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Thermal emission properties of $Al_2O_3/Er_3Al_5O_{12}$ eutectic ceramics

Narihito Nakagawa [a,*], Hideki Ohtsubo [a], Yoshiharu Waku [a], Hiroo Yugami [b]

[a] *Ube Research Laboratory, Ube Industries Ltd., 1978-5 Kogushi, Ube City, 755-8633 Yamaguchi, Japan*
[b] *Graduate school of Engineering, Tohoku University, Aoba-ku, Sendai 980-8579, Japan*

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Abstract

The mechanical properties and thermal stability of the $Al_2O_3/Er_3Al_5O_{12}$ (EAG) eutectic ceramics have been investigated at very high temperature. The emissive properties of this eutectic ceramics have also been measured and its possibilities of application to an emitter have been discussed. The present eutectic ceramic has excellent high-temperature strength characteristics, showing that tensile yielding stress is approximately 300 MPa at 1650 °C and superior thermal stability at 1700 °C in an air atmosphere. The present material shows strong selective emission bands at wavelength 1.5 μm due to Er^{3+} ion. The emission bands of this material are nearly coincident with the sensitive region of GaSb PV cell, therefore, the Al_2O_3/EAG eutectic ceramic can be regarded as one of the promising emitter materials in TPV systems.

Keywords: Mechanical properties; Thermophotovoltaic

1. Introduction

TPV generation systems have been studied as one of the new generation systems of electricity.[1–4] TPV systems have no moving parts, high power density and a wide-ranging heat source. A specific feature of interest with the rare-earth oxides, for example, Er_2O_3, Yb_2O_3 and Ho_2O_3 is the strong band emission, which ranges from the visible to the near-infrared wavelength region.[5,6] These bands permit strong thermal excitation at high temperatures. Therefore, their use as selective spectral radiation sources has become a subject of increasing interest.

Authors have already reported eutectic ceramics such as $Al_2O_3/Y_3Al_5O_{12}$ (YAG) or Al_2O_3/$GdAlO_3$ (GAP) or $Al_2O_3/Er_3Al_5O_{12}$ (EAG) with neither colonies nor grain boundaries, fabricated by using a unidirectional solidification. The eutectic ceramics have a microstructure, in which continuous networks of single-crystal Al_2O_3 phases and single-crystal oxide compounds (YAG, GAP, EAG) interpenetrate without grain boundaries. Therefore, the eutectic ceramics have excellent high-temperature strength characteristics, creep resistance, oxidation resistance and thermal stability at 1700 °C in an air atmosphere.[7–13]

The material containing 18 mole% of Er_2O_3 shows a strong emission peak at 1.5 μm of wavelength, so the $Al_2O_3/Er_3Al_5O_{12}$ eutectic ceramic, which has superior high temperature characteristics can be expected as one of materials for rare-earth selective emitters.

The first objective of this study is to investigate tensile high-temperature strength behavior from 1200 to 1750 °C and thermal stability at 1700 °C for 1000 h for the $Al_2O_3/Er_3Al_5O_{12}$ eutectic ceramic. The secondary objective is to evaluate thermal emission properties of this material[14,15] from 1200 to 1600 °C and examine the possibility of application to a selective emitter for a burner TPV generation system with GaSb cells.

2. Experimental

2.1. Raw powder

Commercially available α-Al_2O_3 powders (AKP-30, produced by Sumitomo Chemical Co. Ltd.) and Er_2O_3 powders (Er_2O_3-RU, submicron-type, produced by Shin-Etsu Chemical Co. Ltd.) were mixed to a mole ratio of

* Corresponding author. Tel.: +81 836 31 6139; fax: +81 836 31 6153.
E-mail address: 26359u@ube-ind.co.jp (N. Nakagawa).

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$Al_2O_3/Er_2O_3 = 81/19$, and wet ball milling using ethanol was carried out to obtain a homogeneous mixed powder. The slurry obtained was dried in a rotary evaporator to remove the ethanol. To obtain a cylindrical ingot, preliminary melting was performed in a molybdenum crucible (50 mm in outside diameter by 200 mm in height by 5 mm in thickness) heated by high-frequency induction heating.

