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Spectrally selective, matched emitters for thermophotovoltaic energy conversion processed by tape casting

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The thermophotovoltaic (TPV) generator converts radiant energy from a high temperature emitter element into electric power using infrared responding photovoltaic cells. Spectral control is a primary issue in TPV applications. Conventional TPV generators have relied on filters to achieve selectivity and spectral control with near-blackbody ceramic emitters. Several practical problems have limited the success of this approach, particularly the present lack of a satisfactory wide-band infrared filter. A new, spectrally selective emitter is described in this work, and will be called the "bandgap matched" emitter because its emissive power spectrum is very efficiently matched with the infrared response of the GaSb photovoltaic cell. The superior spectral efficiency has been achieved with a novel combination of spectrally active, transition metal dopants within an infrared-transparent magnesium oxide ceramic matrix. High mechanical integrity, thermal shock resistance, excellent heat transfer characteristics, and near-ideal spectral efficiency have been achieved by fabricating composite Co- or Ni-doped MgO from thin ceramic ribbons made by the tape casting process. *© 2001 Kluwer Academic Publishers*

1. Introduction

The thermophotovoltaic (TPV) generator [1] has become the subject of intensive research and development because it promises to be a very clean and quiet source of electrical power [2–4]. The TPV generator has no moving parts, and TPV conversion systems can use a wide variety of energy sources including methane, hydrogen, radioisotope [5], wood powder [6], and direct concentrated sunlight [7]. Even when more environmentally harmful hydrocarbon fuels such as propane or diesel fuel [8] are used with TPV energy conversion systems, the fuel can still be burned in a continuous way that greatly reduces many toxic emissions. There is evidence, for example, that the toxic NO_x emissions produced by internal combustion engines can be nearly eliminated by substituting TPV conversion systems [9] that operate at temperatures below 1400°C. With the recent commercial production of large quantities of GaSb infrared photovoltaic cells [10], and the invention of "Bandgap Matched Emitters" [11, 12]. TPV energy conversion may soon provide a practical solution to some of the energy issues that we face.

2. Background

Fig. 1 shows the portion of a theoretical 1600 K blackbody radiation spectrum that can be converted into useful electrical energy by an infrared-responding GaSb photovoltaic cell [10] with bandgap energy of 0.73 eV. The convertible portion of the spectrum for a Si cell with bandgap energy 1.12 eV is also included for comparison. An emitter with a blackbody emissive power spectrum radiates the theoretical maximum amount of energy at each wavelength at a given temperature, and can be described by Planck's Law. The integrated area under the emissive power curve within any wavelength range is equal to the total power that is radiated within that same range.

The GaSb photovoltaic cell absorbs more of the incident photons and generates far more electrical power than the Si cell when exposed to the same 1600 K radiant emitter, due to the smaller bandgap energy of the GaSb cell. The increased current that is generated in the GaSb cell more than compensates for the decreased open circuit voltage that is a consequence of the reduced bandgap energy. The "ideal" radiant emitter for use with GaSb photovoltaic cells would have an emissive power spectrum that very nearly duplicates the shaded portion of the diagram in Fig. 1, that is high emissivity between 1.0 μm and 1.7 μm and minimal emissions at wavelengths greater than 1.7 μm.

Full-spectrum or near-blackbody type emitters are used in most conventional TPV generator designs, and the problem of spectral control is the most challenging design requirement. High conductivity, polycrystalline silicon carbide (SiC) ceramic elements are frequently chosen as the emitter material [13]. These SiC elements are similar to the high temperature heating elements used in electric furnaces. SiC is an attractive material for

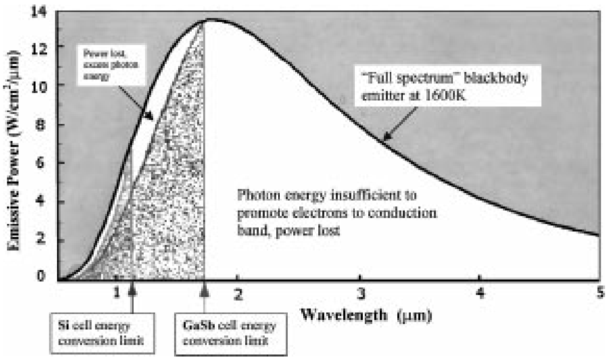

Figure 1 Emissive power curve for a 1600 K theoretical blackbody, and the utilization of radiant energy by GaSb and Si photovoltaic cells.

TPV emitter applications because it has exceptionally high thermal shock resistance, and because it has the ability to resist decomposition in air atmospheres up to a temperature of about 1600°C.

In theory at least, full-spectrum emitters can work efficiently with photovoltaic cells if infrared filters can be devised that effectively reflect nearly all of the non-convertible radiation back to the emitter. At this time however, no high-efficiency ($>10\%$) TPV generator is readily available on the commercial market. The primary reason for this is that it appears to be impossible to build practical infrared filters that can perform adequately under the rigorous demands of the TPV generator environment. Low conversion efficiencies stem from the decreased emitter temperatures that result when non-convertible radiation is not contained and recycled by the spectral filters. Inadequate spectral filters also can lead to unmanageable heat loads on the PV cells, filters, insulating materials and other generator components.

Researchers in the field recognized at an early stage that it would be better not to emit any radiation at non-convertible wavelengths in the first place, and began work on developing "spectrally selective" emitters. Spectrally selective emitters take advantage of the ability of certain rare earth oxides to radiate in a relatively narrow predetermined wavelength range when thermally excited at high temperatures (1500–2000°C). Guazzoni [14, 15] appears to have published some of the first work on spectrally selective emitters when he identified several of the rare earth oxides including erbium oxide and ytterbium oxide as possible candidates for spectrally selective emitters in TPV systems that employed germanium or silicon photovoltaic cells.

These first spectrally selective emitters did not give the improvements over blackbody emitters and filter combinations that researchers hoped for. Problems with poor spectral efficiencies and fracturing under thermal stress were persistent. The tendency for mechanical failure and fracturing is common to most dense oxide ceramics in bulk monolithic form (non-fiber, non-composite, etc.), and is caused by the build-up of stress generated by the severe thermal gradients that are present during operation of the TPV system.

Significant advances were made by fabricating erbia, ytterbia, holmia, and neodymia rare earth oxide emitters in a small diameter (approx. 10 μm) fibrous form [16]. The thin ceramic fibers are said to couple well to the combustion products of a flame because of the high thermal transfer coefficient associated with these small diameter elements [16]. The filamentary structures are also thermally stress tolerant because no significant thermal stress can be built up across the diameter of the very small diameter filaments, and flexing relieves stress build-up along the axis of the filament.

