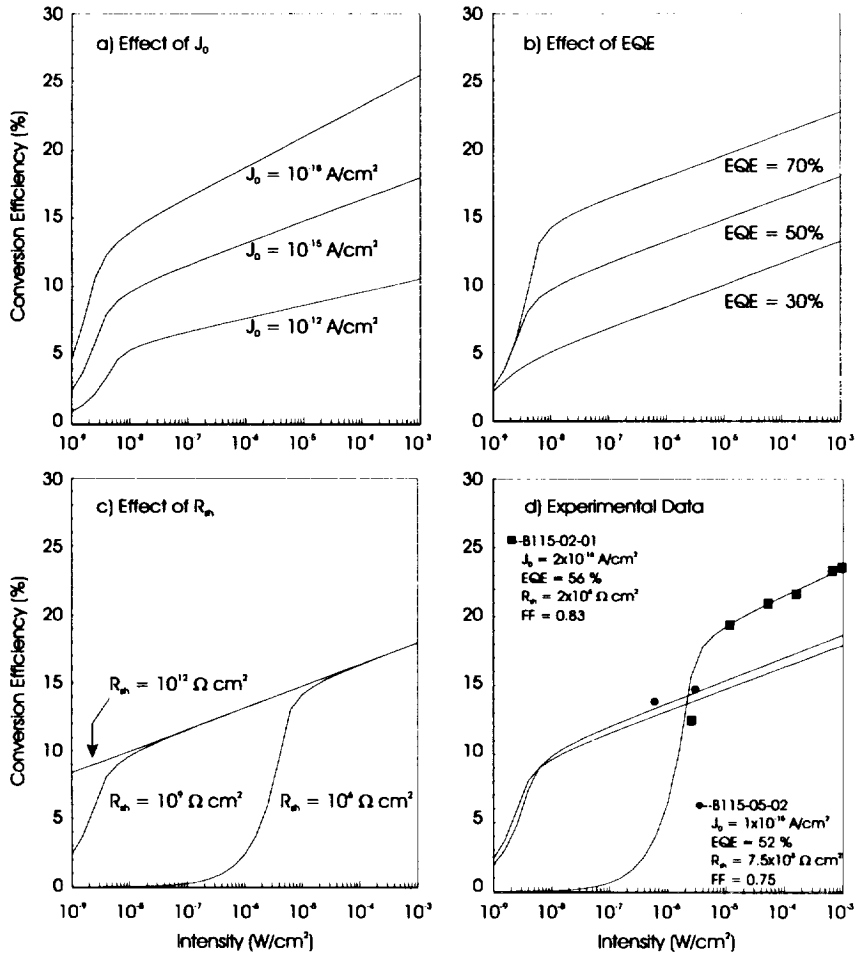

Figure 3. Effects of model parameters on predicted device conversion efficiency.

At a given light intensity conversion efficiency is linearly proportional to the external quantum efficiency (EQE) of the device. The fill factor also affects conversion efficiency linearly. The EQE is affected by surface recombination, the diffusion length of the emitter and base material, and the depth of the junction. For this application, the fill factor is mainly affected by the quality of the contacts at low current levels. Reducing J_{02} increases the voltage of the device at a given light intensity. The efficiency increase is less, it is log-linear (i.e. $\Phi \cdot \ln\Phi$) with the flux. The reverse saturation current depends on the carrier concentration of the material and the diffusion length in the material. The shunt resistance of the diode determines a threshold intensity for efficient conversion. The shunt resistance of the device seems to be mainly determined by the isolation technique utilized, and the depth of the junction.

The results of this modelling were used to determine the device parameters necessary to achieve 30% conversion efficiency for the "indirect conversion" β-battery. These are summarized in Table 2. For reference, parameters corresponding to the middle curves in the Figure 3 graphs ae also shown.

Table 2. Device Modeling Results

Device Parameter	Middle Curves	30% Conversion Efficiency
Reverse Saturation Current	10^{-15} A/cm^2	10^{-18} A/cm^2
External Quantum Efficiency	50%	80%
Shunt Resistance	10^9 Ω-cm^2	10^9 Ω-cm^2
Fill Factor @ 10^{-6} watts/cm^2	70%	80%

Device Results

Gallium phosphide layers were grown by liquid phase epitaxy and p/n junction devices were fabricated and characterized for low light intensity power conversion. AstroPower has demonstrated GaP based energy conversion efficiency of 440 nm blue light of 23.54% at 968 μW/cm^2 and 14.59% at 2.85 μW/cm^2.

Representative quantum efficiency curves of devices produced during this program are displayed in Figure 4. The external quantum efficiency (EQE) of GaP devices can be increased up to 20% by the application of an optimized AR coating, resulting in 70 to 80% EQE in the 380 to 480 nm spectral range.

