Far-infrared emission of Ti-based oxides

Seunghhee Lee a, Yongseon Kim b,c, Shinhoo Kang b,*

a Department of Biomedical Engineering, College of Medicine, Seoul National University, Seoul 151-742, Republic of Korea
b Department of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul 151-742, Republic of Korea
c Samsung SDI Co., Ltd., Young in-si, Gyeonggi-do 446-577, Republic of Korea

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A B S T R A C T
Various Ti-based oxides were used as far-infrared (FIR) radiation sources. The temperature increases and emissivities of aluminum panels coated with these oxides were measured. To explain their different FIR emissivities, the electronic energy levels of these oxides were calculated using the direct-variational Xα molecular orbital method. Ti2O3 and TiO were found to be more effective materials as FIR sources than was TiO2 in the wavelength range 3–7 μm. The wide band gap of TiO2 is the cause of its relatively low emissivity.

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1. Introduction

Far-infrared (FIR) radiation is electromagnetic radiation with wavelengths longer than near-infrared (NIR) radiation. Such radiation commonly exhibits strong thermal interaction with organic materials. The classification of the Commission Internationale de l’Eclairage divides the infrared (IR) region into three regions: the NIR region with wavelengths in the range 0.78–1.4 μm, the FIR region with wavelengths in the range 3.08–1000 μm, and an intermediate region. FIR radiation with wavelengths in the range 3.0–30 μm is generally used for industrial applications, whereas FIR radiation with wavelengths in the range 50–1000 μm is rarely used. [1–4] According to the Stefan–Boltzmann law, the flux density of radiant energy emitted by a black body emitter is proportional to the fourth power of its absolute temperature (T4). Wien’s displacement law states that the wavelength at which the maximum energy density occurs decreases with increasing temperature.[5,6]

The FIR region corresponds to energies that can generate vibrational motion of atomic clusters and molecules. When a material is exposed to radiation from a heat source, its constituent atoms or molecules absorb the energy together with their associated electrons, resulting in vibrational motions of the atoms or molecules, thereby exciting their electrons. A portion of the absorbed energy is then re-emitted as a low-energy spectrum that contains FIR radiation. When the frequency of this re-emitted FIR radiation coincides with the resonance frequency of the material, resonance occurs and energy is transferred to the material. This energy can be re-emitted by varying the dipole moment of the material, being generally emitted as heat. Electromagnetic radiation with a frequency that does not coincide with the vibrational frequency of the material passes through and/or is reflected.[7–9]

The main concern in utilizing FIR radiation is how to control the radiation level of a specific wavelength or wavelength range to ensure resonance with a material. To this end, natural materials with high emissivities have been investigated and used as mixtures. In applications, attention has focused on solving practical problems associated with thermal expansion mismatch, thermal shock, and poor mechanical strength. However, FIR radiation has been insufficiently studied, despite it being widely used in industrial and medical applications.

In this study, Ti-based oxides were selected to investigate FIR generation and energy transfer mechanisms because there are various oxide compounds to compare with the same constituent elements. Further, some of these materials are known as good far-infrared materials. In an effort to understand the FIR generation, the electronic energy states of these oxides were calculated by a first-principles method known as the discrete variational (DV) Xα molecular orbital method. This method approximates the exchange–correlation interaction with the Xα potential proposed by Slater [10] and solves the Schrödinger equation numerically through the Hartree–Fock–Slater method. This allows one to obtain reliable information regarding the transfer of electrons among the atoms, the extent of contribution of each atomic orbital to the formation of molecular orbitals, and the electronic energy levels.
2. Experimentals

TiO (99.9% purity, <5 μm, Aldrich), TiO2 (>99% purity, anatase, <110 μm, Aldrich), and Ti2O3 (99.9% purity, <110 μm, Aldrich) powders were used in the experiments. Two grams of each powder were mixed with the same weight of a binder material made from water glass (sodium silicate solution: Na2SiO3) and water in a weight ratio of 1:10. These mixtures were then uniformly coated on 0.5-mm-thick aluminum square panels of 200 × 200 mm.

