

**Material candidates for thermally robust applications of selective thermophotovoltaic emitters**Minsu Oh , John McElearney, Amanda Lemire , and Thomas E. Vandervelde \**Renewable Energy and Applied Photonics Labs, Department of Electrical and Computer Engineering, Tufts University, Medford, Massachusetts 02155, USA* (Received 27 April 2022; revised 24 August 2022; accepted 27 September 2022; published 7 November 2022)

As the majority of the input energy in power generation or energy consumption processes goes to waste as heat, thermophotovoltaic (TPV) devices enable energy recovery from (waste) heat. In TPV devices, the power output and conversion efficiency are impacted by thermal emitters. Since TPV devices operate at higher temperatures, emitters that can withstand hot environments without significant degradation of their emission performance are required. Refractory metals are commonly used as the emitter material due to their higher melting point and optical properties. This paper reviews physical and chemical properties of 15 refractory metals that may affect the emitter's performance at high temperatures: melting point, crystal structure, lattice constant, standard reduction potential, diffusion coefficient, Young's modulus, thermal expansion coefficient, and refractive index. Biological hazards and prices of the metals are also explored. Then, selective TPV emitters fabricated with the refractory metals are compared regarding their thermal stability. Finally, material properties are discussed toward achieving thermally robust TPV emitters.

DOI: [10.1103/PhysRevMaterials.6.110201](https://doi.org/10.1103/PhysRevMaterials.6.110201)**I. INTRODUCTION**

Lawrence Livermore National Laboratory in the United States reports that more than 65% of the total energy input in power generation or energy consumption processes is lost to heat [1]. This percentage indicates that there are enormous opportunities for energy recovery from (waste) heat if we can convert it into power [2–7]. Energy recovery from waste heat will not only lead to more power available but also to less fossil fuel being burned in power plants [4,8]. Thus, the capability of thermophotovoltaics (TPVs) to convert waste heat into electricity has brought an excitement to the energy research community [9–13]. Figure 1 describes the energy flow with a TPV device and its key components for operation: a thermal emitter and a photodiode. In a TPV device, Fig. 1(b), the emitter absorbs thermal energy from the heat source via conduction, convection, and/or radiation [14,15] and radiates photons based on its emission spectrum [14]. Then, using the photovoltaic effect, the diode generates electricity by absorbing the photons with energies greater than the band gap [16]. In TPV devices, which typically operate with heat sources at temperatures higher than 900 K [8], the emitter is physically closest to the heat source. TPV emitters, therefore, must withstand the hot environment to maintain their stable operation. For this reason, materials with a relatively high melting point are often used to make TPV emitters [17]. In general, metals have larger extinction coefficients, the imaginary part of the refractive index, and a higher melting point. In subwavelength structures, large extinction coefficients of the material can induce higher emission. The optical properties of subwavelength structures can also be engineered by changing their

dimensions. Thus, metal-based subwavelength structures have the advantage of higher, engineerable emission. This is useful for various heat source temperatures since the wavelength at which thermal radiation energy peaks varies as a function of temperature.

This work reviews thermal stability and optical performance of TPV emitters fabricated with refractory metals. The performance degradation of TPV emitters is found to be due mostly to their chemical reaction or/and mechanical deformation at high temperatures. The material properties responsible for degradation are characterized as lattice constant, reduction potential, diffusion coefficient, Young's modulus, or thermal expansion coefficient. In the first half of this paper, we introduce these material properties and identify metals with a melting point higher than 1700 °C, i.e., refractory metals. We then collect the material property data of refractory metals available in the literature. Biological concerns, due to the high-temperature operation of TPV devices, and prices of the metals are explored as well. After that, we proceed to review TPV emitters fabricated with refractory metals. Finally, we discuss the material properties for realizing thermally robust TPV emitters.

**A. Subwavelength structures**

Upon the interaction between an object and light, every spatial point of the object that the light hits produces its own optical response, also known as Huygens principle. Thus, the sum of responses from all those points determines the overall optical response of the object. As illustrated in Fig. 2, we compare optical responses of two types of objects: bulk structures and subwavelength structures. For bulk structures, Fig. 2(a), where the structure dimensions are much larger than the wavelength of interest, their optical responses can be calculated by

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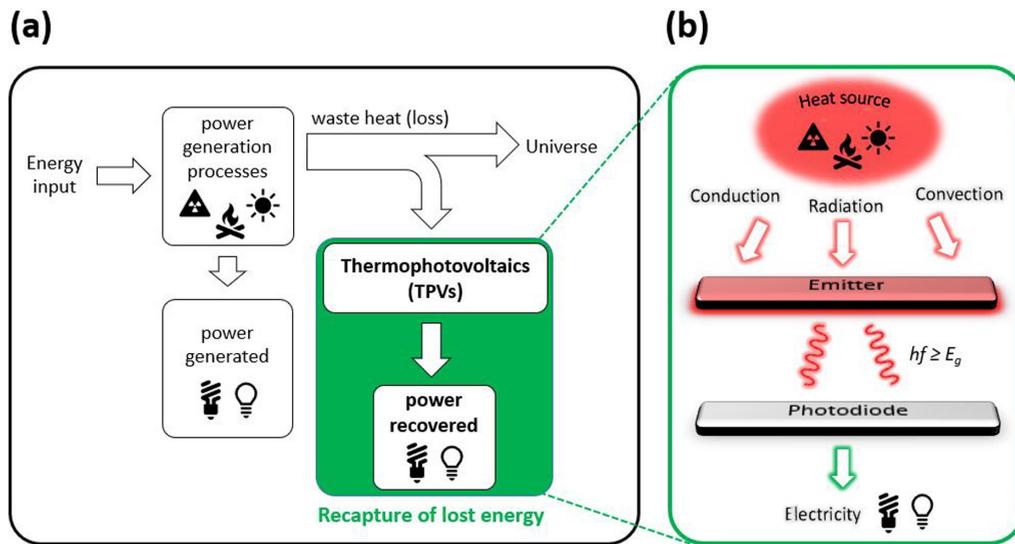


FIG. 1. Thermophotovoltaic (TPV) waste heat recovery. (a) Energy flow with TPVs. (b) Key components of a TPV device.  $hf$  and  $E_g$  are photon energy and band gap energy, respectively.

relatively simple equations, such as Fresnel coefficients (for reflection and transmission) [18] or absorption coefficient (for absorption) [19]. For a given angle, wavelength, and polarization of the incident light, the optical responses of a bulk structure are determined by its refractive index and thickness. This, as the refractive index is an intrinsic property of a material, fundamentally limits the “engineerability” of the optical interaction of bulk structures. However, as the dimensions of a structure decrease close to the wavelength, its optical responses start to become different compared to when it was a bulk structure. Structures with dimensions smaller than the wavelength are called subwavelength structures, Fig. 2(b). The optical responses of subwavelength structures are determined not only by the refractive index and thickness but also by the dimensions, shape, and spatial distribution of the structure elements. Therefore, compared to bulk structures, subwavelength structures allow arbitrary manipulation of their optical responses with more degrees of freedom. For this reason, subwavelength structures, also known as metamaterials (MMs) or photonic crystals (PhCs), are commonly used to create emitters with the desired emission spectrum.

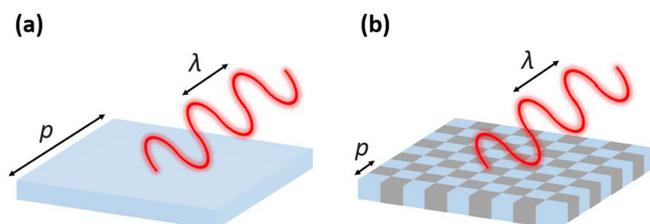


FIG. 2. Comparison of a bulk structure (a) and a subwavelength structure (b).  $\lambda$  is the wavelength of the incident light. The size of  $p$  relative to  $\lambda$  distinguishes bulk and subwavelength structures. Objects in blue and gray represent different materials.

### B. Crystal structure and phase

A crystal (or lattice) structure is a unique pattern of atomic arrangement of the material. Because a crystal structure is determined by how atoms are arranged with respect to their neighboring atoms, different orientations of an atomic stack do not render a different crystal structure. In other words, whether an atomic stack is facing south or north, they are still the same crystal structure. In particular, a region where the atoms are stacked in the same direction is referred to as a grain. A material may have one or multiple grains while they all have the same crystal structure. Materials with a single grain are referred to as single crystals while those with multiple grains are called polycrystals. Figure 3 illustrates these crystallographic differences between single crystals and polycrystals that have the same crystal structure. For single crystals, in general, unless the crystal structure allows isotropy, some material properties are dependent on the crystallographic orientation or the direction of measurement [20]. For example, the refractive index and thermal expansion coefficients are independent of orientations in the face-centered cubic (fcc) and body-centered cubic (bcc) structures while they vary with the orientation in single crystals

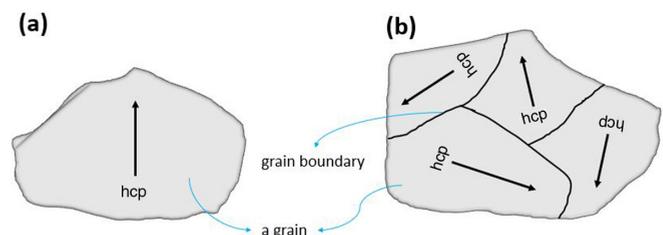


FIG. 3. Grains of a single crystal (a) and a polycrystal (b). Black arrows in the grains represent the orientation of the atomic stacking within that grain. All grains are in the hexagonal close-packed (hcp) structure.

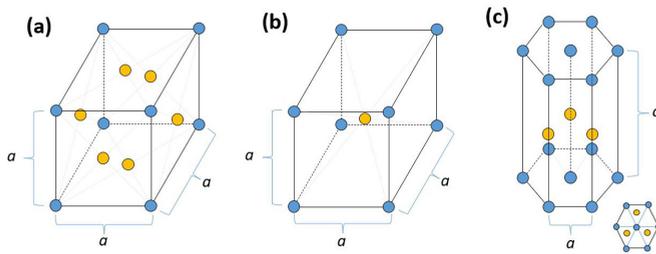


FIG. 4. Conventional unit cells for the fcc (a), bcc (b), and hcp (c) lattices. The coloring of the spheres is meant only to guide the eye—it is not meant to imply different atoms. Given their symmetry, the fcc and bcc lattices are typically given a single lattice constant, marked  $a$ , which applies along all three Cartesian axes. The hcp is marked with both its in-plane,  $a$ , and out-of-plane,  $c$ , lattice constants. The inset in (c) is a top view of the hcp unit cell.

with the hexagonal close-packed (hcp) structure [21,22]. Polycrystals with randomized grain directions, however, behave isotropically and exhibit somewhat averaged magnitude of their orientation-dependent properties [20]. Furthermore, thermally excited atoms in two or more neighboring grains in polycrystals can rearrange and form a united, larger grain [23]. This phenomenon, called grain growth, is sometimes used to suppress diffusion by annealing the material at higher temperatures [24]. Diffusion is discussed in detail in Sec. I E.