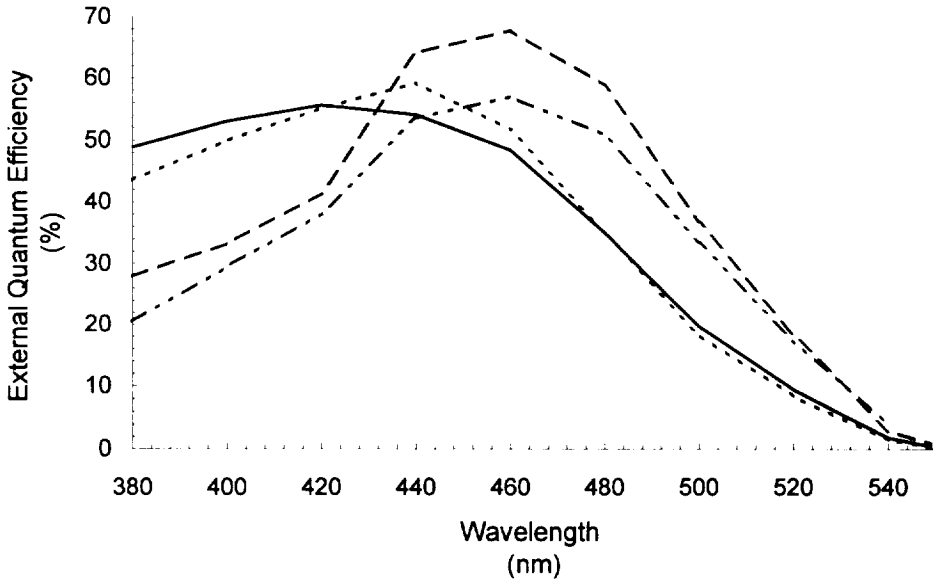

Figure 4. Quantum efficiency of some devices produced during the research program (no AR).

The J-V curves of device B115-05 illuminated by different wavelengths of light are displayed in Figure 5. This device has good shunt resistance, but the reverse saturation current is higher so that the photogenerated voltages are lower. Note that the conversion efficiency of 2.85 μW/cm^2 440 nm light is 14.59%. This color and intensity of light is barely visible to the naked eye.

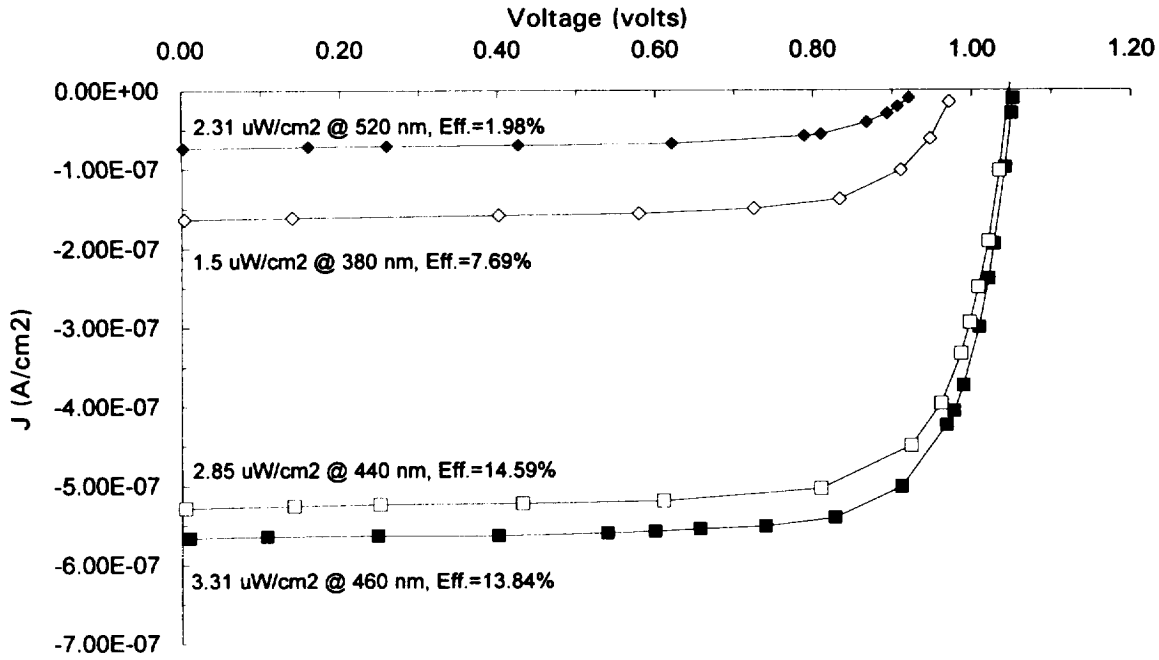

Figure 7. Conversion efficiency of device B115-05 for different wavelengths and intensities of monochromatic light.