The fibrous, rare earth oxide type emitters appear to suffer from several important disadvantages, however. Light structures composed of the small diameter, fibrous emitters tend to be rather fragile and are easily damaged, particularly under the pressure of high velocity combustion byproducts. The fundamental problem that has plagued the use of selective line (rare earth) emitters in TPV systems has been the structural integrity of these systems [17]. The light-emitting mantle in a typical gas-burning lantern is a familiar example of a fibrous ceramic emitter that is easily broken, and must be frequently replaced. Fibrous rare earth selective emitters also tend to require structural materials such as quartz fibers [17], or some other ceramic matrix material for support, and this tends to give rise to higher levels of non-convertible radiation at wavelengths longer than about 4 μm. Another inherent disadvantage is that the use of ytterbia, erbia, or other rare earth oxides results in only narrow "line-type" emissions at the convertible wavelengths where emissive power should be maximized. Other researchers [18] have developed "Superemissive" light pipes (SELP) and reported attractive optical power densities of 12.0 W/cm^2 for an ErAG/YAG single crystal $Er_3Al_3O_{12}$ emitter heated by high temperature methane–oxygen torches. Due to the narrow line-type emissions of the rare earth oxides, it appears to be necessary to operate the SELP, and other rare earth oxide emitters, at excessively high temperatures (2073 K for ErAG/YAG) in order to achieve high emissive power densities. In reference to the rare earth metal oxide emitters and the excessively high operating temperatures, it has been observed that a disadvantage of this type of emitter is the high evaporation rate, and this leads to a short lifetime [19].

It is believed that the low photovoltaic convertible power of erbium oxide emitters is due to the narrow line emissions, and that one of the ways to increase the photovoltaic convertible power is to broaden the line emissions [20]. One approach has been to develop a "Multiple-Dopant Selective Emitter" with a mixture of erbia and holmia rare earth oxides that exhibit high emittance peaks at 1.55 μm for erbia and 2.01 μm for holmia [20]. Unfortunately, the holmia emissions are outside of the conversion range for the simpler, low-cost GaSb photovoltaic cells [21] or Ge cells, and more complex ternary InGaAs, or quaternary GaInAsSb photovoltaic cells [22] are required. Er-YAG and erbia, reinforced with alumina, thick film emitters have also been fabricated. An optimum selective emitter thickness is said to be about (0.15–0.4 mm) for obtaining maximum emittance [23–25].

Recent measurements (to be published elsewhere by the authors) indicate that the emittance of the new Ni-doped MgO tape cast emitters can be greater than 0.85 at a near optimal wavelength of about 1.4 μm. This value is significantly higher than the value of approximately 0.55 that was reported by Guazzoni [14] for monolithic erbium oxide at a temperature of 1540 K.

There are three critical design requirements that must be satisfied for spectrally selective emitters to be useful in a practical energy conversion system. First, the emitter must be chemically stable. Emitter materials must be resistant to decomposition at temperatures that may reach well above 1400°C, and in the presence of reactive hot gas combustion byproducts, particularly carbon monoxide. Second, the emitter must maintain its mechanical integrity and operate reliably when subjected to severe thermal gradients during transient and continuous operation. The heat transfer rates from the hot combustion reaction to the emitter must be as high as possible, and this usually implies emitter elements with relatively small dimensions and/or high thermal conductivity. Finally, the spectral selectivity of the emitter should be optimized or "matched" with respect to the energy bandgap of the photovoltaic cells to attain the highest conversion efficiency for a given rate of energy input or fuel consumed.

The central objective of this work has been to meet all these critical requirements by developing a novel emitter material and taking advantage of the ceramic tape casting technique to make durable new matched emitter structures from thin, woven ceramic ribbons. The experimental results that will be presented here indicate significant efficiency gains over conventional systems.

3. Experimental procedure

3.1. Fabrication of tape cast matched emitters

Matched emitters are fabricated by starting with a high purity, infrared-transparent, refractory ceramic host, such as magnesium oxide. To obtain strong spectral emissions at the optimal wavelengths, the infrared-transparent host is doped with small amounts of Co_3O_4 or NiO transition-metal oxides. Initial experiments involving a range of doping concentrations and various transition metal oxides indicate that the best spectral performance is obtained with 2 wt.% Co_3O_4, or 4 wt.% NiO, in an MgO host.

The flow chart in Fig. 2 outlines the process that was developed for non-aqueous tape casting of MgO. The first step is to dry mix several hundred grams of the host material, "fused" MgO powder, particle size $<40\ \mu$m, purity $>99.85\%$, (Accumet Materials Co., Ossining, NY), with 2–4 wt.% of the dopant, Co_3O_4 or NiO transition metal oxide powders (Mallinckrodt Baker, Inc., Phillipsburg, NJ). The powders were then added into a mixture of xylene (Fisher Scientific, Pittsburgh, PA) and methanol (McCormick Distilling Co., Weston, MO) as solvents containing 3.3 wt.% "blown Z-3 menhaden fish oil" dispersant (Werner G. Smith, Inc., Cleveland, OH). The solvent mixture used in this work was about 81 wt.% xylene to 19 wt.% methanol. The solvent mixture was previously optimized for creating a steric suspension with the menhaden fish oil dispersant [26, 27]. The slurry is then roll-milled with cylindrical zirconia grinding media (YZ-110HS, 9.5 mm diameter, Norton Advanced Ceramics, Export, PA) for 24 hours. Binder and plasticizers are then added and the slurry is roll-milled again for 16 hours. The amount of binder to be added to the slurry is about 7 wt.% polyvinyl butyral (Butvar B-98, Solutia, Inc., St. Louis, MO), based on the total weight of the solvents. A plasticizer mixture is also added to the slurry consisting of 3.5 wt.% polyethylene glycol 400 (Union Carbide, Danbury, Ct.) and 3.5 wt.% butyl benzyl phthalate (Solutia, Inc., St. Louis, MO) again based on the total weight of the solvents. The slurry is then decanted from the grinding media, and de-aired for about 4 minutes in vacuum before it is ready to cast.