A homogeneous portion of a material with uniform physical and chemical characteristics is defined as a phase [20]. In practice, a phase of a crystalline solid can be understood as its distinguishing crystal structure [20]. For example, Zr and Hf have the hcp lattice at room temperature, referred to as  $\alpha$ -Zr and  $\alpha$ -Hf, respectively. As the temperature increases, the lattice structure of these metals changes into the bcc structure ( $\beta$ -Zr and  $\beta$ -Hf)—the phase transition temperatures are 863 °C and 2115 °C for Zr [25] and Hf [26], respectively. Since the atomic arrangement changes upon the phase transition, a phase change may cause abrupt changes of material properties such as lattice constants, volume [27,28], or optical properties [29,30].

### C. Lattice constant

For a given crystal lattice, we define the unit cell as any repeatable shape that can recreate the lattice solely by translation between lattice points, i.e., without rotation or mirroring. It follows that there are multiple possible unit cells for any crystal structure; for example, the smallest cell possible, or with a minimum volume, is defined as the primitive cell [31]. By construction, the primitive cell contains only one lattice point. To achieve this, the primitive cell requires that lattice points only sit on the vertices of the cell [32]. For some crystal structures, this can obscure important structural information about the lattice in its totality. To better reflect the overall structure and symmetry of the crystal, compared to “primitive cell,” “conventional unit cell” is often used instead. The conventional unit cells for the fcc, bcc, and hcp crystal structures are shown in Fig. 4. The dimension of the unit cell in a particular crystallographic direction is then defined as the crystal’s lattice constant in that direction, i.e., the distance between adjacent unit cells. In the fcc or bcc structure, the lattice

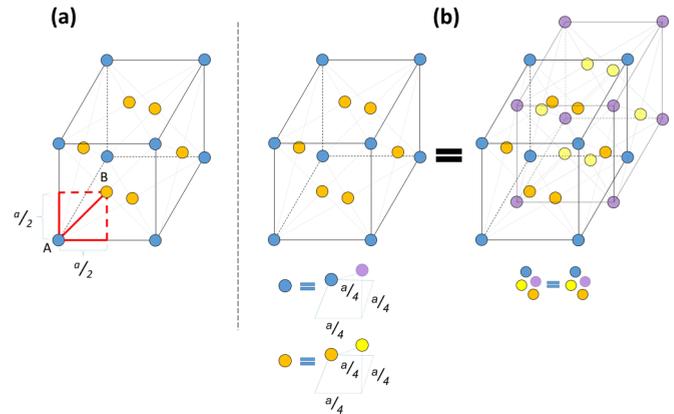


FIG. 5. (a) An fcc lattice where the nearest neighbor distance is marked in red. (b) The diamond cubic lattice is represented by a single fcc with a two-atom basis (left) and with a single-atom basis and the accompanying interlocked fcc lattices (right).

constant is equal along all three axes (marked  $a$  in Fig. 4), while the hcp lattice has different lattice constants between in-plane (marked  $a$ ) and out-of-plane (marked  $c$ ) directions. For this paper, the listed lattice constants in Table I refer to those defined by conventional unit cells.

It should be noted that the lattice constant is typically not equal to the spacing between adjacent atoms. For example, in the fcc lattice, the shortest distance between two atoms is the distance between any corner atom and the center atom (labeled A and B in Fig. 5) on one of the adjoining faces. The distance between these two atoms is  $\frac{\sqrt{2}a}{2}$ , with  $a$  being the lattice constant. This distinction can become especially important in the case of a crystal with a multiatom basis. A crystal’s basis indicates how many atoms sit on each lattice site. For example, the diamond cubic structure is essentially two interlocking fcc lattices with a single atom on every lattice site. It can alternatively be described as a single fcc lattice with two atoms sitting on each lattice site, separated by a distance of  $\frac{a}{4}$  in each direction. Thus, for the case of the two-atom basis, the nearest neighbor distance would be  $\frac{\sqrt{3}a}{4}$ , from a blue sphere to a purple one, in Fig. 5(b). As these both sit on the same lattice site, however, the lattice constant remains simply  $a$ .

For devices consisting of multiple layers of materials, materials should be chosen to avoid significant lattice mismatch—a difference in lattice constant between adjacent layers—to minimize stress caused by lattice mismatch at the interfaces. Growing layers with significantly different lattice constants, greater than 1% or so, can introduce excessive strain into the crystal [33]. For sufficiently thick layers, this strain can lead to the epilayer delaminating from the underlying stack [34,35]. This effect can also be caused, or exacerbated, by differences in rates of thermal expansion. Two materials with acceptably matched lattice constants at a given temperature can become mismatched, if one is changing at a much higher rate than the other. Thus, an ideal emitter should have well-matched lattice constants between constituent materials at room, growth, and operating temperatures to ensure device integrity. Figure 6 shows the delamination process and some examples of delaminated layers.

TABLE I. Physical and chemical properties of the 15 refractory metals.  $T_m$  is melting point. For the crystal structure, fcc, bcc, and hcp stand for face-centered cubic, body-centered cubic, and hexagonal close-packed, respectively. For the standard reduction potential, efforts were made to show reactions that involve similar oxidation states, mostly IV, of the metals for objective comparison. Self-diffusion refers to diffusion of the atom in the same-element matrix, diffusion of Cr atoms in a Cr matrix, for example. s.c. and p.c. stand for single crystal and polycrystal, respectively. CTE shown is the coefficient of linear thermal expansion. While some references report material properties at temperatures specified and some do not, indicating room temperature, values in this table are presumably at room temperature unless otherwise specified. For biological hazard, “high” is given if the material is radioactive or reported as lethal. Blank cells indicate that there is no reported or little known information to the best of our knowledge.

$T_m$ (°C) [52]	Crystal structure	Lattice constant (Å)	Standard reduction potential (V)	Self-diffusion coefficient at 1000 °C ( $10^{-15}$ cm <sup>2</sup> /s)	Young's modulus (p.c.) (GPa) [53,54]	CTE at 25 °C ( $10^{-6}$ /K)	Biological hazard	Price (USD/g) [52]	Reported emitters
V	bcc	3.02 [55]	-0.242 [52] $V_2O_5 + 10H^+ + 10e^- \rightleftharpoons 2V + 5H_2O$	81.7 (s.c.) [56] 81.5 (p.c.) [57]	128	8.4 [58]	mid [59]	3	[60]
Cr	bcc	2.88 [55]	-0.188 [52] $CrO_2 + 4H^+ + 4e^- \rightleftharpoons Cr + 2H_2O$	0.945 (s.c.) [61]	279	4.9 [58]	mid [59]	1	[62-65]
Zr <sup>a</sup>	hcp ( $\alpha$ -Zr) bcc ( $\beta$ -Zr)	$a = b = 3.24$ $c = 5.17$ ( $\alpha$ -Zr) [66]	-1.473 [42] $ZrO_2 + 4H^+ + 4e^- \rightleftharpoons Zr + 2H_2O$	$1.49 \times 10^6$ ( $\beta$ -Zr, p.c.) [61]	97	5.7 ( $\alpha$ -Zr, p.c.) [58]	mid [59]	4	-
Nb	bcc	3.30 [55]	-0.690 [52] $NbO_2 + 4H^+ + 4e^- \rightleftharpoons Nb + 2H_2O$	0.036 (s.c. or p.c.) [57]	105	7.3 [58]	mid [67]	0.5	[68]
Mo	bcc	3.15 [55]	-0.152 [52] $MoO_2 + 4H^+ + 4e^- \rightleftharpoons Mo + 4H_2O$	$1.5 \times 10^{-4}$ <sup>b</sup> (s.c.) [61] $2.4 \times 10^{-4}$ <sup>b</sup> (p.c.) [57]	325	4.8 [58]	mid [59]	0.16	[69-73]
Tc	hcp	$a = b = 2.76$ $c = 4.42$ [66]	+0.272 [74] $TcO_2 + 4H^+ + 4e^- \rightleftharpoons Tc + 2H_2O$	-	376	-	High (radioactive)	100	-
Ru	hcp	$a = b = 2.73$ $c = 4.31$ [66]	+0.788 [52] $RuO_2 + 4H^+ + 4e^- \rightleftharpoons Ru + 2H_2O$	-	420	6.4 (p.c.) [58]	-	25	[75]
Rh	fcc	3.80 [55]	+0.758 [52] $Rh^{3+} + 3e^- \rightleftharpoons Rh$	-	275	8.2 [58]	mid [59]	180	-
Hf <sup>a</sup>	hcp ( $\alpha$ -Hf) bcc ( $\beta$ -Hf)	$a = b = 3.20$ $c = 5.08$ ( $\alpha$ -Hf) [66]	-1.591 [42] $HfO_2 + 4H^+ + 4e^- \rightleftharpoons Hf + 2H_2O$	$  c 0.56$ <sup>b</sup> ( $\alpha$ -Hf, s.c.) [61] $\perp c 1.43$ <sup>b</sup> ( $\alpha$ -Hf, s.c.) [61] $3.09$ ( $\alpha$ -Hf, p.c.) [57]	139	6.0 ( $\alpha$ -Hf, p.c.) [76]	mid [77]	2	-
Ta	bcc	3.31 [55]	-0.752 [42] $Ta_2O_5 + 10H^+ + 10e^- \rightleftharpoons 2Ta + 5H_2O$	$8.7 \times 10^{-4}$ (s.c.) [61] $1.4 \times 10^{-3}$ <sup>b</sup> (p.c.) [61] $1.02 \times 10^{-8}$ <sup>b</sup> (s.c.) [61]	186	6.3 [58]	mid [78]	2	[72,79-81]
W	bcc	3.16 [55]	-0.119 [52] $WO_2 + 4H^+ + 4e^- \rightleftharpoons W + 2H_2O$	$1.9 \times 10^{-4}$ <sup>b</sup> (p.c.) [82,83]	411	4.5 [58]	Low to mid [59,84]	2.9	[39,46,49,65,70,72,85-100]
Re	hcp	$a = b = 2.78$ $c = 4.50$ [66]	+0.251 [74] $ReO_2 + 4H^+ + 4e^- \rightleftharpoons Re + 2H_2O$	-	470	6.2 (p.c.) [58]	-	16	-
Os	hcp	$a = b = 2.76$ $c = 4.36$ [66]	+0.687 [74] $OsO_2 + 4H^+ + 4e^- \rightleftharpoons Os + 2H_2O$	-	550	5.1 (p.c.) [58]	Low to high <sup>c</sup> [101]	100	-
Ir	fcc	3.84 [55]	+0.73 [42] $IrO_2 + 4H^+ + 4e^- \rightleftharpoons Ir + 2H_2O$	$3.7 \times 10^{-4}$ <sup>b</sup> (s.c.) [57]	528	6.8 [53]	Mid [102]	100	[103-105]
Pt	fcc	3.92 [55]	+0.92 [42] $PtO_2 + 4H^+ + 4e^- \rightleftharpoons Pt + 2H_2O$	$1235$ (p.c.) [61]	190	8.8 [58]	Low to mid [25]	15	[106-111]

<sup>a</sup>The crystal structures of Zr and Hf change from hcp ( $\alpha$  phase), at room temperature, into bcc ( $\beta$  phase) at 863 °C [25] and 2115 °C [26], respectively.