Fig. 1 shows a schematic diagram of the experimental setup used to measure the thermal response of FIR irradiation of objects. The coated aluminum panels were used as FIR sources by maintaining them at 250 °C using a thermal control system. The other aluminum disks (diameter: 200 mm; thickness: 0.5 mm) were painted with nitrocellulose lacquer (Samwha, Korea) to a thickness of 20 μm and were used as the objects to be heated by FIR radiation. One of these painted disks was placed 30, 60, or 90 cm away from the FIR source panel. The change in the temperature of the painted disk was monitored using a thermometer (1316, TES, Taiwan), with five measurements for each sample.

The radiation spectra from FIR source panels coated with various Ti-based oxide powders were obtained in the wavelength range 4000–400 cm⁻¹ using an FT-IR (Fourier-transform infrared spectrometer, Midac, 2200, USA) at 250 °C. Spectra with a resolution of 8 cm⁻¹ were obtained by scanning each sample 20 times and averaging the results. Visible light emission was also measured using a spectrophotometer (Jasco, FP-6500, Japan).

Electronic energy levels were calculated by first-principles calculations using the DV-Xα molecular orbital method. [Ti2O20]3⁻, [Ti13O50]64⁻, and [TiO6O20]3⁻ cluster models were used for TiO, Ti2O3, and anatase TiO2, respectively. The radiation wavelength was estimated from the simulation results.

3. Results and discussion

3.1. Radiation properties of Ti-based oxides

The temperature measurement sensitivity of the experimental setup was checked using an unpainted aluminum disk. When a FIR aluminum panel coated with TiO was heated to 250 °C, the temperatures of unpainted disks positioned 30, 60, and 90 cm from the TiO-coated FIR panel increased by 0.9, 0.67, and 0.5 °C, respectively. These results with corresponding standard deviations of 5 measurements demonstrate that the experimental setup provides reasonably accurate temperature measurement, although the measured temperature changes are not very large. The amount of FIR radiation absorbed by the unpainted aluminum disk was found to be insignificant. In contrast, the aluminum disks painted with nitrocellulose lacquer absorbed a considerable amount of FIR radiation. The lacquer increased FIR absorption, resulting in a marked increase in the temperature of the aluminum disks.

Table 1 summarizes the temperature increases of the painted aluminum disks heated by FIR radiation from aluminum panels coated with the three oxide coatings. The temperature rise stabilized within 90 s; thus, the temperature measurements were performed after 90 s. When an uncoated aluminum panel was used as an FIR source by heating it to 250 °C, the temperature of a painted disk located 30 cm from the FIR disk increased by 2.03 °C. The temperature increase was 4.25 °C when an aluminum panel coated with water–glass binder was used as the FIR source.

Significant increases in the temperature were observed when Ti-based oxides were added to the water–glass binder. When aluminum panels were coated with binders containing 2 g of TiO2, Ti2O3, or TiO, the temperature increase of the painted disks were 12.58, 20.94, and 17.95 °C at a distance of 30 cm, respectively. The measurements performed at 60 and 90 cm revealed similar trends for the three oxide coatings (see Table 1). This finding indicates that the FIR radiation efficiency depends on the material used as an FIR source.

TiO2 powders with average particles sizes of 54 and 100 μm were also examined to investigate the effect of particle size on the FIR radiation energy. The temperature changes using TiO2 powders with average particles sizes of 54 and 100 μm were 12.58 and 12.34 °C, respectively, yielding similar values. This finding indicates that FIR radiation from a material is independent of the material's size or shape; that is, the FIR properties are not significantly affected by the surface area and/or transmittance of the powder.

Thus, the observed temperature increases must be due to the interaction between the FIR radiation and the nitrocellulose lacquer. FIR radiation having the same frequency as that of molecular vibrations in the nitrocellulose lacquer generates resonant motions, resulting in heating of the lacquer and subsequently of the aluminum disks. The thermal energies acquired by the disks are estimated to be 471,784 and 672 J for TiO2, Ti2O3, or TiO, respectively, using the equation of $Q = c·m·ΔT$, where $c$ is the specific heat capacity of aluminum, $m$ mass and $ΔT$ is the temperature increase.