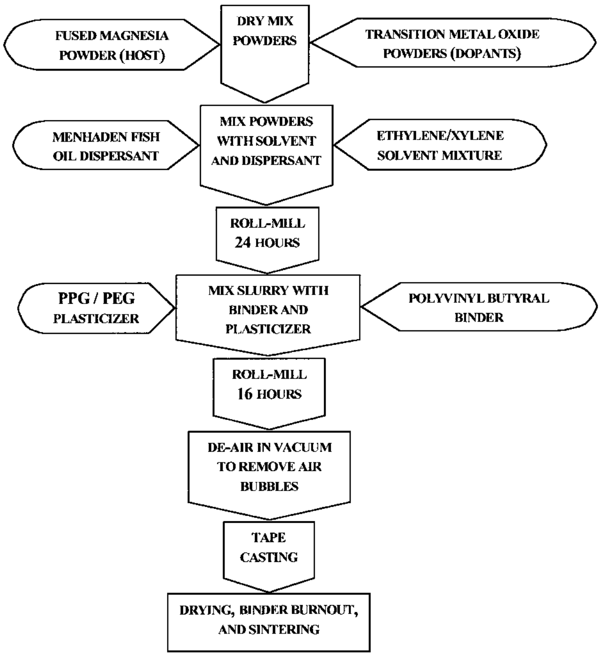

Figure 2 Flow chart of tape casting process used to produce thin, flexible, ceramic powder loaded sheets.

Tape casting is carried out on a commercially available unit manufactured by Richard E. Mistler, Inc., (Model TTC-1000). When casting magnesia slips, the gap on the single 10 cm doctor blade is typically set between 0.6–0.7 mm with the run speed at 40 cm per minute. The airflow rate is about 90–120 cc/min., and the casting is done on a silicone-coated Mylar® carrier sheet that allows for easy release of the ceramic tapes after drying.

The green tape cast sheet is placed between an upper and a lower refractory ceramic substrate, or "setters", before firing. The green MgO tapes are sintered at a nominal temperature of 1520°C for 2 hours in an air atmosphere, after a 3-hour binder-burnout step at 498°C. During the firing process, the setters prevent severe warping of the tape cast ceramic that would otherwise occur without the setters to press the ceramic tape flat during fusion and densification. High-purity, zero-porosity zirconia setter plates (TYK Inc., Japan), approx. $10 \times 10 \times 0.1$ cm, are used because they are resistant to warping and the diffusion of any volatile components in the tape cast ceramic. The "green" ceramic tape is delicate after binder burnout, and very little shear stress at the interface of the setter and the tape can be tolerated when the ceramic tape begins to

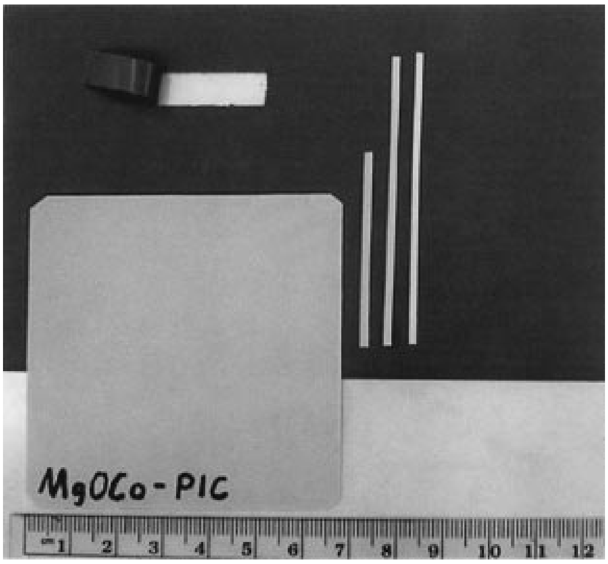

Figure 3 Picture of Co_3O_4-doped MgO tape after casting and drying with thin ceramic plate and ribbons produced by sintering tape at 1520°C.

shrink and densify. The top setter generally needs to have a total weight of less than 50 grams with a surface area of 100 cm^2 in order to prevent cracking the tape cast ceramic.

A buffer sheet material containing setter powders and binders was used for sintering the MgO tapes between the setter plates [28]. Zirconia setter powders with an average particle size of about 12–18 μm (Teledyne-Wah Chang, Albany, OR) are dispersed in a water-based hydroxypropyl methocellulose binder (Methocel F4M, Dow Chemical Co., Midland, MI). The approximately spherical particles act as an anti-friction, anti-sticking medium that facilitates densification and uniform shrinkage of the ceramic tapes. The zirconia setter powders are deposited in a thin, highly uniform layer on the green tapes during the methocellulose binder burnout. Fig. 3 shows cobalt-doped MgO sheets and ribbons before and after sintering.

Tape cast, yttria stabilized zirconia (YSZ) ribbons were also used for strengthening and fixing the magnesia ribbons to construct co-woven emitters. Smaller panels do not appear to require strengthening with the YSZ ribbons, however panels larger than about 10 cm can be reinforced with a co-woven structure, particularly when gas combustion products are forced to flow through the panel surface. The YSZ tapes were made in a manner similar to the processing of MgO tapes, using zirconia powders (Tosoh TZ-3Y) and sintering at 1520°C in air for 2 hours, after a binder-burnout step at 490°C for 3 hours. The thin, high-density, stabilized zirconia (3 mol% Yttria) ribbons have exhibited superior resistance to fracture under thermal stress or shock when compared to tests conducted on similar ceramic substrates made out of high purity alumina, mullite, spinel (magnesium aluminate), YAG, and magnesium oxide.

Fig. 4 shows an example of a "woven" matched emitter panel constructed from tape cast ribbons in the prefired form, and then sintered at high temperature to form a rigid ceramic structure that is highly resistant to thermal stress failure. The ceramic ribbons are free to flex or expand to relieve the build up of thermal stress, and the vents created by weaving the ribbons provides for excellent thermal coupling with the gas combustion products.

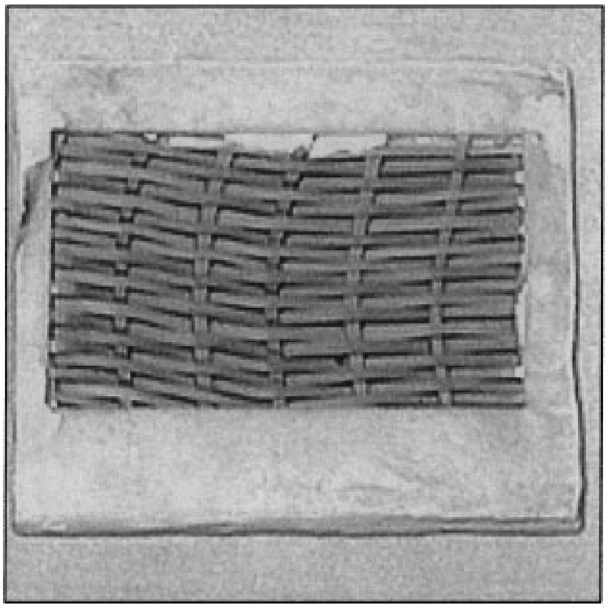

Figure 4 Matched emitter panel made from woven tape cast ribbons, after sintering. The panel size is approximately 10 cm by 5 cm.