<sup>b</sup>The value is extrapolated for 1000 °C (1273 K) based on the data in the reference.

<sup>c</sup>When heated, Os oxidizes into the volatile compound OsO<sub>4</sub> (osmium tetroxide). Although Os itself is innocuous, OsO<sub>4</sub> is reported as highly toxic and lethal in animal testing [101].

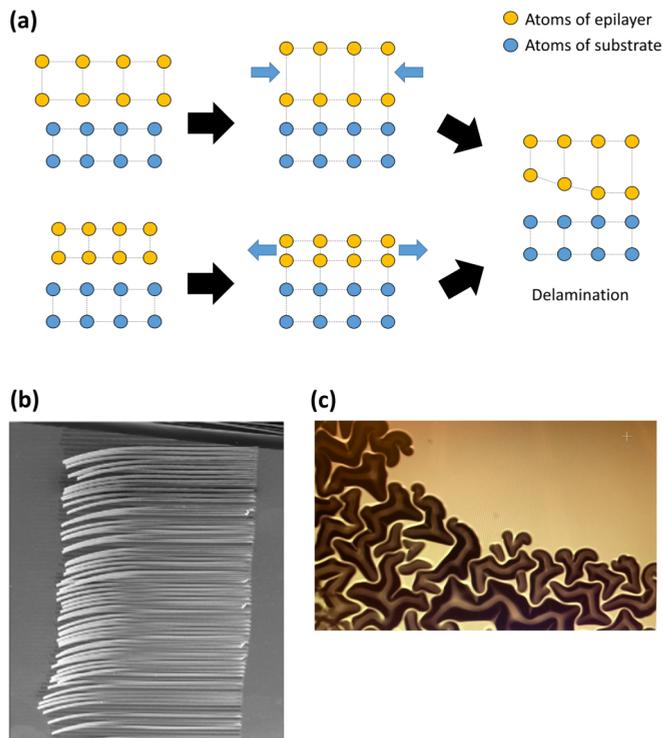


FIG. 6. (a) A schematic view of lattice-mismatch-induced strain. Top: an epilayer with a lattice constant greater than that of the underlayer undergoes compressive strain (blue arrows), shrinking the in-plane lattice constant and stretching the out-of-plane constant. Bottom: an epilayer with a lattice constant smaller than that of the underlayer undergoes tensile strain (blue arrows), stretching the in-plane and shrinking the out-of-plane lattice constants, respectively. (b) Delamination of thin strips of Ni from a Au/Si substrate (reprinted with permission from Ref. [35]). (c) Delamination of a thin Si layer from a quartz substrate.

#### D. Standard reduction potential

The standard reduction potential (SRP) of a chemical species is the magnitude of the electrical potential involved in transferring electrons to the species' cation to reduce it to a neutral state. SRPs are defined with reference to the reduction of protons into  $H_2$ : An electrode comprising a Pt crystal submerged in aqueous 1M HCl with  $H_2$  gas bubbled through at 1 atm is defined as having a standard potential of zero and is called the standard hydrogen electrode (SHE) [36]. To measure the SRP of a metallic species, the SHE is connected to an electrode of the species across a voltmeter. The electrode being measured is submerged in a solution of a salt containing the species in question; silver, for example, may be measured in a solution of  $AgNO_3$ . The solutions at each electrode are connected by a salt bridge to maintain charge neutrality. The full system of electrodes and electrolytic solutions is called a galvanic cell. Assembling a galvanic cell produces a spontaneous current flow between the electrodes [37]. The direction of the current flow depends on the species under examination: If it is more easily reduced than hydrogen,  $H_2$  gas dissociates at the Pt electrode and electrons flow to the electrode of interest. The species cations combine with the electrons

and form a layer of neutral material on the electrode. The voltmeter output while the reaction progresses is the reduction potential, and for a spontaneous reaction in which the species under study is reduced, the SRP is positive. For species which are less easily reduced than  $H_2$ , the reaction would proceed spontaneously in reverse: The species electrode oxidizes and sends electrons to the SHE to reduce hydrogen ions to  $H_2$ . The recorded SRP would be negative. Therefore, a species with a higher SRP is more resistant to oxidation. As oxidation or reduction is a spontaneous reaction, TPV emitters fabricated with a material with a lower reduction potential, such as W, may suffer optical performance degradation due to oxidation [38–40]. The SRPs, furthermore, are presented as half reactions, as can be seen in Table I. The half reaction for the SHE, for example, is written as  $2H^+ + 2e^- \rightleftharpoons H_2$ ,  $E^\circ = 0$  V, where  $E^\circ$  is the SRP. In principle, reduction reactions are reversible, with the same potential energy barrier in either direction. Thus, for a given species, its standard oxidation potential is therefore equal in magnitude as its SRP with an opposite sign. Since SRP is an intensive property, the magnitude of the recorded voltage is independent of the size of the electrodes used. While temperature can impact the SRP, its effects are relatively small [41,42].

#### E. Diffusion

Diffusion is a translational movement of a thermally excited atom (or atoms) where the atoms move to other locations. As atoms move through the volume or surface of a material, diffusion is responsible for physical or chemical reactions such as grain growth [43] or oxidation [38]. According to the Maxwell-Boltzmann distribution [44], at thermal equilibrium, some of the atoms in the material have higher kinetic energy than others. The atoms with higher kinetic energy may have enough energy to break their atomic bonding with neighboring atoms and move to other locations. As thermal energy fuels this kinetic movement, a higher temperature causes more diffusion. The relationship between diffusion and temperature is given by  $D = A \exp(-Q/k_B T)$ .  $D$  is the diffusion coefficient (the higher the value, the more diffusion),  $A$  is a temperature-independent constant,  $Q$  is the activation energy for diffusion,  $k_B$  is the Boltzmann constant, and  $T$  is temperature [20]. As the likelihood of diffusion increases exponentially as a function of temperature, structures with small dimensions, such as metamaterial emitters, can be deformed due to diffusion at high temperatures [45–47]. In particular, the diffusion coefficient of a material is higher when the material is polycrystalline than when it is single-crystalline. This is because grain boundaries, where the number density of atoms is lower than that inside a grain, behave as a tunnel through which atoms can move more easily [48]. For this reason, at high temperatures, the optical performance of nanostructured polycrystalline emitters can degrade more rapidly than single-crystalline nanostructures [49].

#### F. Thermal expansion and Young's modulus

As thermal energy causes movement of atoms, the average distance between atoms increases as the temperature

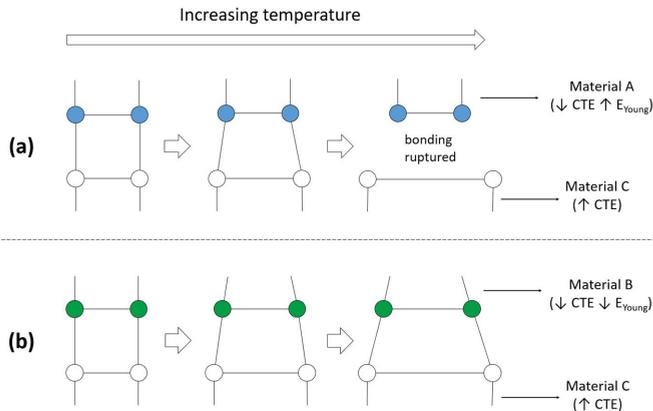


FIG. 7. Delamination due to a higher Young’s modulus upon thermal expansion. Materials with a higher (a) and lower (b) Young’s modulus are compared. Atoms and atomic bonding are represented by balls and lines, respectively. The upward (↑) and downward (↓) arrows represent high and low values of the property, respectively.

increases. This results in expansion of the material dimensions, referred to as thermal expansion. Upon heating, the expansion of a material in length is measured as the coefficient of linear thermal expansion,  $\alpha_L$ , typically referred to as CTE. The coefficient is defined as  $\alpha_L = \frac{1}{L_0} \frac{dL}{dT}$ , where  $L_0$  is the length of the material before the temperature change, and  $dL$  and  $dT$  are variations in length and temperature, respectively. As different materials may have different CTEs, thermal expansion can create stress at interfaces between jointed materials. If the stress is too high, the atomic bonding at the interface may rupture, which can cause the materials to delaminate. This can lead to permanent fracture and severe optical performance degradation of TPV emitters consisted of multiple layers [50]. Moreover, the resistance of a material to one-dimensional tensile or compressive stress in the elastic regime is measured as Young’s modulus,  $E_{\text{Young}}$ , defined as applied stress divided by the strain [51]. Thus, at a given strain, materials with a higher Young’s modulus are under more stress than those with a lower modulus. This indicates that a higher Young’s modulus may contribute to delamination at interfaces upon thermal expansion. Figure 7 illustrates delamination due to a higher Young’s modulus.

## II. REFRACTORY METALS

The 15 refractory metals with a melting point higher than 1700 °C are shown in Fig. 8. The physical and chemical properties of these metals for TPV applications are shown in Table I along with their biological hazard and typical prices. References to some emitters fabricated with the refractory metals are also given. These emitters are discussed in Sec. III regarding their optical performance and thermal degradation. The material properties of the refractory metals are also plotted in Fig. 9. Figure 10 shows the refractive index of the metals. The  $n$  and  $k$  are real and imaginary parts of the refractive index, respectively. For fcc and bcc metals, being single crystalline or polycrystalline does not affect their refractive index due to the symmetry of their lattice structure [21].

H																	He															
Li	Be	<b>Refractory metals</b> ( $T_m > 1700^\circ\text{C}$ )										B	C	N	O	F	Ne															
Na	Mg																	Al	Si	P	S	Cl	Ar									
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr															
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe															
Cs	Ba																	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

FIG. 8. Periodic Table of elements. Metals with a melting point ( $T_m$ ) higher than 1700 °C are boxed in red.