2.2. Unidirectional solidification of Al_2O_3/EAG eutectic ceramic

Fig. 1 shows schematic drawing of the Bridgman type unidirectional solidification apparatus. All the unidirectional solidification experiments were carried out by using the advanced alloy crystalline structure controlling equipment at the Japan Ultra-high Temperature Materials Research Center (573-3 Okiube, Ube City, Yamaguchi Prefecture, 755-0001 Japan). A cylindrical ingot obtained was inserted into the molybdenum mold, which was installed in a vacuum chamber and then the molybdenum crucible heated by a graphite susceptor heated by high-frequency induction coils. The dimensions of the molybdenum crucible are the same as that used in preliminary melting. After sustaining the melt temperature at 1960 °C (about 100 °C above melting point) for 30 min, unidirectional solidification was completed by lowered of the molybdenum crucible at the speed of 5 mm/h. We fabricated the cylindrical ingot with 40 mm in diameter and 70 mm in length of the Al_2O_3/EAG eutectic ceramic.

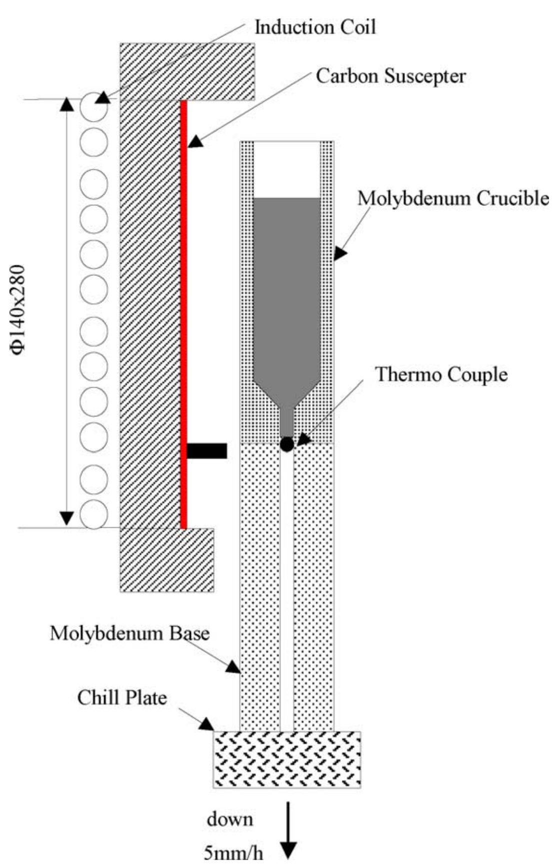

Fig. 1. Schematic drawing of the Bridgman type unidirectional solidification apparatus.

2.3. Mechanical testing method and microstructural characterization

The specimens used for tensile tests were selected so that their axial direction was parallel to the solidification direction. The dimensions of the tensile test specimen were shown in Fig. 2. The tests were carried out using the high-temperature uniaxial tension-compression and flexural test system (modified creep and fatigue machine, type 8562 produced by Instron) at the Japan Ultra-high Temperature Materials Research Center. The tensile tests were carried out from 1200 to 1750 °C in an argon atmosphere at a crosshead speed of 0.5 mm/min.

The thermal stability of the microstructure of the Al_2O_3/EAG eutectic ceramic was examined from microstructural changes after heat treatments at 1700 °C until 1000 h in an air atmosphere. The microstructure of the eutectic ceramic was observed by using scanning electron microscope (SEM). The high-resolution transmission electron microscope (HRTEM) observations of the interface structure between the phases were carried out with a JEM-2010 microscope.

2.4. Optical characterization

The plate specimens used for emissive test were fabricated so that their plane was perpendicular to the solidification direction. The dimensions of the test specimen were 10 mm × 10 mm × 0.3 mm. Fig. 3 shows the apparatus of thermal radiation spectrum measurements equipped with a FT-IR spectrometer. A specimen installed at the sample holder, which is constructed of SiC and Pt plates were heated by a natural gas burner. The intensity of thermal radiation was normalized be a standard black body furnace. The emission from specimen was detected by Fourier transform infrared (FT-IR) spectrophotometer. The emission spectrum measured is converted into an emissive power spectrum with the apparatus coefficient. To determine apparatus coefficient, the emission spectrum were measured by utilizing a black

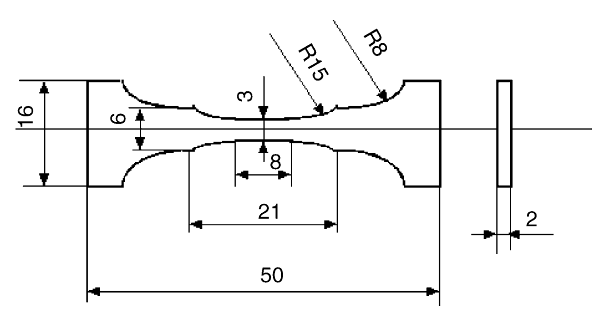

Fig. 2. Dimensions of the tensile test specimen.