3.2. Spectral emissive power measurements for single ribbons

Making accurate measurements of emitter surface temperatures has proven to be a formidable task. There is still debate among researchers over the best method to use. Conventional optical pyrometry is not reliable unless the emissivity can be accurately estimated or otherwise determined for the emitter prior to the temperature measurement. It is quite difficult in general however, to obtain an accurate emissivity value for spectrally selective emitters because their emissive power spectrums will (by definition) deviate radically from the theoretical Planck's Law or blackbody spectrum.

Useful spectral information has been obtained based on "relative" emissive power measurements that compare potential emitter materials with a standard sample under fixed test conditions. In this type of measurement, the objective is to hold the geometry of the experiment, including the optics and the dimensions of the ribbons as near constant as possible. Under these conditions the view factors should be constant, and the emissive power measurements are therefore absolute except for a common scaling factor.

The ceramic ribbon under test is held in a fixed position and heated with the flame from an air-propane torch. The thermally excited emitter ribbon appears much brighter than the emissions from the nearly "non-luminous" air-propane flame. The fuel flow to the torch should be adjustable and continuously regulated. Radiation from the hot ceramic ribbon passes through a water-cooled aperture, a light chopper, a filter wheel, and finally through the entrance slit of a CM110 (CVI Laser, Inc., Albuquerque, NM) digital, scanning monochrometer, where the intensity may be resolved in very narrow wavelength intervals. The intensity at a particular wavelength is detected with a liquid nitrogen cooled InSb/MCT detector (EG&G) and a lock-in amplifier (PAR 5105 Programmable Lock-In Amplifier). The intensity-wavelength data for multiple scans can be stored in a digital computer and retrieved later for analysis. The optical geometry, ribbon view factor and dimensions, and chemical energy input (air-propane flame) are held as constant as possible for comparative studies. The raw intensity data is converted to relative emissive power as a function of wavelength by calibrating the various instrumentation gain factors with a high-temperature blackbody infrared source.

3.3. Emitter panel measurements

The emitter panel test fixture allows for combustion of the propane or methane fuel to take place in a hollow cylindrical section of a high-temperature fibrous alumina insulating tube. Gas pressure is regulated with an adjustable regulator and flow is controlled with a sensitive rotometer and digital monitor. Interchangeable emitter panels can be tightly fixed to the front face of the combustion chamber, and the back face of the combustion chamber is covered with a sapphire window that is highly transparent from the visible wavelength region and extending to wavelengths as long as 6 or 7 μm. The sapphire window allows viewing of the “hot” side of the emitter panel inside the combustion chamber and acts as a heat shield for photovoltaic cells and other instruments including a radiometer that measures the total radiated power. Energy is transferred from the hot combustion gas to the emitter panel as it passes through vents in the panel. Another infrared transparent sapphire window may be placed in front of the emitter panel to deflect the combustion gas. A water-cooled, NASA calibrated GaSb photovoltaic cell is set at a fixed distance from the emitter panel so that the view-factor is held constant while various emitter panels may be substituted for comparison.

4. Results and discussion

Introducing certain transition-metal ions with incomplete d-orbitals into the host MgO ceramic material creates multiple new energy levels that give rise to strong, extended radiant emissions spanning the wavelengths where energy can be most efficiently converted by an infrared responding GaSb photovoltaic cell. Very low radiant emissions are observed at non-convertible wavelengths when doping concentrations are within an optimum value, and other impurities are minimal. When the level of transition metal dopant is increased beyond about 2 mole percent the spectral selectivity becomes less pronounced, and the emissive power spectrum begins to look more like that of a blackbody emitter. The increased emissivity at wavelengths between approximately 2 and 6 μm is believed to be the result of impurity and dopant interactions, free carrier absorption, defect electronic absorption and defect associations. At a dopant concentration of about 2 wt.% (or 1.1 mole%) NiO in the MgO host, the average nearest neighbor distance is close, about 3 lattice constants, and impurity interactions begin to be significant.

Measurements have shown that the air-propane or air-methane flame used to heat the emitter materials is very nearly non-luminous, except for a narrow but strong emission at the CO and CO_2 molecular resonance wavelengths near 4.26 μm [29]. It is believed that the heat transfer mechanism between the flame and the emitter is primarily kinetic in nature, or due to collisions with hot gas molecules, and not a strong function of the spectral (photon) absorption characteristics of the emitter. One important implication of this conclusion is that the amount of energy transferred to a near-blackbody emitter and a selective emitter should be approximately equivalent, given fixed geometries and combustion parameters, (air-fuel flow to the torch in this case). The steady state temperature of the selective emitter is therefore expected to be much higher when compared to a geometrically similar blackbody emitter. This is because the selective emitter is forced to radiate much more energy than the blackbody emitter at wavelengths in the range between 1 and 2 μm in order to maintain an energy balance. Stated in another way, it should require much less fuel, or input energy for the selective emitter to achieve an emitter temperature similar to the blackbody emitter, and equivalent emissive power levels in the wavelength range (1–2 μm) where energy conversion with GaSb cells is possible.

Fig. 5 shows emissive power spectrums for a cobalt-doped MgO ribbon before and after the spectrum of the air-propane flame has been subtracted. Intense power emissions in the vicinity of 4.3 μm are attributed to O-C-O and O-C molecular vibrations, and the less intense peaks at about 2.7 μm are from H-O-H, O-H, and O-C-O molecular vibrations that are generated during combustion of the propane. Except for a small uncertainty around 4.3 μm, an accurate power spectrum for the ceramic ribbon is left after subtracting the power spectrum of the flame without the ribbon.