## III. SELECTIVE EMITTERS FABRICATED WITH REFRACTORY METALS

This section reviews emitters fabricated with refractory metals. The review focuses on mechanical deformation or/and changes in the emissivity spectrum. The conversion efficiency and power output of TPV devices are not the focus of this work for the following reasons. No single metric is universally used by researchers to report TPV efficiency. The main difference between different metrics is the inclusion [9] or exclusion [121] of the incident power with photon energies smaller than the photodiode’s band gap in the denominator. This means that a TPV device can have different efficiencies depending on which metric is used. Another reason is that there is currently little research on TPV efficiency or power output degradation as a result of the emitter’s thermal degradation, as what most researchers report is the emitter’s mechanical deformation or its emission spectrum change. Nevertheless, degradation in emissivity causes the TPV efficiency and power output to drop [40]. Priority for the review is given to emitters that are reported with experimental results as opposed to simulated results. For metals where there was no reported emitter based on experimental results, to the best of our knowledge, the emitters based on simulated results are reviewed. Oftentimes, the “emissivity” of emitters is reported based on their “absorptivity” as these two properties are equal to each other at a given wavelength, polarization, direction, and temperature due to Kirchhoffs law [106,122]. For this reason, the terms “absorption” and “emission” may be used interchangeably in this paper. Moreover, as different reports in the literature use different terms, we note that the terms “absorptivity”, “absorbance”, or “absorptance” refers to the same numerical value in this paper. The same is true for “emissivity” and “emittance” as well as for “reflectance” and “reflectivity”.

### A. Vanadium (V)

A V-based metamaterial (MM) thermal emitter is numerically reported by Liu *et al.* over the visible to infrared wavelengths [60]. By using alternating nanosized disks of V and SiO<sub>2</sub>, the authors of Ref. [60] demonstrate their emitter’s radiation spectrum similar to that of a blackbody. Figure 11 shows the emitter structure and simulated spectral radiance. The radiation properties of their emitter are attributed to the plasmonic resonance between the metal disks.

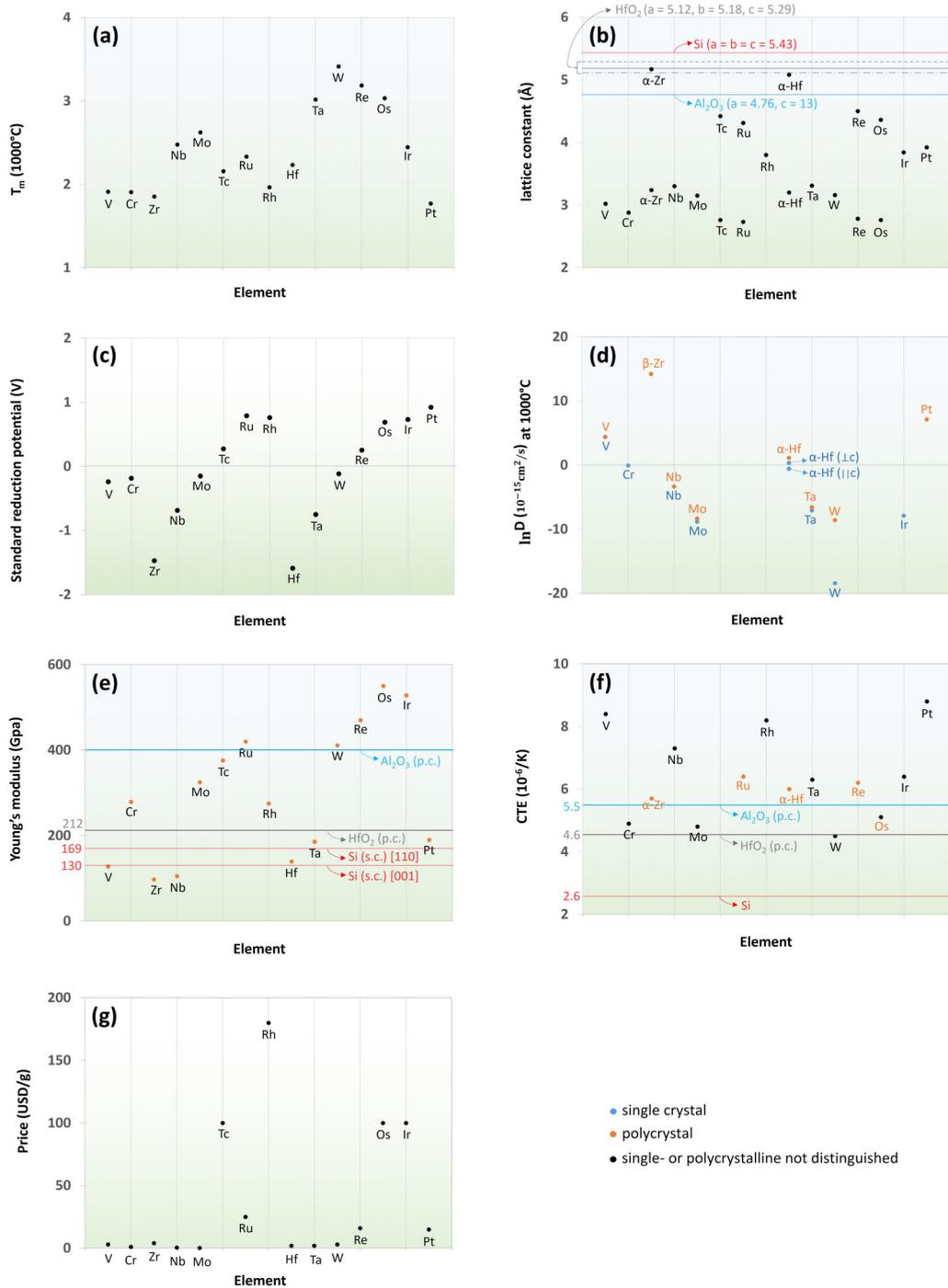


FIG. 9. Properties of the refractory metals from Table I. Melting point (a), lattice constant (b), standard reduction potential (c), self-diffusion coefficient (D) (d), Young’s modulus (e), linear thermal expansion coefficient (CTE) (f), and typical prices (g) are shown. Lattice constants are shown along with those of common substrate or coating materials for TPV emitters: Si [55], HfO<sub>2</sub> [112], and Al<sub>2</sub>O<sub>3</sub> [113]. The Young’s moduli [114–116] and CTEs [113,117,118] of these three materials are shown as well.

**B. Chromium (Cr)**

Based on optical interference between Cr and SiO<sub>2</sub> layers, Deng *et al.* experimentally demonstrated a broadband emitter with measured absorption [62]. As the authors of Ref. [62] report, their emitter’s emissivity is higher than 90% over the wavelength range 0.4–1.4 μm. The emitter structure

and emission results are shown in Fig. 12(a). Meanwhile, focusing on submillimeter wavelengths, a Cr ring resonator was numerically suggested with a potential application as a thermal emitter by Hu *et al.* [63]. The unit cell and absorption spectrum of this ring resonator are shown in Fig. 12(b). Another emitter fabricated with Cr was reported numerically

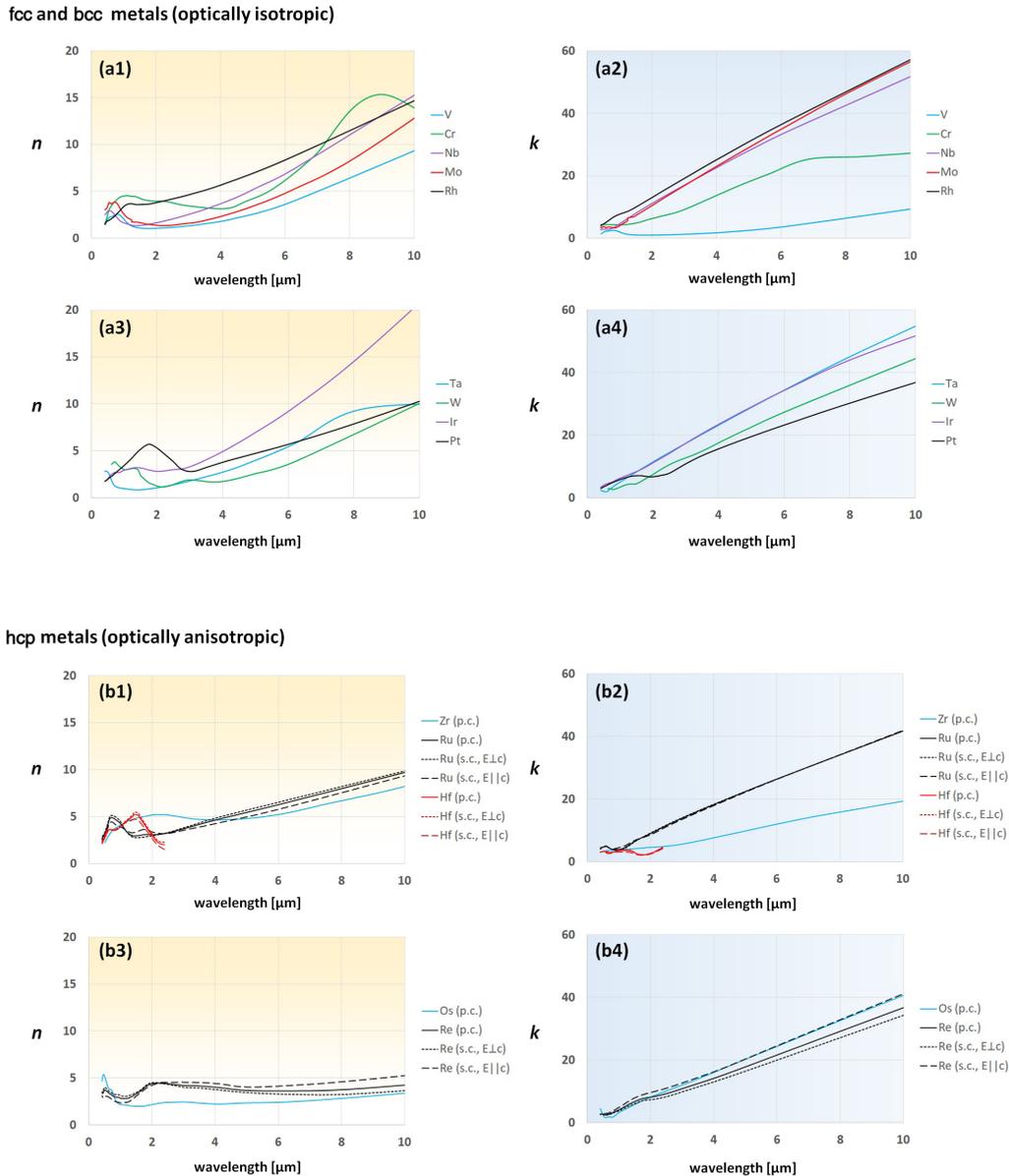


FIG. 10. Refractive index of the refractory metals. Data are separated for optically isotropic (a) and anisotropic (b) metals.  $n$  and  $k$  are real and imaginary parts of the refractive index, respectively. In the legend, s.c. and p.c. stand for single crystal and polycrystal, respectively. The orientation of incident electric field ( $E$ ) relative to the orientation of the longer axis of hcp unit cell, the  $c$  axis, is denoted. Data are from [52,119]. For polycrystalline Ru, Hf, and Re, refractive indices are calculated from the relationships  $\varepsilon = (\varepsilon_{||} + 2\varepsilon_{\perp})/3$  and  $\sqrt{\varepsilon} = n + ik$ , assuming randomized grain orientations [120], where  $\varepsilon$  is permittivity. We note that  $\varepsilon_{||}$  and  $\varepsilon_{\perp}$  are permittivities corresponding to electric fields parallel and perpendicular to the  $c$  axis of the hcp unit cell, respectively [120].

in the visible to infrared spectrum [64], where the emission performance is based on plasmonic resonance.