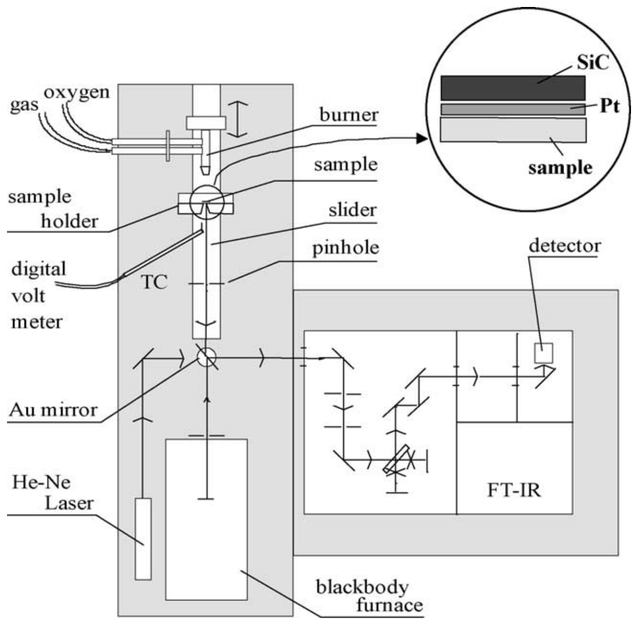

Fig. 3. Apparatus of thermal radiation spectrum measurements equipped with a FT-IR spectrometer.

body furnace. Apparatus coefficients are nearly constant independent of temperatures. Therefore, an apparatus coefficient spectrum at 1227 °C was adopted as a representative value to calculate emissive power spectrum of a specimen. The temperature of a specimen was changed by controlling the distance between the gas burner and the specimen, and measured with a Pt–Rh thermocouple at the surface of the specimen. In order to prevent uneven heating and remove the emission from the gas burner, a composite sample consisting of SiC, Pt and an Al_2O_3/EAG eutectic ceramic plate was used. The Pt plate was inserted between SiC and an Al_2O_3/EAG plate to prevent reaction between SiC and an Al_2O_3/EAG plate as shown in Fig. 3.

2.5. A selective emitter in TPV systems

Single-burner TPV apparatus is composed of an Al_2O_3/EAG emitter, a gas burner and infrared radiator surrounded by GaSb PV cells. A gas burner burnt mixture gases of kerosene and air and heated a specimen. The selective emitter rings with dimensions of 20 mm in outside diameter by 20 mm in height by 2 mm in thickness were produced by polishing with a diamond wheel from the Al_2O_3/EAG cylindrical ingot.

3. Results and discussion

3.1. Microstructure

Fig. 4 shows an SEM image of the microstructure of the unidirectionally solidified Al_2O_3/EAG eutectic ceramics. This composite consists of Al_2O_3 phases with a corundum structure and $Er_3Al_5O_{12}$ phases with a garnet structure; these were determined from X-ray diffraction patterns. And the white area in the SEM image is the $Er_3Al_5O_{12}$ phase, the dark area is the Al_2O_3 phase from EPMA analysis. The dimensions of the microstructure of Al_2O_3/$Er_3Al_5O_{12}$ eutectic ceramics are about 20–30 μm (this dimension is defined as the typical length to the short axis of each domain seen in the cross-section perpendicular to the solidification direction). The X-ray diffraction pattern at plane perpendicular to the solidification direction revealed an only diffraction peak from the (7 3 2) plane of the $Er_3Al_5O_{12}$ and the (1 1 0) plane of the Al_2O_3.