A comparison of the relative emissive power of tape cast matched emitters composed of magnesium oxide host ceramic doped with the addition of 2 wt.% Co_3O_4 in one case, and with 4 wt.% NiO in another case, are shown in Fig. 6. Both of these MgO based emitters have spectral characteristics that would make them very attractive candidates for TPV energy conversion with GaSb PV cells whose cutoff wavelengths for energy conversion are around 1.72 μm. Note that the shaded region in Fig. 1 (useful energy conversion range for GaSb photovoltaic cells) is remarkably well “matched” with the emissive power measurements for the transition metal doped MgO ribbons in Fig. 6. The emissive power curve for a silicon carbide ribbon, (Fig. 7, Sylramic® S200 CMC, Dow Corning), not only closely approximates a theoretical blackbody, but the peak is much lower and has shifted to longer wavelengths compared to transition-metal doped MgO ribbons that were tested under near identical conditions. This is the result that is expected from energy balance considerations [30]. The temperature of an emitter will increase until the total power that is absorbed by the emitter is equivalent to the total power that is being radiated, with a maximum upper limit being set by the flame temperature. If an equivalent amount of heat is transferred into both a blackbody emitter and a selective emitter by the

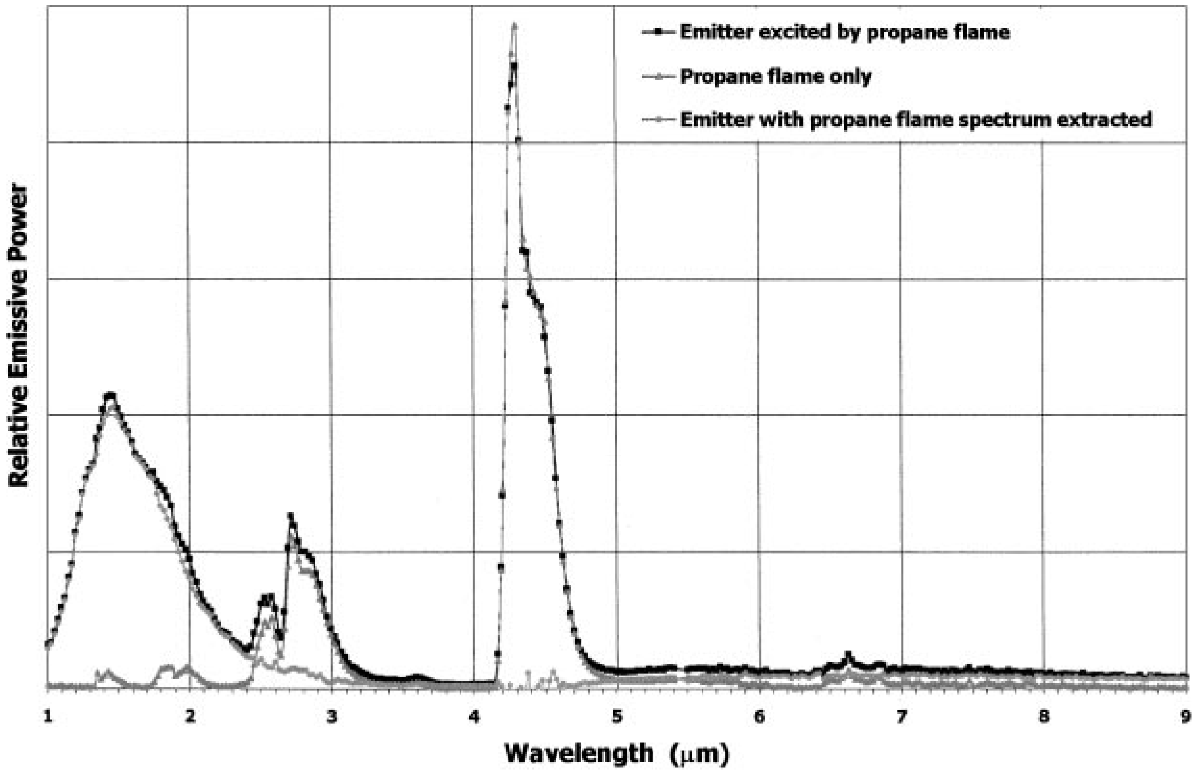

Figure 5 Emissive power measurements of matched emitter ribbon while thermally excited by propane-air flame, and same air-propane flame without emitter ribbon.

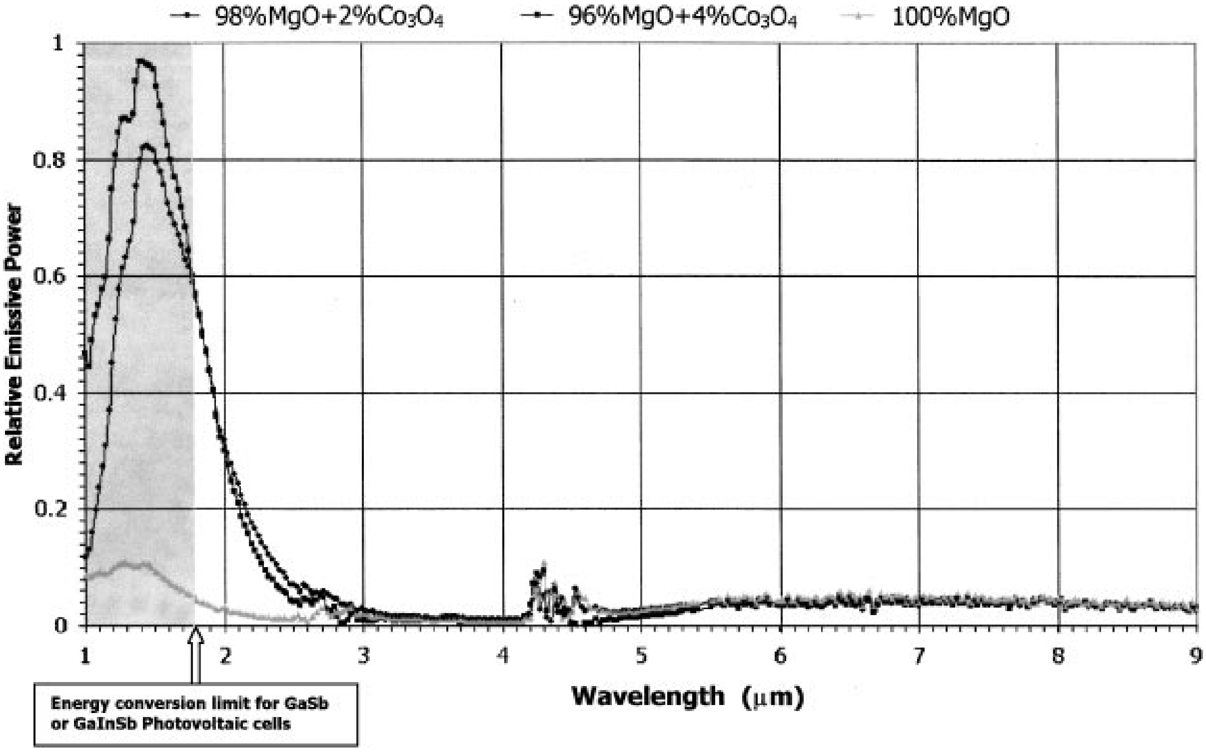

Figure 6 Comparison of relative emissive power for tape cast, Co- and Ni-doped MgO matched emitter ribbons and an un-doped, 99.85% pure MgO emitter ribbon.

gas combustion process, then the temperature of the selective emitter may be expected to rise more rapidly. This is because the chemical structure of the selective emitter is such that it is forced to radiate a larger portion of its energy within a much more limited wavelength range, approximately 1–2 μm, compared to the "non-selective" blackbody emitter. The temperature of the selective emitter is higher (by definition) than the blackbody emitter if the emissive power at any wavelength is greater than the blackbody emitter. The undoped, high-purity MgO ribbon may approach the limits set by the air-propane flame temperature, however radiation from the MgO ribbon is still severely limited by the low emissivity of MgO at wavelengths between 1 and 5 μm.