### C. Niobium (Nb)

While focusing on transmission properties, Nb-based plasmonic MMs with mechanical stability at up to 800 °C in vacuum are experimentally demonstrated by Bagheri *et al.* [68]. The authors report that the mechanical stability of their metamaterials in vacuum can be further improved with a 5 nm thick Al<sub>2</sub>O<sub>3</sub> coating on top of the Nb. The thermal stability

improvements are attributed to the prevention of Nb grain growth due to the coating layer. Annealing results of these Al<sub>2</sub>O<sub>3</sub>-coated MMs are shown in Fig. 13 with measured transmittance. In the figure, little mechanical deformation of Nb features is seen after annealing. In Fig. 13(d), stable transmission properties before and after annealing are seen. Although the authors report with a focus on transmission, it is worth noting that their MMs maintain stable mechanical and optical performance at high temperatures in vacuum. Thus, the results of Ref. [68] may provide insights for creating Nb-based emitters for TPV applications. Additionally, the authors of

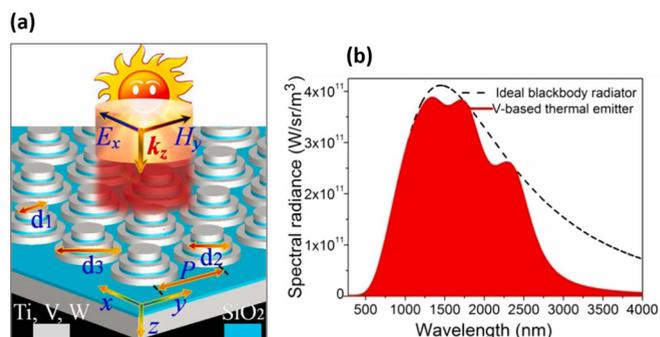


FIG. 11. A V-based emitter. (a) Emitter structure with three nanosized disks. White and blue layers are the metal (either all Ti or V or W) and  $\text{SiO}_2$ , respectively. (b) Simulated spectral radiance curves of the emitter with V disks and a blackbody corresponding to 2000 K. (Reprinted with permission from Ref. [60].)

Ref. [68] state that annealing the structure in air causes oxidation of Nb, which leads to optical performance degradation.

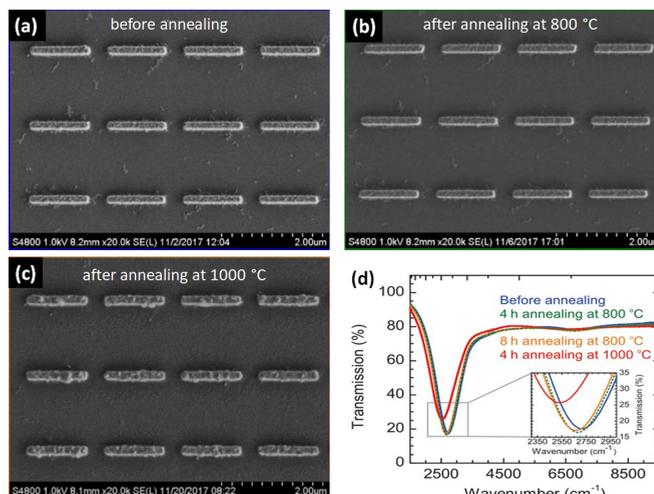


FIG. 13. Nb-based metamaterials with 5 nm thick  $\text{Al}_2\text{O}_3$  coating. (a)–(c) Scanning electron microscopy (SEM) images of the emitter’s top surface before or after annealing in vacuum. (d) Measured transmittance of the emitter before and after annealing. (Reprinted with permission from Ref. [68].) © (2018) American Chemical Society.)

### D. Molybdenum (Mo)

Thermal emission of a plasmonic MM with Mo disks is experimentally reported by Yokoyama *et al.* [69]. Figure 14

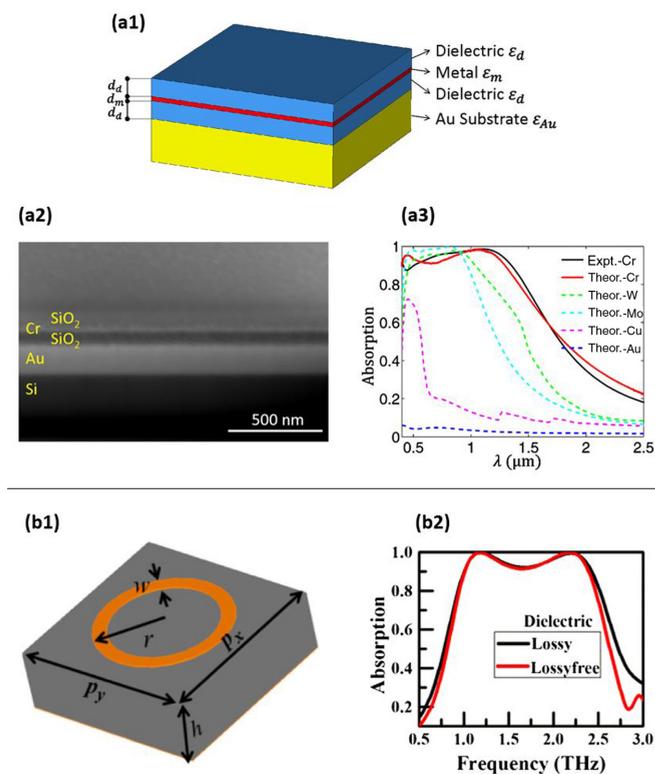


FIG. 12. Cr-based emitters. (a) Emitter with Cr (metal) and  $\text{SiO}_2$  (dielectric) planar layers [62]. The layer structure (a1,a2) and measured absorption (Expt.-Cr) (a3) are shown.  $d_d = 85$  nm and  $d_m = 8$  nm. (b) Emitter with a Cr ring resonator [63]. The unit cell (b1) and simulated absorption (b2) are shown. Materials in orange and gray are Cr and a dielectric, respectively.  $w = 4$   $\mu\text{m}$ ,  $r = 25$   $\mu\text{m}$ ,  $p_x = p_y = 70$   $\mu\text{m}$ , and  $h = 26$   $\mu\text{m}$ . ((a), (b) are reprinted with permission from Refs. [62,63], respectively. © The Optical Society.)

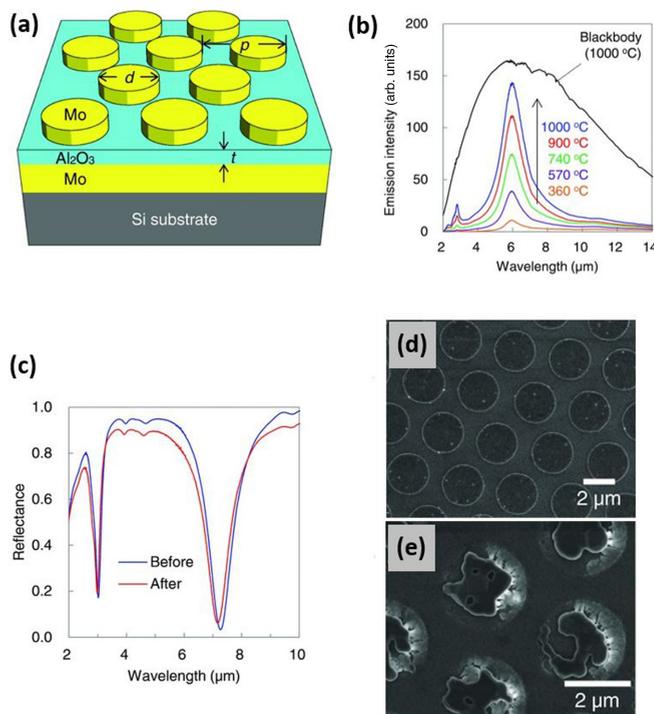


FIG. 14. A Mo-based emitter. (a) Emitter structure. Thicknesses of the top and bottom Mo layers are 100 nm and 1  $\mu\text{m}$ , respectively. (b) Measured emission of the emitter at several temperatures up to 1000 °C in vacuum. (c) Measured reflectance of the emitter before and after annealing at 1000 °C for 3 h in vacuum. (d,e) are SEM images of undeformed and deformed Mo disks after annealing, respectively. (Reprinted with permission from Ref. [69].)

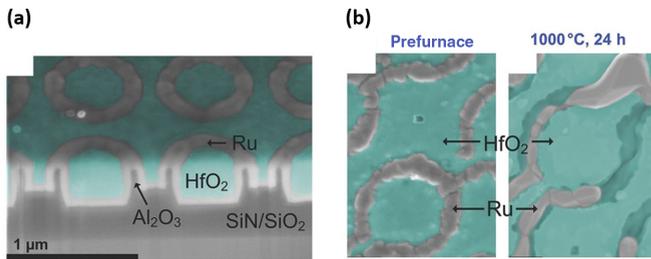


FIG. 15. A Ru-based photonic crystal. (a) A cross-section SEM image at an oblique angle. (b) Top-view SEM images before (left) and after (right) annealing at 1000 °C for 24 h in inert atmosphere (95% Ar + 5% H<sub>2</sub>). (Reprinted with permission from Ref. [75].)

shows their MM structure and results. In Fig. 14(b), stable emission properties are seen up to 1000 °C in vacuum over the wavelength range 2–14 μm. Moreover, in Fig. 14(c), the authors further demonstrate stable reflectance before and after annealing a similar structure at 1000 °C for 3 h in vacuum. After annealing, as stated in Ref. [69], only a small number of Mo disks are deformed while more than 90% of them are undeformed. Scanning electron microscopy (SEM) images of the emitter's surface after annealing are shown in Figs. 14(d) and 14(e). Another nanostructured emitter with a Mo coating on a silica woodpile scaffold is experimentally demonstrated, where the structure is annealed at 650 °C for 2 h in inert atmosphere [70]. The emission is measured at 620 °C over the wavelength range 1.5–2.5 μm. Additionally, by annealing the structure at 650 °C for 2 h under inert atmosphere, the authors of Ref. [70] report that no grain growth of Mo is observed. A few more nanostructured emitters with Mo are reported based on simulation at wavelengths 1–4 μm [71]. Fabrication techniques of three-dimensional nanostructures with Mo are also reported for TPV applications [72]. Besides nanostructured emitters, an emitter based on optical interference effects between thin Mo and HfO<sub>2</sub> layers is demonstrated with measured emission at room temperature [73].