Table 2 shows the radiation emissivities of the oxides measured using an FT-IR spectrometer in different wavelength ranges at 250 °C. The emissivity is defined as the ratio of energy radiated by an object to that radiated by a black body at the same temperature. According to Wien's displacement law, the maximum peak in the radiation energy spectrum shifts to shorter wavelengths, when the surface temperature of a body increases, such that the product of the wavelength of the peak and the temperature is a constant: $λ_m·T = 2987 [μm K]$. [16,17].

![Fig. 1. Schematic view of the experimental system.](image-url)
Since the FIR sources were heated to 250 °C, Wien’s displacement law predicts that the wavelength of the maximum peak will be 5.72 \( \mu \)m. This is consistent with the results of our experiments (see Fig. 2). The difference in the wavelength between that of Fig. 2 and 5.72 \( \mu \)m is due to the fact that Wien’s displacement law is based on the ideal blackbody. However, in the actual material, the maximum wavelength of the peak may shift depending on the electron states and crystal structure of materials. Interestingly, the emissivities of TiO and Ti\(_2\)O\(_3\) are over 0.85, while TiO\(_2\) has a relatively low emissivity of ~0.77 in the wavelength range of 3–7 \( \mu \)m (Table 2). The emissivity of TiO\(_2\) is low compared with its overall emissivity of 0.86 in the range 3–20 \( \mu \)m. Possible reasons for these different emissivities are discussed in the following section in terms of the electronic energy states of the systems.

Photoluminescence (PL) emission spectra of TiO, TiO\(_2\), and Ti\(_2\)O\(_3\) were also obtained to determine their radiation properties in the visible region (Fig. 3). Only TiO\(_2\) showed UV emission at about 400 nm, indicating that electron transitions occur across relatively large energy gaps in TiO\(_2\) crystals. This finding is also explained below using the DV-X\(\alpha\) calculation results.

### 3.2. Energy level calculations by the DV-X\(\alpha\) method

To explain the above experimental results, the electronic energy levels of Ti-based oxide systems were calculated using the DV-X\(\alpha\) molecular orbital method. The cluster models used in these calculations were selected to achieve a good balance between calculation efficiency and accuracy. The models are presented in Fig. 4: [Ti\(_{22}O_{22}\)]\(^{4+}\) was used for the fcc crystal structure of TiO, while [Ti\(_{15}O_{48}\)]\(^{51-}\) was used for trigonal Ti\(_2\)O\(_3\), and [Ti\(_{9}O_{50}\)]\(^{64-}\) was used for tetragonal TiO\(_2\) (anatase). These models contain 40–60 atoms, which is sufficiently large to provide accurate simulation results.

Fig. 5 shows the electronic energy levels calculated by the DV-X\(\alpha\) molecular orbital method and Table 3 gives the energy gaps between the immediate energy. These energy levels are specified relative to the energy level of the highest occupied molecular orbital (HOMO). When electrons are excited by an external source, the radiating energy is determined either by the minimum gap size, \( \Delta E \), or by the sum of the energy gaps. Short-wavelength radiation is also possible depending on the probability of energy transitions.

### Table 2

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>3–7 ( \mu )m</th>
<th>8–10 ( \mu )m</th>
<th>10–11 ( \mu )m</th>
<th>12–13 ( \mu )m</th>
<th>13–20 ( \mu )m</th>
<th>Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black body</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TiO</td>
<td>0.868</td>
<td>0.858</td>
<td>0.878</td>
<td>0.885</td>
<td>0.885</td>
<td>0.872</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.772</td>
<td>0.941</td>
<td>0.958</td>
<td>0.924</td>
<td>0.896</td>
<td>0.860</td>
</tr>
<tr>
<td>Ti(_2)O(_3)</td>
<td>0.865</td>
<td>0.858</td>
<td>0.877</td>
<td>0.884</td>
<td>0.884</td>
<td>0.870</td>
</tr>
</tbody>
</table>

Fig. 2. Emissive powers of Ti-based oxides relative to that of a black body.

Fig. 3. PL spectra of Ti-based oxides (\( \lambda_{ex} = 245 \) nm; all PL spectra were measured under the same measurement conditions).

Fig. 4. Cluster models of the three oxides used in DV-X\(\alpha\) calculations.