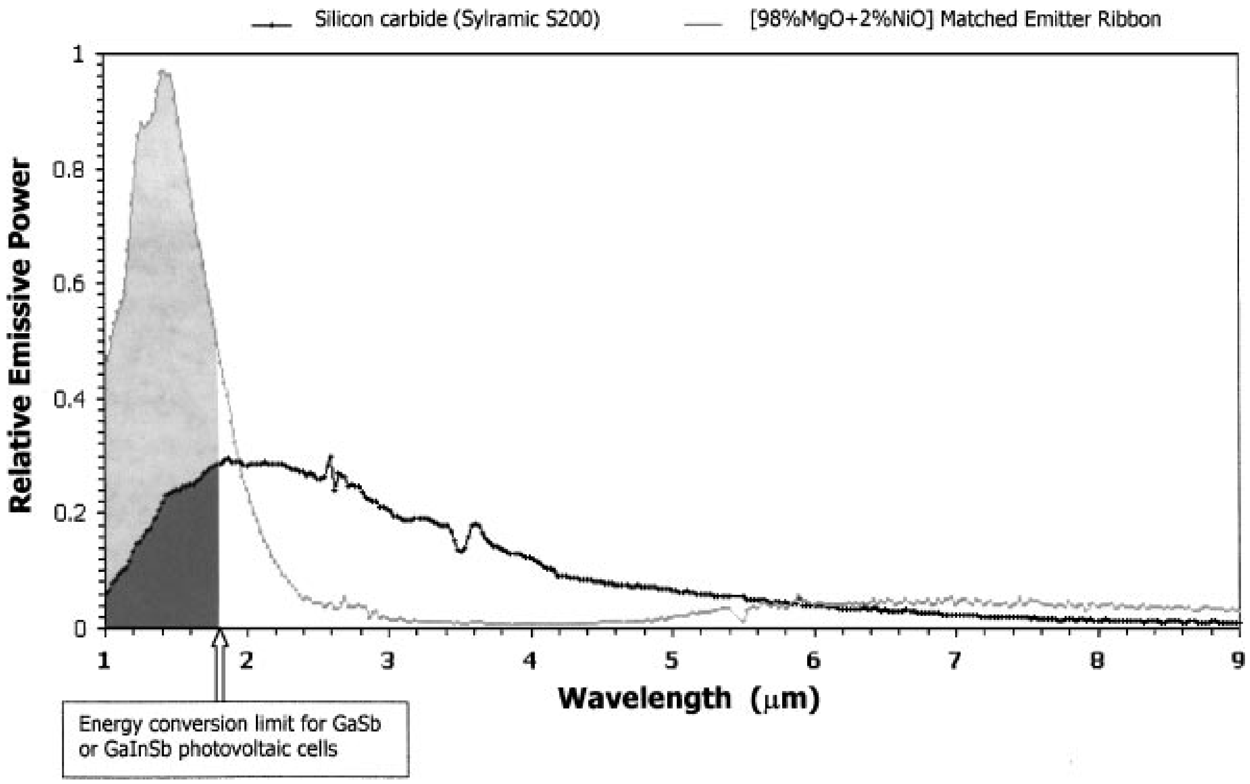

Figure 7 A near-blackbody, SiC ribbon compared with 2 wt.% NiO-doped MgO matched emitter ribbon.

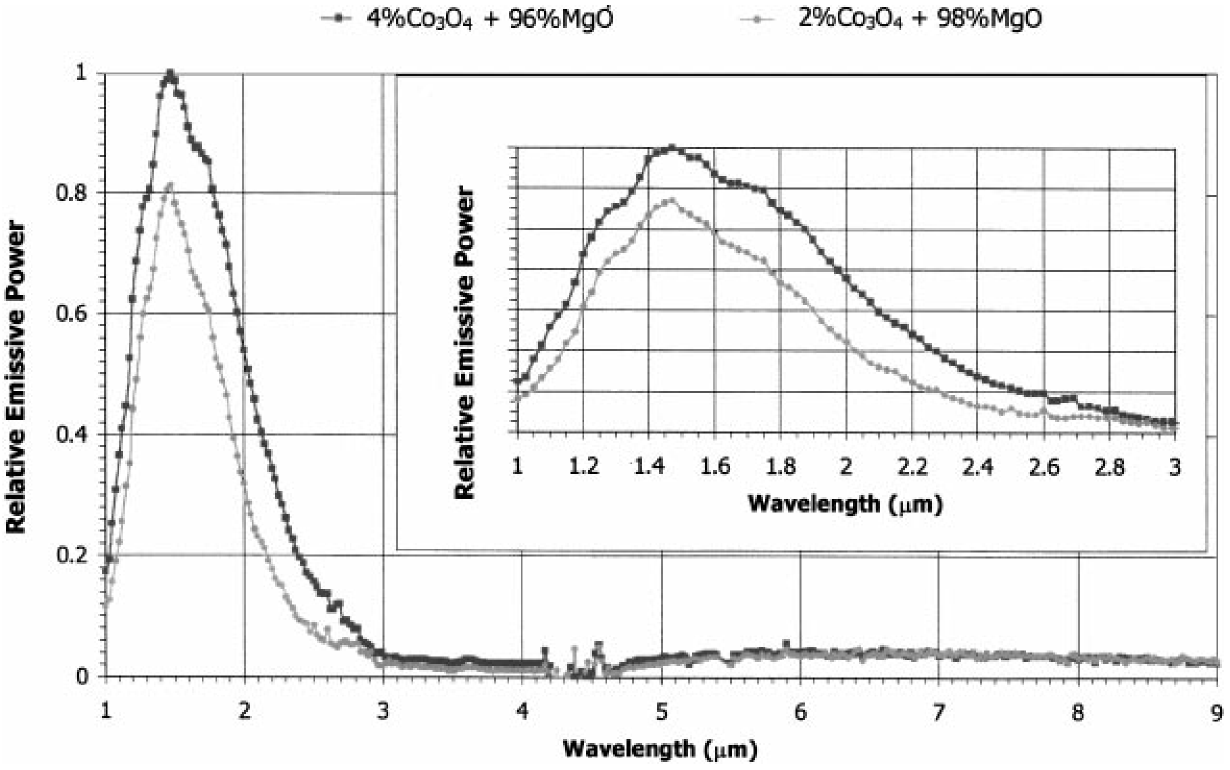

Figure 8 Comparison of relative emissive power for MgO ribbon doped with 2 wt.% and 4 wt.% NiO.