### E. Ruthenium (Ru)

A Ru-based photonic crystal (PhC) absorber is experimentally demonstrated by Chou *et al.* [75]. The absorber is also annealed at 1000 °C for 24 h in inert atmosphere. The results before and after annealing are shown in Fig. 15. The authors report that the mechanical deformation of their absorber is due to surface diffusion and delamination of Ru from HfO<sub>2</sub>. In Ref. [75], TiN is suggested as an adhesion layer, presumably between Ru and HfO<sub>2</sub>, to prevent delamination for their future work. Despite the deformation, the absorption results before and after annealing are reported to be similar.

### F. Tantalum (Ta)

A nanostructured PhC emitter made solely of Ta is experimentally reported by Rinnerbauer *et al.* [79]. The authors etched a polycrystalline Ta wafer, 50.8 mm in diameter and 3 mm thick, into a nanostructured emitter. Before patterning the emitter, the Ta substrate was annealed at 2250 °C for 4 h in vacuum to induce grain growth for improved thermal stability. Grain sizes, after annealing, ranged from 0.1 to 0.5 μm and 1

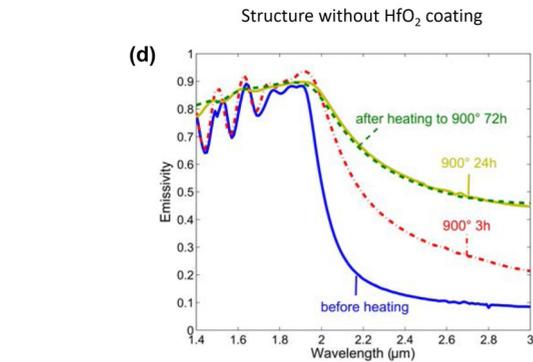
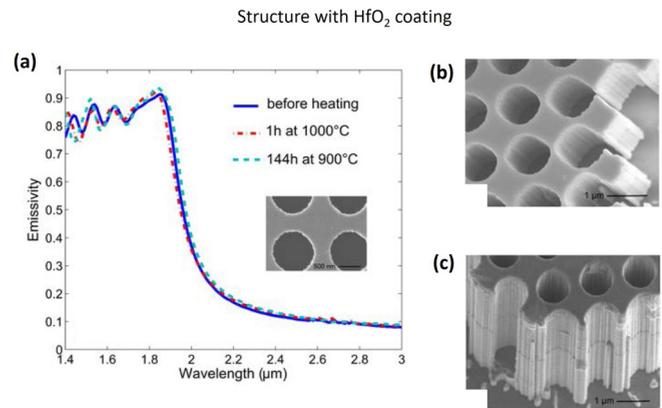


FIG. 16. Ta-based photonic crystal emitters with and without 20 nm thick HfO<sub>2</sub> coating. (a) Emissivity of the HfO<sub>2</sub>-coated structure measured at room temperature before and after annealing in vacuum. (b), (c) are SEM images of the HfO<sub>2</sub>-coated structure (oblique view) before and after annealing at 900 °C for 144 h in vacuum, respectively. (d) Emissivity of the uncoated structure measured at room temperature before and after annealing in vacuum. (Reprinted with permission from Ref. [80]. © The Optical Society.)

to 2 mm. The research group of Ref. [79] further investigated thermal stability of their emitter with and without a 20 nm thick HfO<sub>2</sub> coating layer by annealing the structure in vacuum in their other study [80]. The HfO<sub>2</sub>, deposited on the emitter's surface, prevented surface diffusion of Ta and TaC formation, which was due to the carbon contamination in their vacuum chamber. Without the HfO<sub>2</sub> coating, the authors of Ref. [80] report that the emission properties severely degrade due to the TaC formation. The results before and after annealing the emitter with and without the HfO<sub>2</sub> coating are shown in Fig. 16. Additionally, other nanostructured emitters fabricated with Ta are demonstrated based on simulation [81]. Fabrication techniques of three-dimensional nanostructures with Ta are reported for TPV applications as well [72].

### G. Tungsten (W)

Using a carbon nanotube (CNT) scaffold, Cui *et al.* experimentally demonstrated the thermal stability of their W-based PhCs [97]. W is deposited on an Al<sub>2</sub>O<sub>3</sub>-coated CNT scaffold. The results before and after annealing the structure at 1000 °C in vacuum with He gas are shown in Fig. 17(a). In their x-ray diffraction (XRD) results, Fig. 17(a3), the slight

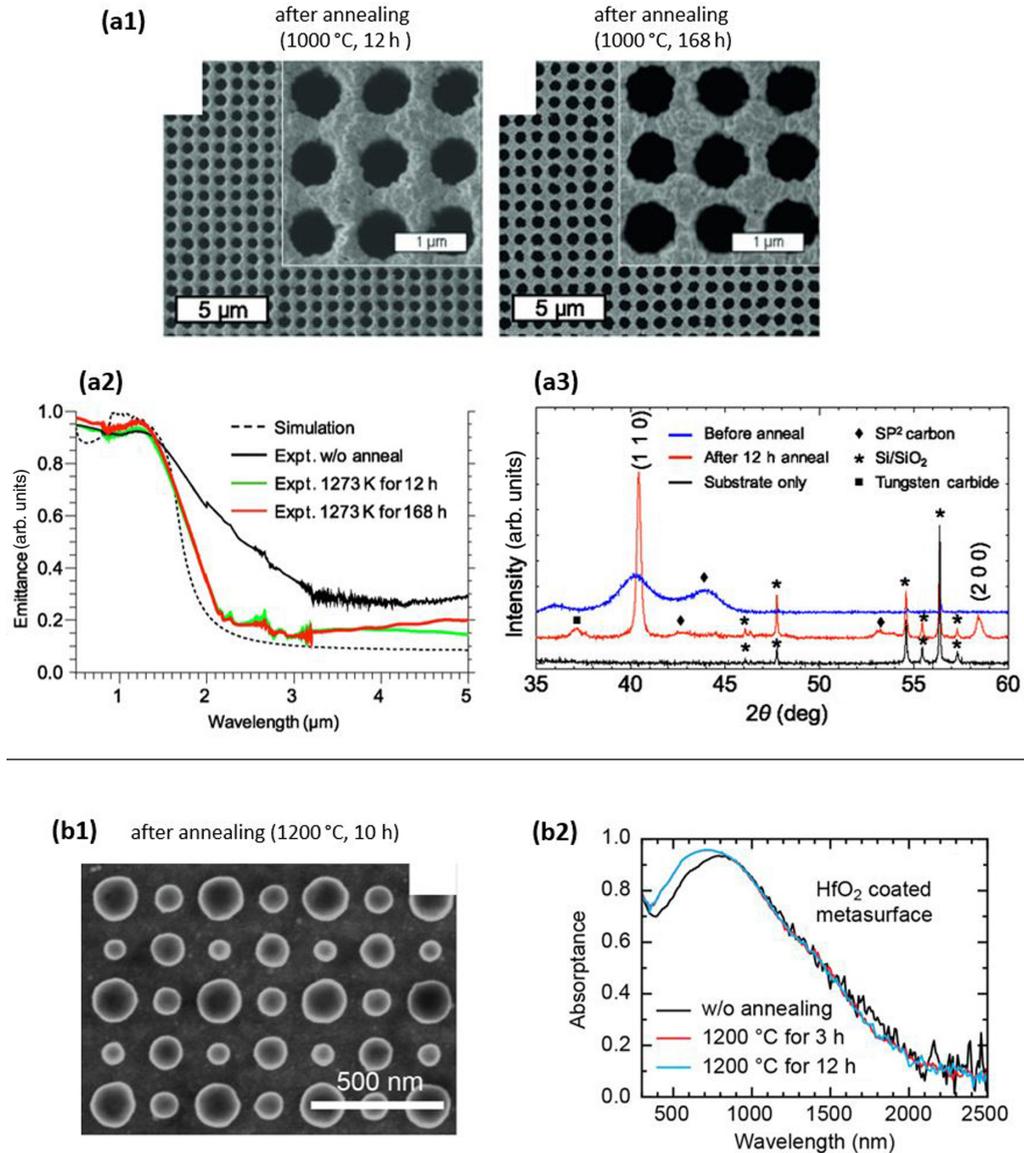


FIG. 17. W-based nanostructures for TPV emitters. (a) Results of the W-CNT structure (no surface coating of W) before and after annealing in vacuum [97]. SEM images (a1), measured emittance (a2), and XRD peaks (a3) are shown. The blue and red curves in the XRD results correspond to W. (b) Results of the 20 nm thick HfO<sub>2</sub>-coated metasurface before and after annealing in vacuum [98]. An SEM image (b1) and measured absorbance (b2) are shown. ((a), (b) are reprinted with permission from Refs. [97,98], respectively.)

shift and narrowing of the W (110) peak after annealing are due to the stress release and grain growth of nanosized W grains. Meanwhile, Chang *et al.* conducted a rigorous investigation of W-based metasurfaces with and without a 20 nm thick HfO<sub>2</sub> coating at 1200 °C in vacuum [98]. HfO<sub>2</sub> is used to prevent evaporation of W. Figure 17(b) shows the absorption results of their HfO<sub>2</sub>-coated metasurface before and after annealing in vacuum. Reference [98] also compares the absorbance of their metasurfaces fabricated by two different deposition techniques for tungsten: sputtering and electron beam evaporation. In addition to these structures, numerous emitters fabricated with W are demonstrated with their performance based on optical interference [39,46,99], complicated three-dimensional structures [70,72], and simulation [85–89,100] for high-temperature applications. Nanostructured emitters made solely of bulk W are reported

as well [49,90]. Moreover, there are a great deal of studies on W-based emitters for near-field TPV applications [65,91–94,96]. Near-field TPVs is distinguished from typical TPVs in that the spacing between the emitter and photodiode is on the nano- or micrometer scale. One advantage of near-field TPVs is that the energy transfer from the emitter can exceed the theoretical blackbody limit [12,65]. One study experimentally shows that the TPV power output increases as the emitter-to-diode spacing decreases, where the emitter was in vacuum [65].