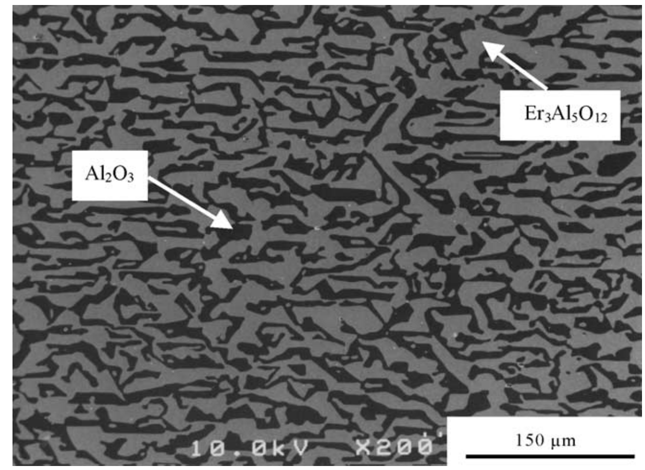

Fig. 4. SEM images of microstructure of cross-section perpendicular to the solidification direction of the Al_2O_3/EAG eutectic ceramics.

Fig. 5 shows a SEM micrograph, which illustrates the three-dimensional configuration of the $Er_3Al_5O_{12}$ phase in the Al_2O_3/$Er_3Al_5O_{12}$ eutectic ceramics from which Al_2O_3 phases had been removed by heat-treating in graphite powders at 1650 °C for 2 h. The configuration of the

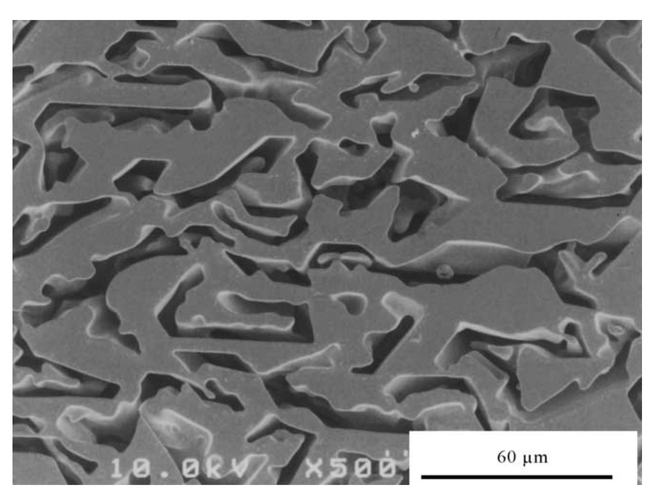

Fig. 5. SEM photographs of the three-dimensional configuration of the EAG phases in the Al_2O_3/EAG eutectic ceramics.

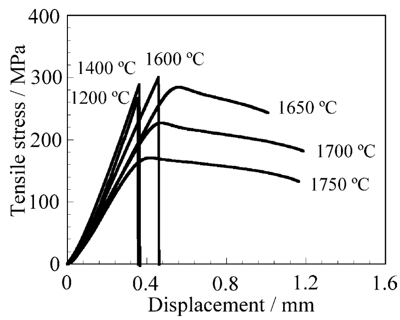

Fig. 6. Typical stress-displacement curves of the Al_2O_3/EAG eutectic ceramics obtained from tensile tests from 1200 to 1750 °C.

$Er_3Al_5O_{12}$ phase is a three-dimensionally connected porous structure of irregular shape. Therefore, we can conclude that the microstructure of the unidirectionally solidified Al_2O_3/$Er_3Al_5O_{12}$ eutectic ceramics consists of single-crystal Al_2O_3 phases and single-crystal $Er_3Al_5O_{12}$ phases with neither colonies nor pores.

3.2. High temperature tensile strength and thermal stability

Fig. 6 shows the stress-displacement curves observed in the tensile tests of a unidirectionally solidified Al_2O_3/EAG eutectic ceramics from 1200 to 1750 °C. The present materials show a brittle fracture from 1200 to 1600 °C as shown in Fig. 6. Tensile strength was approximately 300 MPa and independent of testing temperatures from 1200 to 1600 °C. While the materials shows substantial plastic deformation above 1650 °C. The tensile yield stress was very high stress of approximately 300 MPa at 1650 °C and thereafter decreases with an increase in temperature.