Although Co- and Ni-doped MgO emitters have not yet been rigorously tested with respect to evaporation of the dopants at prolonged high temperatures, the preliminary testing indicates that the chemical stability is very satisfactory at the operating temperatures around 1400°C.

Figs 8 and 9 show the spectral effects of increasing the amount of transition-metal oxide that is added to the MgO host ceramic ribbons. At low concentrations an increase in the amount of transition-metal dopant causes the peak emissions to increase and the emission bands broaden and shift to slightly lower wavelengths. Previous measurements [12] with Co-doped $MgAl_2O_4$ indicated that as the level of transition-metal dopant is increased beyond a few mole percent, the emissive power tends to saturate at a peak value and the emissions

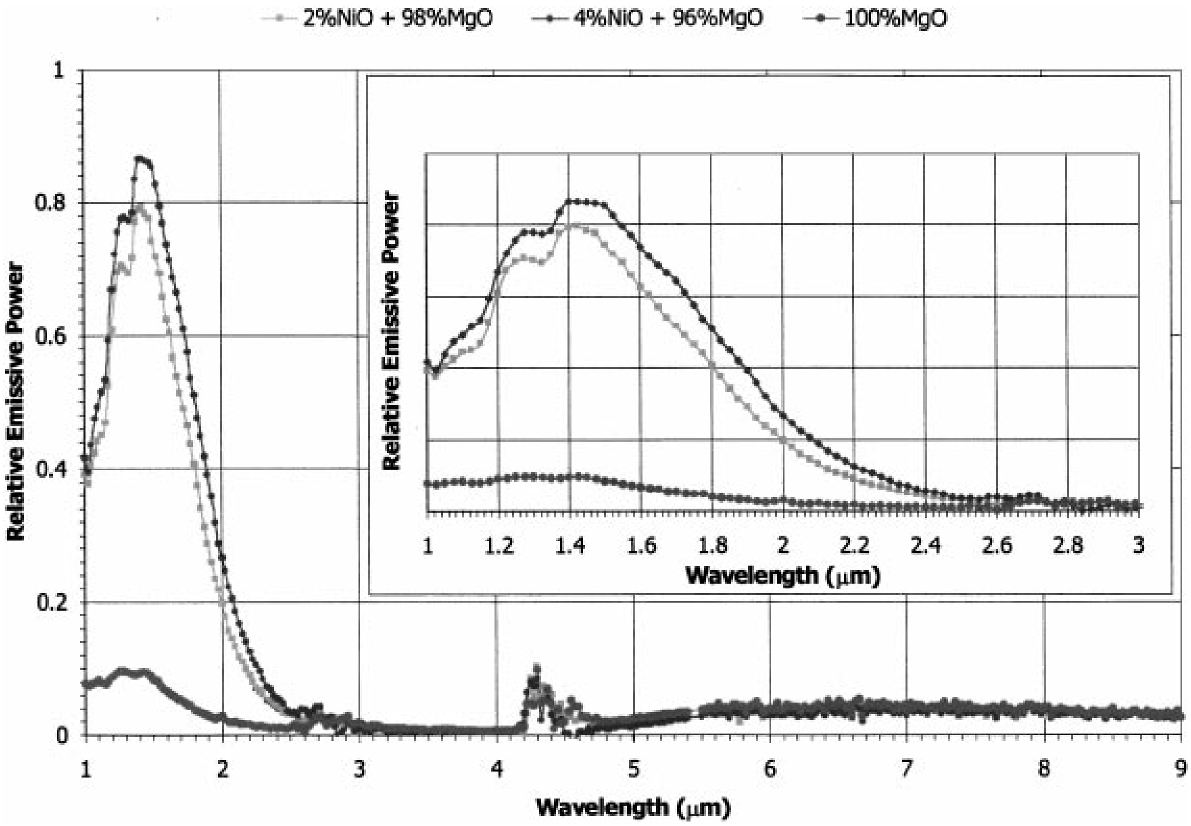

Figure 9 Comparison of relative emissive power for MgO ribbon doped with 2 wt.% and 4 wt.% Co_3O_4.

at longer wavelengths rise rapidly until the spectrum approaches that of a blackbody.

It is believed that the very low radiation levels exhibited by tape cast MgO ceramic ribbons at longer non-convertible wavelengths is due in part to the fact that tape cast emitters can be made very thin in at least one dimension. When the thickness of the emitter is decreased, this reduces the amount of unwanted impurities or defects that can contribute significantly to the spectral emissive power at longer wavelengths, (this effect is similar in principle with the reduced emissions that are observed with ceramic fibers and thick film emitters). The suppression of radiation at non-convertible wavelengths translates into reduced waste-heat loads on TPV generator components and increased system efficiency.

Predicting the performance of a particular emitter design in a real TPV energy conversion system is a complex issue, and measurements of spectral efficiency alone are not conclusive. Many factors determine the overall energy conversion efficiency of a TPV generator. Experience has shown that the chemical-to-electrical conversion efficiency of an air-propane burning TPV generator is a strong function of the way that heat is transferred from the combustion gasses to the emitter and the geometry of the radiation collection system. In order to gain confidence in the new, transition-metal doped MgO matched emitters, a test fixture that includes the "essential elements" of a practical TPV energy conversion system was constructed.

A GaSb photovoltaic cell may be placed in front of the emitter panel that is under test, and the short circuit current in the cell indicates the intensity of radiation (and the amount of useful power) that is being emitted by a particular panel at convertible wavelengths. The actual current measurements that are reported in Table I are very attenuated because the 1 cm^2 GaSb cell is placed at a relatively large distance, about 14 cm, from the emitter panel and the aspect ratio is small. It is possible to obtain much more impressive short circuit currents if the GaSb cell is placed very near the matched emitter panel, however comparisons are less accurate because it is then necessary to precisely duplicate the separation distance and aspect ratio for each test panel. A radiometer can be substituted for the GaSb photovoltaic cell to measure the total emissive power that is being radiated over practically the full spectrum (~0–30 μm). The ratio of GaSb cell current to total radiated power correlates directly with the overall thermochemical-to-electrical efficiency that can be obtained with a particular emitter panel.