### H. Iridium (Ir)

A wafer-area emitter fabricated with Ir is experimentally demonstrated with its absorption measured at room temperature in the visible to near-infrared spectrum by Oh and Vandervelde [103]. The absorption results are due to optical

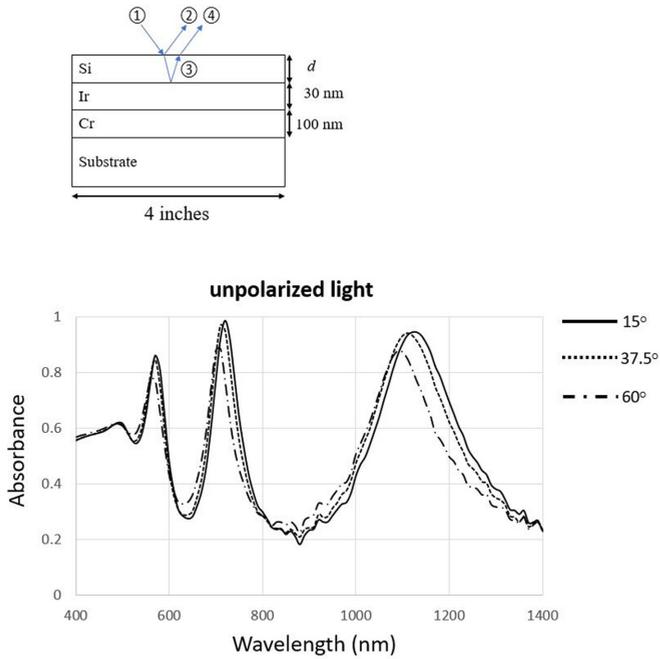


FIG. 18. An Ir-based emitter. Absorbance results (for  $d = 225$  nm) measured at room temperature are shown for unpolarized light. The incidence angles are denoted in the legend. (Reprinted with permission from Ref. [103].)

interference effects. Ir is used due to its higher resistance to oxidation. Figure 18 shows the emitter structure and absorbance spectrum in Ref. [103]. The research group of Ref. [103] also numerically proposes plasmonic MMs based on Ir for TPV applications at wavelengths near 2–7  $\mu\text{m}$  [104]. They show that the absorbance spectrum of their plasmonic MMs can be engineered by changing the width of the top features as the plasmonic resonance is responsible for their selective emission. Similar structures containing Ir are reported based on simulation for longer wavelengths [105].

I. Platinum (Pt)

A Pt-based MM emitter with two-dimensional patterns is experimentally demonstrated at wavelengths near 600–1600 nm by Shemelya *et al.* [106]. The authors report the optical properties of their emitter at high temperatures as well as before and after annealing. Figure 19(a) shows their emitter structure and emissivity results. Compared to two-dimensionally patterned MMs, three-dimensionally patterned MM emitters fabricated with Pt are demonstrated by Garín *et al.* at wavelengths near 2–10  $\mu\text{m}$  [107]. The authors of Ref. [107] present optical and microstructure results of their emitters after annealing in air and in  $\text{N}_2$  atmosphere, which are shown in Fig. 19(b). The effects of a dielectric coating on Pt-based MMs are also studied by other research groups [108,109]. By annealing their emitter at 1027  $^\circ\text{C}$  for up to 12 min in Ar atmosphere, the authors of Ref. [108] show improved thermal stability of their Pt-based MMs with 150 nm thick  $\text{Al}_2\text{O}_3$  coating (Fig. 20). Other Pt-based emitters are experimentally demonstrated at relatively low temperatures [110,111].

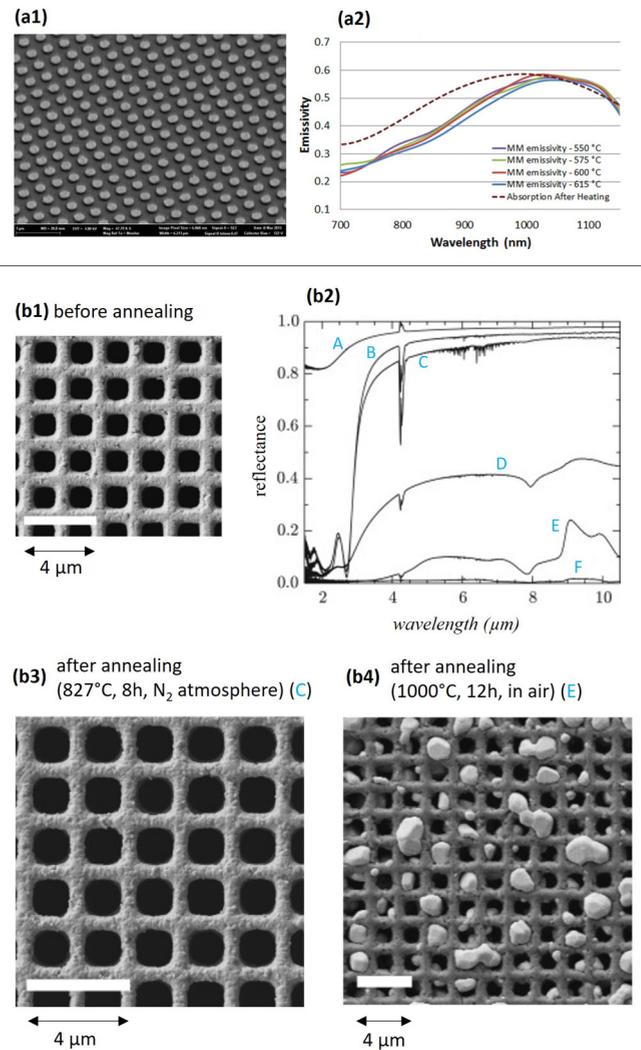


FIG. 19. Pt-based emitters (without surface coating). (a) Surface SEM image (a1) and measured emissivity (a2) of the two-dimensionally patterned metamaterial [106]. (b) Results of the three-dimensionally patterned metamaterial [107]. Surface SEM images before (b1) and after (b3), (b4) annealing with corresponding measured reflectance (b2) are shown. Annealing conditions are written on top of each SEM image. ((a), (b) are reprinted with permission from Refs. [106,107], respectively.)

IV. DISCUSSION

A. Crystal structure

This work finds that most refractory emitters are fabricated with fcc or bcc metals. While these two crystal structures are optically isotropic, there remains a question as to how the anisotropic optical properties of hcp metals will affect the emitter’s performance. As discussed in Secs. IB and IE, metals undergo grain growth at higher temperatures, and (polycrystalline) hcp metals become more anisotropic. We remind the readers that TPV emitters typically operate at temperatures around 900 K. For this reason, significant grain growth is expected to occur in emitters during their operation. As a result of grain growth, the (polycrystalline) hcp metal’s refractive index would change in preference of the dominant

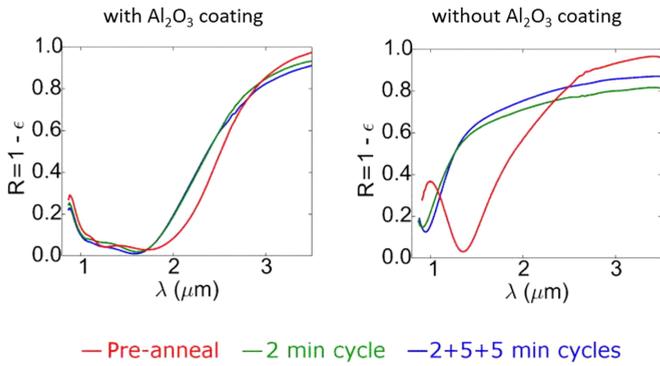


FIG. 20. Measured reflectance ( $R$ ) of Pt-based MM emitters with and without 150 nm thick  $\text{Al}_2\text{O}_3$  coating after annealing at  $1027^\circ\text{C}$  in Ar atmosphere. The legend shows annealing time, where the font color corresponds to the plot color.  $\epsilon$  is emissivity. (Reprinted with permission from Ref. [108].)

grains' crystallographic orientations, as seen in Fig. 10. The refractive index variation is not desired since the emitter's optical performance is impacted by the materials' refractive index and it may lose its initially designed emission properties as a result of grain growth. Therefore, fcc or bcc metals may be preferable to hcp metals. However, for some hcp metals where the refractive index does not vary as much with grain orientations, Ru for example [75], the above concern could be reduced.

### B. Phase change

Zr and Hf undergo phase change from hcp into bcc at  $863^\circ\text{C}$  and  $2115^\circ\text{C}$ , respectively. The bcc structure has a benefit of being optically isotropic. However, a phase transition involves abrupt changes in material properties such as lattice constants or volume. Since these changes can cause stress at interfaces between different materials, a phase change could lead to delamination and permanent fracture of the emitter. For this reason, caution is needed when using phase-changing materials in TPV emitters. However, if the operation temperature is far below the phase transition temperature, the above concern could be reduced.

### C. Oxidation

TPV emitters operate in a hot environment where their performance can degrade due to oxidation. For this reason, oxidation is probably one of the most important aspects to overcome for practical deployment of TPV technology in air. Several studies suggest that the oxidation rate of materials can vary due to stress in the oxide layer [123–125]. While these studies mainly focus on oxidation of bulk materials, the oxidation of thin films may be more sensitive to stress since oxygen diffusion into the film, in addition to its oxide layer, is also affected by stress. The stress in a thin film is dependent on numerous factors such as CTE or Young's modulus differences between the film and substrate, which we discuss in detail in Sec. IV E, as well as deposition parameters [126] and thickness of the film. If an adhesion/buffer layer is used between the film and substrate, it also affects the stress

in the film. Moreover, studies on metal oxidation report their results based on experimental parameters which vary largely from study to study, such as oxygen pressure, temperature, or annealing time [127–130], to which the oxidation rate is sensitive. We also note that it was hard to find a study that compares oxidation characteristics of various refractory metal thin films with the same thickness on the same substrate for varying deposition parameters. For these reasons, it may be hard to directly compare oxidation characteristics of thin metal films, which are commonly used to fabricate selective TPV emitters. The standard reduction potential (SRP), however, as discussed in Sec. ID, are measured at specific experimental conditions,  $25^\circ\text{C}$ , 1 atm gas pressure, and solution concentration 1 mol/l [52]. For this reason, the SRPs could serve as a more objective measure to compare metal oxidation for TPV emitters.

### D. Diffusion

Compared to diffusion through the volume of a material, surface diffusion depends on numerous factors such as geometry [47], surface energy [47], or surface contamination [131]. Surface contamination also impacts surface energy, which then affects the surface diffusion rate [46]. By assuming no surface contamination, Ref. [47] shows how the surface diffusion rate of a PhC emitter changes as a function of surface geometry, and how that affects its initially designed emissivity spectrum. As the study finds, the surface diffusion rate is proportional to the diffusion coefficient of the material, which is discussed in Sec. II above. Since surface diffusion is dependent on numerous factors, a rigorous investigation of the surface diffusion properties of emitters fabricated with various subwavelength patterns is expected to be highly time consuming. Perhaps this explains the scarcity of the relevant data. However, the diffusion coefficient is one of the dominant parameters for surface diffusion and is independent of surface energy or contamination [47]. For this reason, the diffusion coefficient could serve as a more objective measure in estimating the mechanical stability of TPV emitters against diffusion. In addition, as discussed in Sec. III, refractory oxide coating layers contribute to reducing surface diffusion of metals. This can help emitters retain their initially designed structure.