At the low operating current levels for this type of device, a high series resistance can be disregarded, although the contacts must be ohmic. However, high shunt resistance is critical for low energy conversion efficiency.

A window layer was incorporated in the device design to passivate the surface of the device. The growth of a thin layer of AlGaP on the surface of the diode has also been found to significantly reduce surface recombination. This can be attributed to a combination of band bending effects and the possible formation of a passivating oxide.

A measurement of V_{oc} vs. J_{sc}, Figure 6, at varying light intensities is used to determine J_{02} and the shunt resistance of the device. This technique eliminates the effects of series resistance on the J-V characteristic and permits a straight forward determination of the diode ideality factor n and saturation current density J_o. In general, such a plot will exhibit several distinct regions with characteristic values of n and J. Under low forward bias, $n \approx 2$ and Jo is the depletion region

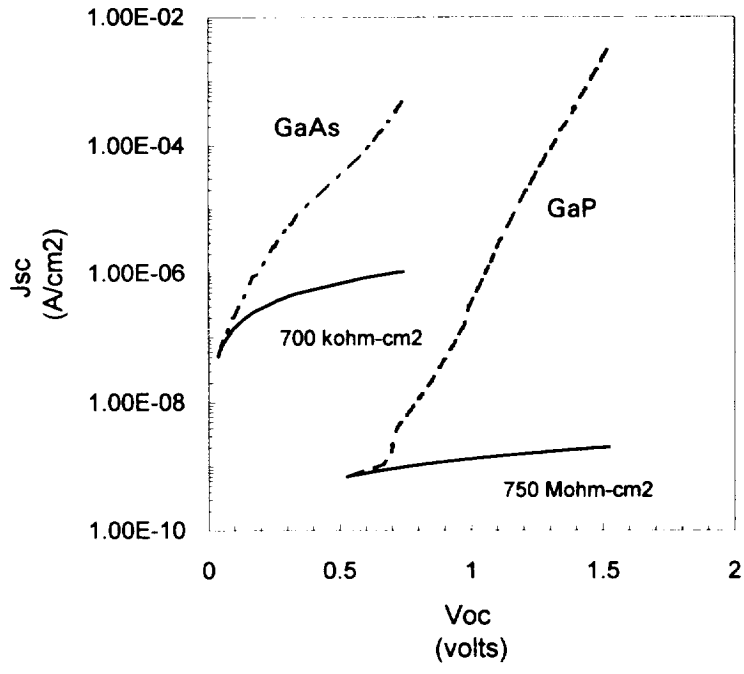

Figure 6. log J_{sc} versus V_{oc} for GaAs and GaP devices.

recombination current. Under high forward bias, $n \approx 1$ and J_0 is due to the recombination of injected minority carriers in the quasi-neutral region of the base layer. High bandgap materials rarely display n = 1 behavior. Figure 6 displays log Jsc vs. Voc for a GaAs solar cell and a GaP energy converter. The light intensity varies from ~ 1 $\mu W/cm^2$ to 100 mW/cm^2. There is no evidence of n = 1 behavior for either device. R_{shunt} is extracted from Ohm's Law. J_{02} is determined by the y-intercept. At room temperature, the n = 2 slope is 120 mV/decade of current.

The diffusion length of the base material is estimated from the absorption edge portion of the quantum efficiency curve. Due to some details in the experimental process, the values obtained are "characteristic" of the true value of the diffusion length. A proprietary growth enhancement has been found to both increase the short wavelength current generation of the device by promoting good window layer formation and to increase the long wavelength response of the device by increasing the diffusion length of the material. The "diffusion lengths" of the enhanced growth devices measured during this program are twice those of non-enhanced growths.

A twelve cell array was fabricated using GaP devices grown by the non-enhanced technique. This array consisted of devices in a two-string configuration. The cells were current matched at an operating point of 0.8 volts while illuminated by an 8.24 $\mu W/cm^2$ ZnS:Ag light source. The fabricated array had a better performance than the predicted values from the individual cell test data due to a current boost from the reduced shading for wire bonded interconnects compared to the probe station. The details of the current matching data are in Table 2. Figure 7 displays the J-V and P-V curve of the array illuminated by the phosphor light source. Since this array was fabricated from devices without growth enhancement, it is expected that an array with at least double the efficiency could be fabricated. Two devices (B115-50-01 and B-115-05-02), from enhanced growth runs, that were not incorporated into the array are included to show the efficiency achievable with this material at its present state of development. Array efficiencies above 20% should be achievable. For reference a GaAs cell is also included.