Fig. 7 shows SEM images showing the microstructure of the cross-section perpendicular to the solidification direction of an Al_2O_3/EAG eutectic ceramic after 500, 750 and 1000 h of heat treatment at 1700 °C in an air atmosphere. The specimens used for the heat treatment were obtained from the same cylindrical ingot as that of tensile specimens. Even after 1000 h of heat treatment, no grain growth of the microstructure and void formation were observed. In contrast, a sintered composite with the same chemical composition shows grain growth and there are many pores lead to reduction of strength at 1700 °C only for 50 h.[12] It has been reported that a unidirectionally solidified Al_2O_3/$Er_3Al_5O_{12}$ eutectic fibers (19.5 mole% Er_2O_3) has superior flexural strength, creep resistance at high temperatures, and is a candidate for high-temperature structural materials. However, coarsening occurred during creep tests at temperatures above 1500 °C[16] The present materials were shown to be very stable during lengthy exposure at high temperature of 1700 °C in an air atmosphere. This stability was obtained by the following means: a unique microstructure consisting of three-dimensionally continuous and complexly entangled single-crystal Al_2O_3 and single-crystal EAG; and the fact that no amorphous phase were formed at the interface boundary between the Al_2O_3 phase

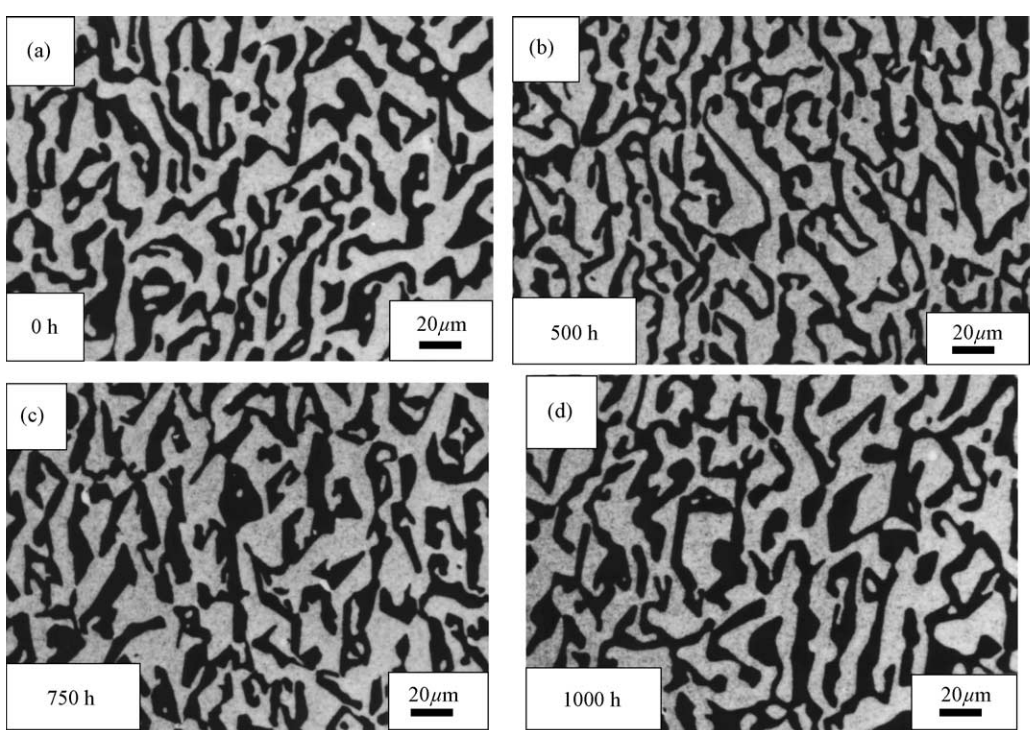

Fig. 7. SEM images showing microstructural change of cross-section perpendicular to the solidification of the Al_2O_3/EAG eutectic ceramics before and after heat treatment until 1000 h at 1700 °C in an air atmosphere.