### E. Thermal expansion and stress

Different materials may have different CTEs. Stress at material interfaces due to different thermal expansion rates can cause delamination or destruction of the structure upon temperature changes. Therefore, researchers have taken CTE into account to minimize stress in their emitters. For example, if the CTE difference is too high, a material that has an in-between CTE is used as an adhesion (or buffer) layer [132]. In addition to CTE, stress-strain responses of the material, such as Young's modulus, may also contribute to delamination. For example, we compare delamination results of Ti and Ir on a sapphire substrate. Although the sapphire's CTE is better matched to the Ir's than the Ti's, it was reported that Ti improves adhesion between a sapphire substrate and an Ir layer, which delaminated off the sapphire without Ti [50]. The CTEs and Young's moduli of these materials are shown in Table II. The Young's modulus of Ir is more than four times larger

TABLE II. Coefficient of linear thermal expansion (CTE) and Young’s modulus of Ti [53], Ir, and sapphire [113]. Given values are for polycrystals at room temperature.

	Ti	Ir	Sapphire
CTE ( $10^{-6}/K$ )	8.35	6.8	5.5
Young’s modulus (GPa)	120	528	400

than that of Ti. This, despite the better CTE match with the sapphire’s, can create more stress at the Ir/sapphire interface. To map the relative stress in these layers at an increased temperature, we performed a simulation. Figure 21 shows the simulated relative stress for Ir, Ti, and Ir/Ti layers on a sapphire substrate at 100 °C. The Ir/sapphire structure is under a higher stress, Fig. 21(a), than that of the Ti/sapphire, Fig. 21(b). These results may be interpreted as the higher Young’s modulus of Ir is responsible for the observed delamination in Ref. [50]. Interestingly, more stress is present at the Ir/Ti interface, Fig. 21(c), than that at the Ir/sapphire interface, Fig. 21(a). However, as discussed above, Ir/Ti on a sapphire did not delaminate while Ir on a sapphire delaminated. This may be attributed to the fact that both Ir and Ti are metals and therefore, they bond more strongly via metallic bonding than Ir (metallic bonding) and sapphire (ionic bonding) do. While many of the failure issues arise at interfaces, some emitters are made solely of one material with micro- or nanopatterns directly etched into the metal substrate [49,79,80,90]—referred to as a “single-material emitter” hereafter. These emitters may have the advantage of no delamination compared to emitters consisting of multiple materials and interfaces.

F. Material cost

While the physical and chemical properties of materials determine the emitter’s performance, enabling TPV applications on a larger scale may require lower material cost [133]. Considering only the metal prices in an emitter, metals with a lower price (per weight) such as Nb, Mo, or Ta, for example, as shown in Fig. 9(g), seem the best candidates to manufacture TPV emitters for a lower cost. However, because it is the amount of materials used that determines the cost, emitter design is also an important factor. For example, Table III and

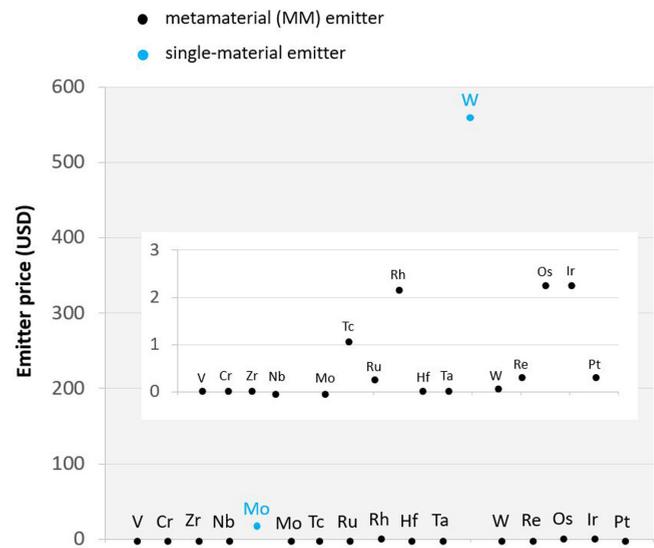


FIG. 22. Price comparison of TPV emitters from Table III. The constituent material of the emitter is denoted by the element symbol on top of each data point.

Fig. 22 compare prices of several emitters regarding the actual amount of metals used. The emitter price ( $P$ ) is calculated by the relationship  $P = P_o A t \rho$ , where  $P_o$  is metal price per unit weight,  $A$  is emitter surface area,  $t$  is emitter thickness, and  $\rho$  is metal density. It is evident that single-material emitters tend to have much higher prices compared to metamaterial (MM) emitters due to the larger amount of material used. Thus, although single-material emitters have the advantage of no delamination, as discussed in Sec. IVE, they result in higher material cost. On the contrary, MM emitters can have a much lower material cost although they may be more prone to delamination. Furthermore, we compare Rh (180 USD/g) and Mo (0.16 USD/g), the most expensive and cheapest metals among the 15 refractory metals in this study, respectively. Rh is 1125 times more expensive than Mo per unit weight. However, the price comparison in Table III suggests that Rh-based MM emitters can be even cheaper than Mo-based single-material emitters. Therefore, we conclude that the metal price (per unit weight) should not be the only factor to look at when determining material cost. Since the total cost is

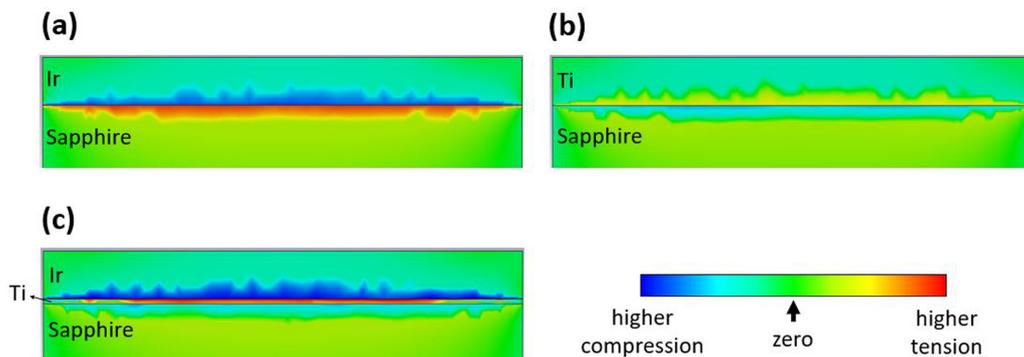


FIG. 21. Simulated relative stress in layers at 100 °C. Thickness ratio of the layers used in simulation is Ir:sapphire = 1:10 (a), Ti:sapphire = 1:10 (b), and Ir:Ti:sapphire = 1:0.1:10 (c). Note that the resulting screenshots are cut at the sapphire. Layers are assumed to have been deposited at room temperature. Material properties at room temperature are used for simplified simulation.

TABLE III. Price comparison of refractory-metal-based emitters. Density data are from Ref. [52]. The thicknesses 1 mm (for single-material emitters) and 100 nm (for metamaterial emitters) are chosen as they are typical thicknesses of metal substrates and metal thin films in a metamaterial, respectively. “MM” in “emitter type” column stands for metamaterial. Emitter price assumes only the prices of the used metals in the emitter.

Metal	Density ( $\rho$ ) (g/cm <sup>3</sup> )	Price per unit weight ( $P_o$ ) (USD/g)	Emitter surface area ( $A$ ) (cm <sup>2</sup> )	Emitter thickness ( $t$ )	Emitter price ( $P$ ) (USD)	Emitter type
V	6.0	3	100	100 nm	0.018	MM
Cr	7.15	1	100	100 nm	0.0072	MM
Zr	6.52	4	100	100 nm	0.026	MM
Nb	8.57	0.5	100	100 nm	0.0043	MM
Mo	10.2	0.16	100	1 mm	16.3	Single material
Mo	10.2	0.16	100	100 nm	0.0016	MM
Tc	11	100	100	100 nm	1.1	MM
Ru	12.1	25	100	100 nm	0.30	MM
Rh	12.4	180	100	100 nm	2.2	MM
Hf	13.3	2	100	100 nm	0.027	MM
Ta	16.4	2	100	100 nm	0.033	MM
W	19.3	2.9	100	1 mm	560	Single-material
W	19.3	2.9	100	100 nm	0.056	MM
Re	20.8	16	100	100 nm	0.33	MM
Os	22.59	100	100	100 nm	2.26	MM
Ir	22.56	100	100	100 nm	2.26	MM
Pt	21.5	15	100	100 nm	0.32	MM

more important than the cost per weight, both emitter design and metal price should be considered.

## V. SUMMARY AND OUTLOOK

This work reviews selective TPV emitters fabricated with refractory metals and their thermal stability. The emitter’s performance can degrade due to a variety of reasons, such as mechanical deformation or chemical reaction. A good material for TPV emitters may be the ones with the following properties: higher melting point, higher SRP, lower diffusion coefficient, and lower  $E_{\text{Young}}$  as well as lower price. Lattice constants and CTE should also be matched between layers to minimize stress. Moreover, the material should not experience a phase change at its operating temperature since it can lead to mechanical destruction. Larger grains are also preferred to reduce diffusion, summarized in Fig. 23.

As shown in Table I and Fig. 9, all refractory metals in this review have both desired and undesired properties. This indicates that a specific property (or properties) may need to be more (or less) weighted when deciding on the material. For example, the oxidation resistance may be less important for TPV applications in outer space [134,135]. For applications in air, however, oxidation resistance should be one of the most important criteria. This work finds that a dominant majority of TPV emitters reported in the literature are based on refractory metals that have poor oxidation resistance; SRP smaller than zero. Most of these emitters are tested in vacuum or inert atmosphere. While they demonstrate their utility in nonoxidizing atmosphere, the thermal stability of these emitters may need to be tested in air for their applications in air. Many sites for potential deployment of TPV energy harvesting are industrial high-temperature processes [2–7] and power plants [8], which are under air. Therefore, more research would be

needed on emitters fabricated with oxidation-resistant materials, i.e., refractory metals with a positive, higher SRP such as Ru, Rh, or Ir, for example. These metals are costly compared to the metals that are widely studied for TPV emitters. However, as discussed in Sec. IV F, material cost can be significantly reduced by using metamaterial emitters.

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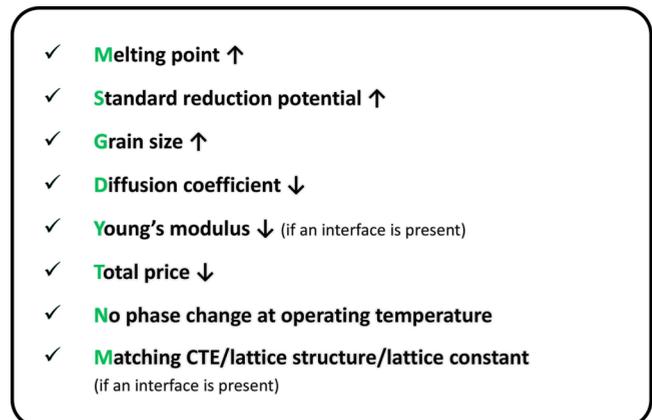


FIG. 23. Desired properties for a good material candidate for TPV emitters. Upward (↑) and downward (↓) arrows indicate higher and lower, respectively.

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