An attempt was made to quantify the effect of spectral selectivity on conversion efficiency, and test the energy

TABLE I Emitter panel measurements

Emitter	Total Radiated Power[a] (W)	Cell Current[b] (mA)	Fuel Flow (slpm)
4 wt.% Co_3O_4 – doped MgO tape cast ribbon panel	0.054	2.40	0.24
Same as above, after coating with 840-Z blackbody paint	0.054	1.28	

[a] Radiometer full-spectrum detector.
[b] GaSb photovoltaic cell.

balance principle with panels made from tape cast matched emitter ribbons. The results of one experiment are reported in Table I. According to the radiometer detector, the *total power* radiated by a panel constructed from cobalt-doped MgO ribbons remained unchanged after the same panel was coated with a thin layer of high-temperature "blackbody paint" (840-Z black, available from Aremco, Inc., Ossining, NY). In contrast to the total radiated power, it was found that the emitter panel generated only about *half* the useful electrical current in a GaSb photovoltaic cell after it had been coated with the "blackbody paint". All other parameters, including air-fuel flow to the combustion chamber and configuration geometry were held as constant as possible. The fact that the total radiated power remained unchanged, regardless of whether the panel is spectrally selective or painted with the blackbody coating, is an indication that the total energy (heat) transferred from the air-propane flame is not strongly dependent on the spectral selectivity of the emitter. Furthermore, the fact that the spectrally selective, "uncoated" emitter panel also generates nearly twice as much current in the GaSb cell is an indication that the spectrally selective panel is forced to reach higher temperatures and radiate more energy at convertible wavelengths before an energy balance is reached.

Fig. 10 is a photograph of the emitter panel constructed from cobalt-doped tape cast ribbons, as viewed through the sapphire window of the combustion chamber. Fig. 11 is a photograph of the same emitter panel as Fig. 10, at the same fuel flow setting, that has been coated with a thin layer of the commercially available, high-temperature "blackbody paint" (840Z-black, Aremco, Inc., Ossining, NY). The side-by-side comparison of Figs 10 and 11 clearly shows that the selective emitter is visually much brighter *before* the blackbody coating is applied, although the total thermal mass and geometry are nearly identical.

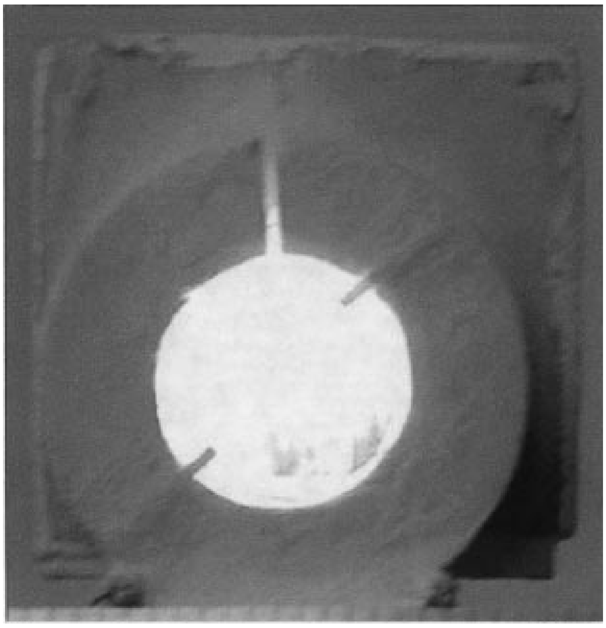

Figure 10 Matched emitter panel constructed from cobalt-doped MgO tape cast ribbons, viewed from combustion chamber of test fixture. The diameter of the inner window is about 2.5 cm.

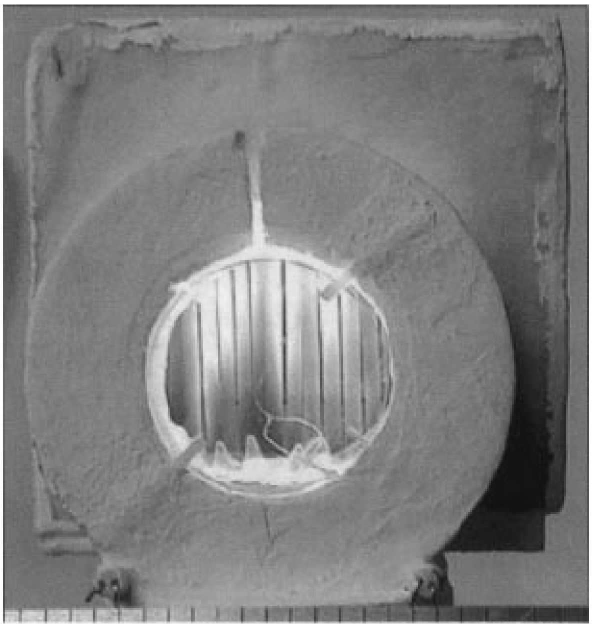

Figure 11 Same emitter panel as Fig. 10 after coating panel with thin layer of high-temperature "blackbody paint", (840Z-black, Aremco, Inc., Ossining, NY).

Of course, visual brightness does not always necessarily imply that the emissivity is also high at the near infrared wavelengths between 1 and 2 μm, where energy conversion is possible with GaSb photovoltaic cells. The human eye only responds to radiation in the visible range between approximately 435 and 670 nm. In this case however, at least for the Co- and Ni-doped MgO emitters, it happens that "visual brightness" does correlate well with "convertible emissive power" in the near infrared range between 1 and 2 μm.

5. Conclusions

A new thermally excited emitter material for TPV energy conversion has been described and termed the "matched emitter" because its emissive power spectrum is very efficiently matched with the portion of the spectrum that can be converted into electrical energy by infrared responding photovoltaic cells (GaSb or GaInSb-types for example). It has been shown that doping concentrations of 2–4 wt.% of Co_3O_4 or NiO within an infrared transparent MgO host can produce matched emitters with continuous, strong radiant emissions in the optimal energy range between 1 and 2 μm, and minimal radiation at non-convertible wavelengths.

Emitters for TPV energy conversion have been fabricated in the form of thin tape cast ribbons. A novel process for producing slips and tape casting MgO has been developed, as well as techniques for sintering the tapes and ribbons. Matched emitters have been constructed by weaving Co- or Ni-doped MgO tape cast ribbons into flat panels. The matched emitter panels and ribbons show heat transfer properties and thermal shock resistance that is superior to solid or monolithic panels.

The measured thermal-to-electrical energy conversion efficiency was reduced to nearly half its original value when spectrally selective emitter panels made from Co_3O_4 doped MgO tape cast ribbons were coated with a high-temperature blackbody paint.

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