Table 3. Cell data for array elements illuminated by ≅ 8.24 $\mu W/cm^2$ ZnS:Ag light

Array Position	Cell	V_{oc} (V)	I_{sc} (nA)	V_{mp} (V)	I_{mp} (nA)	I at 0.8V (nA)	FF	η (%)
A1	B114-14-05	0.99	51	0.8	45	45	0.72	4.37
A2	B114-10-05	1.03	54	0.8	48	48	0.69	4.66
A3	B114-10-07	0.95	52	0.8	48	48	0.78	4.66
A4	B114-12-05	1.00	51	0.9	44	49	0.77	4.81
A5	B114-10-04	1.03	51	0.8	50	50	0.76	4.86
A6	B114-14-01	1.04	53	0.8	50	50	0.73	4.86
B1	B114-12-04	1.06	52	0.9	46	51	0.75	5.03
B2	B114-12-02	1.01	52	0.9	47	52	0.80	5.14
B3	B114-12-01	1.12	53	0.9	53	52	0.76	5.46
B4	B114-14-02	1.14	54	1.0	50	53	0.81	6.07
B5	B114-10-01	1.08	55	0.9	52	54	0.79	5.68
B6	B114-10-03	1.16	55	1.0	51	55	0.80	6.19
Array		**6.27**	**145***	**5.25**	**116**	**121 @ 4.8 V**	**0.56**	**5.52**
	B115-02-01	1.19	106	0.9	100	104	0.71	10.93
	B115-05-02	1.11	111	0.9	108	109	0.79	11.8
	GaAs cell	0.24	251	0.2	159		0.52	3.86

* Current boost is due to the elimination of probe shading after array fabrication.

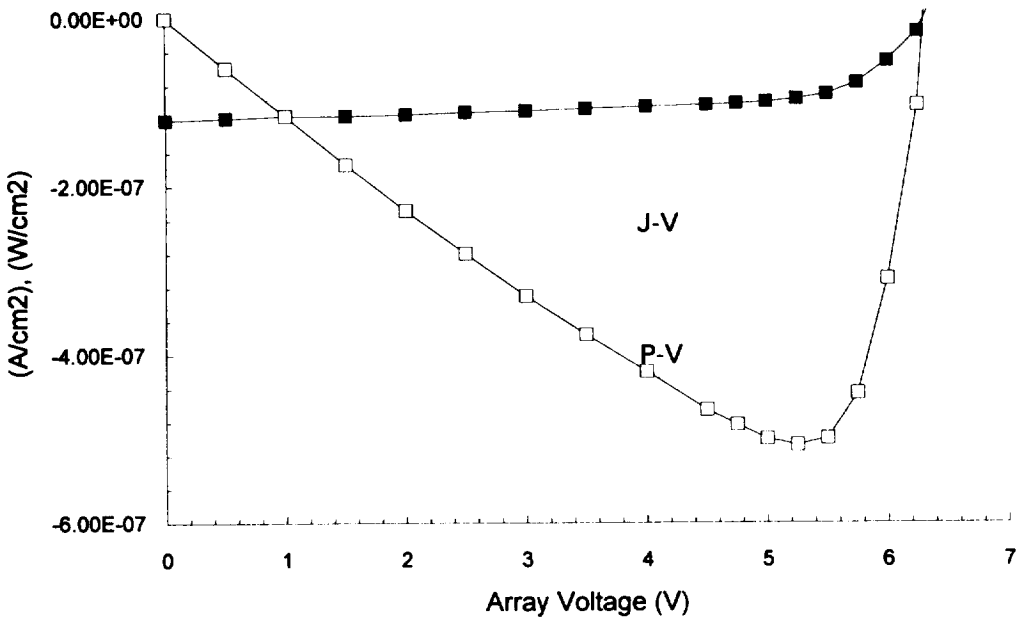

Figure 8. Prototype array illuminated by the ZnS:Ag phosphor.

CONCLUSIONS

Completion of the Phase I program resulted in a prototype 5 volt array based on a non-optimized photodiode structure for the indirect conversion of tritium beta decay to electrical power. Future programs will concentrate on β-battery system design, optimization of the photodiode energy converter, and the manufacturing solutions required for the economic production of the large semiconductor material quantities needed for the β-battery.

The β-battery design encompasses unique advantages. For low power applications, the proposed beta battery has six times less volume than $LiSO_2$ batteries. An optimized β-battery requires 60 cm^3 per mW while a lithium battery requires 360 cm^3 per mW (ref. 8). These batteries can be used in applications where an instrument package is to be left unattended for years in a remote location (such as at the bottom of the ocean or embedded in a roadway for the Intelligent Vehicle Highway System) with an intermittent telemetry stream or a low power housekeeping load. This type of battery will also prove useful in deep space probe power systems. The beta battery also has widespread commercial potential as an on-board power supply to maintain non-volatile memory.

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SESSION VII

CELL/MATERIAL PROPERTIES