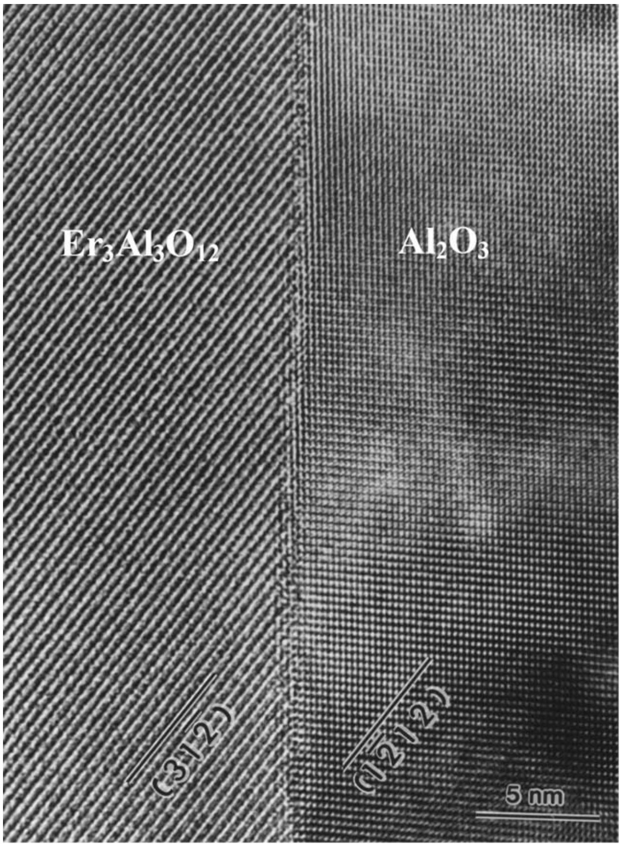

Fig. 8. High-resolution TEM images of the interface boundary between the Al_2O_3 phase and EAG phase.

and EAG phase shown in high-resolution TEM images of Fig. 8.

3.3. Thermal emission properties

Fig. 9 shows the relation between the spectral emissive power and wavelength of the Al_2O_3/EAG eutectic ceramics. The thermal emissive power normal to the sample surface was measured by the apparatus shown in Fig. 3. The strong absorption peak is observed at 1.5 μm of wavelength caused by the 4f-electron orbit of Er^{3+}, because these absorption bands behave emission bands when Er^{3+} is thermally excited. The emissive power at 1.5 μm of wavelength becomes stronger with a rise of temperatures and shows around 180 W/m^2 μm at 1557 °C.

The selective emission efficiency, η, is defined as the ratio of the power emitted in the sensitive region of PV cell to the total emissive power. The temperature dependence of selective emitter efficiency of the present material is shown in Fig. 10. The selective emission efficiency for the Al_2O_3/EAG eutectic ceramics estimated from the relation between efficiency and temperature in Fig. 10 is almost the same 18.3% as 18.7% of NASA's YAG-Er/Ho materials.[6] The selective emission efficiency increases with increasing temperature. Furthermore, Al_2O_3/EAG eutectic ceramics have almost the same 21% as NASA's $Er_3Al_5O_{12}$ single crystal emitter[17] in the same temperature range The Al_2O_3/EAG eutectic ceramics display good mechanical strength, thermal stability and machinability compared with the NASA's YAG-Er/Ho emitter material and the $Er_3Al_5O_{12}$ single crystal. In addition, the present materials show good emission efficiency at 19% at a mole ratio of Er_2O_3 less than 40% of Er or Er/Ho of Er/Ho emitter material. From the result, it is confirmed that the Al_2O_3/EAG eutectic ceramic has one of the promising materials as a selective emitter for TPV generation system with GaSb cells.

3.4. TPV experimental apparatus to portable generators

The single-burner TPV experimental apparatus is shown in Fig. 11. The cylindrical Al_2O_3/EAG eutectic ceramics emitters were heated up to 1400 °C by burning the kerosene. Fig. 12 shows the relationship between voltage and current at 1400 °C measured using this apparatus. This experimental apparatus demonstrate around 4.2% efficiency. From this experiment, it can be concluded that the Al_2O_3/EAG eutectic ceramics has one of the promising materials showing good selective emitter characteristics. For actual use for the TPV system, however, the selective emitter characteristics of the Al_2O_3/EAG eutectic ceramics must be improved more.

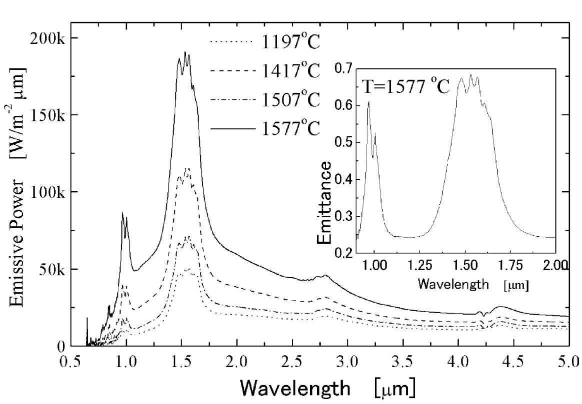

Fig. 9. Spectral emissive power of the Al_2O_3/EAG eutectic ceramics.