Fig. 5. Electronic energy levels of Ti-based oxides calculated by DV-X\(\alpha\).
from excited states to low-energy states. Most of the excited energy generally dissipates as heat during transitions to the ground state. This heat would be expressed as an infrared spectrum.

In the FIR range of 3–7 μm shown in Table 2, it is possible for energy to be emitted by transitions between energy states separated by 0.177–0.412 eV. This amount of energy can be emitted only by the electronic states in TiO and Ti2O3 because the energy gaps between vacant levels are in the ranges 0.003–0.103 eV and 0.020–0.511 eV for TiO and Ti2O3, respectively, according to Table 3. In addition, the above-mentioned energy can also be absorbed by these oxides.

In the case of TiO, the energy gaps between the vacant levels, ΔEi, are very small and uniform (−0.05 eV), making this oxide suitable for use as an FIR source for long wavelengths over 20 μm. TiO2 also has a dense distribution of energy levels (Fig. 5); however, unlike TiO, it has a few intermediate-sized energy gaps (ΔEi = 0.2–0.5 eV) and some small energy gaps (<0.05 eV) (see Table 3). This implies that Ti2O3 may emit both NIR radiation with wavelengths of ~2 μm and FIR radiation with wavelengths over 20 μm.

However, a 3.3 eV band gap exists between the HOMO and lowest unoccupied molecular orbital (LUMO) levels in TiO2 (Table 3b). This is about the same as the measured band gap (~3.2 eV)[18,19]; however, it offers a good explanation for the low emissivity of the TiO2 system in the wavelength region of 3–7 μm. The energy transfer across this band gap generates UV emission rather than infrared emission. The wavelength of radiation generated by band-to-band transitions of electrons will be

Table 3  
Band gap energies and energy levels of Ti-based oxides.

<table>
<thead>
<tr>
<th>(a) TiO</th>
<th>(b) TiO2</th>
<th>(c) Ti2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ei</td>
<td>Energy (eV)</td>
<td>ΔEi</td>
</tr>
<tr>
<td>E320</td>
<td>9.3221</td>
<td>0.012</td>
</tr>
<tr>
<td>E321</td>
<td>9.2102</td>
<td>0.045</td>
</tr>
<tr>
<td>E322</td>
<td>9.1650</td>
<td>0.080</td>
</tr>
<tr>
<td>E323</td>
<td>9.0852</td>
<td>0.003</td>
</tr>
<tr>
<td>E324</td>
<td>9.0817</td>
<td>0.046</td>
</tr>
<tr>
<td>E325</td>
<td>9.0360</td>
<td>0.015</td>
</tr>
<tr>
<td>E326</td>
<td>9.0210</td>
<td>0.006</td>
</tr>
<tr>
<td>E327</td>
<td>9.0153</td>
<td>0.025</td>
</tr>
<tr>
<td>E328</td>
<td>8.9904</td>
<td>0.103</td>
</tr>
<tr>
<td>E329</td>
<td>8.8870</td>
<td>0.076</td>
</tr>
<tr>
<td>E330</td>
<td>8.8115</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Where ΔEi = Eei – Ein.

The conclusions of this study are given below:

1. When an aluminum disk was coated with TiO2, Ti2O3, or TiO and used as an FIR source at 250 °C, the temperature increase of the painted aluminum disk was 12.58, 20.94, and 17.95 °C at a distance of 30 cm, respectively. This indicates that Ti2O3 and TiO are more effective materials for FIR sources than is TiO2.

2. The radiation emissivities of the oxides were measured using an FT-IR spectrometer at 250 C in different wavelength ranges. The emissivities of TiO and Ti2O3 are over 0.85, whereas TiO2 has a relatively low emissivity of ~0.77 in the wavelength range 3–7 μm. This finding is consistent with the temperature increases observed in the painted disks.

3. The energy gaps between vacant levels are calculated to be in the range 0.003–0.103 eV and 0.020–0.511 eV for TiO and Ti2O3, respectively. In contrast, TiO2 has a wide band gap and some narrow gaps. Energy transfer across this wide gap generates UV emission. The band gap is the cause of the relatively low infrared emission.

4. TiO could be used as an FIR source for long wavelengths over 20 μm, while Ti2O3 could be used as an NIR source for wavelengths ~2 μm and an FIR source for wavelengths over 20 μm.

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