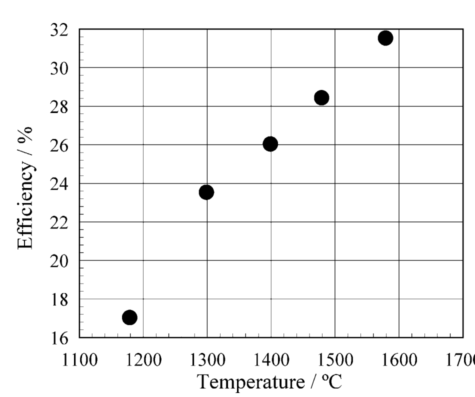

Fig. 10. Temperature dependence of emitter efficiency.

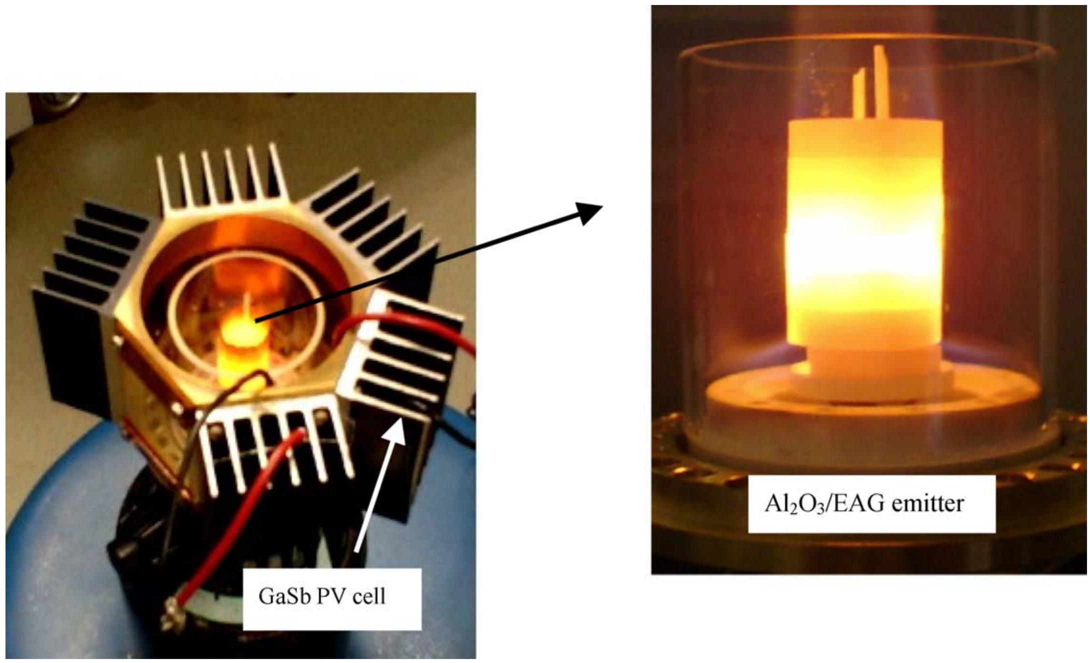

Fig. 11. General view of the single-burner TPV experimental apparatus.

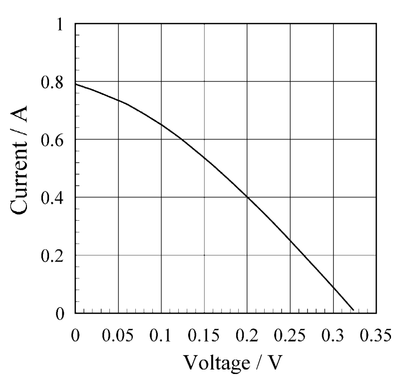

Fig. 12. Relationship voltage and current at 1400 °C.

4. Conclusions

A unidirectionally solidified $Al_2O_3/Er_3Al_5O_{12}$ eutectic ceramics has excellent high-temperature tensile strength and thermal stability at very high temperatures.

This material has a strong selective emission band at wavelength 1.5 μm caused by the existence of Er^{3+} ions. These emission bands match up the sensitive region of GaSb PV cell, therefore, Al_2O_3/EAG eutectic ceramics is one of the promising materials as an emitter material for TPV systems.

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