Shift in low-frequency vibrational spectra of transition-metal zirconium compounds

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The far-infrared terahertz (THz) spectra of ZrC, ZrN, ZrO2, and ZrF4 have been measured using terahertz time-domain spectroscopy. The characterization of the frequency-dependent power absorption, index of refraction and complex dielectric function in the frequency range 0.1–2.0 THz are obtained. A standard Drude-Lorentz model gives a good fit on the transmission measurement results. We first observe the shift in the low-frequency vibrational spectra of different zirconium compounds. We analyze that the influence of the anion on the vibration modes causes the shift in low-frequency vibrational spectra of zirconic compounds. © 2005 American Institute of Physics.

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The refractory transition-metal compounds are a very interesting class of materials both for theoretical and experimental investigations because they combine various unique physical and chemical properties such as high melting point, chemical stability, and corrosion resistance.1 ZrC is a high temperature structural material with a very high melting point at 3420 °C and striking mechanical properties, extreme hardness combined with metallic electrical, and thermal conductivities. Zirconium nitride crystallizes in the rock salt structure and has high hardness, good resistance to wear, oxidation and corrosion, good chemical stability and golden color. Zirconia (ZrO2) possesses a wide range of applications in structural and functional engineering. ZrO2 films have been used as hard coatings on recording media, buffer layer in structural and functional engineering. ZrO2 films have been used as hard coatings on recording media, buffer layer for high temperature oxide superconductors, and so on. 2, 3 A lot of methods have been employed to studies the various properties of zirconic compounds, but little research has been done on their optical characteristics in the Terahertz (THz) region.

In this letter, we report the characterization of the THz spectra of several compounds based on zirconium, namely, ZrF4, ZrO2, ZrC, and ZrN over frequency region from 0.1 to 2.0 THz using THz time-domain spectroscopy (THz-TDS). THz-TDS transmission measurements have been demonstrated as an effective technique for characterizing various materials including semiconductor materials, chemical vapors, nanostructures, and conducting polymers.5–8 Its applications have also involved tomographic imaging, label free genetic analysis, cellular level imaging, and biological sensing.9 We present the measurements of the far-infrared (far-IR) THz spectra of the above four compounds and the Drude-Lorentz model describing the observed complex dielectric properties.

ZrF4, ZrO2, ZrC, and ZrN used in this study were purchased from Sigma-Aldrich and used without further purification. The samples were prepared by milling the crystals powder carefully and made into pellets with thickness between 1.1 and 3.0 mm by applying an approximate pressure of 50 MPa with an oil press. All procedures were carried out well in a dry condition. A standard Terahertz time domain spectroscopy apparatus for far-IR transmission measurements is used. The setup and corresponding experimental data analysis method have been discussed in detail in previous reports.10,11 In brief, the laser was model-locked Ti:sapphire system that provided 100-fs pulses at a wavelength of 800 nm with average power of 700 mW and a repetition rate of 80 MHz. Pulsed THz radiation was produced by illuminating the GaAs photoconductor antenna and detected in a ZnTe crystal via electro-optical sampling. The spectrometer has a useful bandwidth of 0.1–2.2 THz and a spectral resolution of better than 40 GHz. The THz beam path was purged with dry nitrogen in order to minimize absorption by water vapor.

As an example, we first discuss ZrF4 sample. As shown in Fig. 1, the measured power absorption a(ω), index of refraction n(ω), and the complex dielectric constant ε(ω) of ZrF4 are obtained at room temperature. The marked absorption peak is seen in the far-IR region around 1.48 THz, which corresponds to a characteristic change of the index of refraction. The measured absorption, index of refraction, and complex dielectric can be fitted using the Drude-Lorentz model.

The frequency-dependent complex dielectric constant ε(ω) is described by the Drude-Lorentz model as12

$$
\varepsilon(\omega) = \varepsilon_c - \frac{\omega_p^2}{\omega(\omega + i\gamma)} - \sum_j \frac{\omega_{pj}^2}{(\omega^2 - \omega_j^2) + i\Gamma_j\omega},
$$

(1)

where εc represents the frequency-independent optical dielectric constant. The first and second terms are well known as a Drude model for a good metal. In the simple Drude model, the key parameters describing the dynamics of free carriers in a material are plasma frequency ωp and the relaxation rate of the charge carries γ.12,13 The motion of localized charge carries is ascribed to the third term, the Lorentz harmonic oscillators, where ωpj, ωj, and Γj are, respectively, oscillator strength, the center frequency, and spectral width. The general relationship between the complex dielectric function and the complex refraction is14

$$
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = [n(\omega) + ik(\omega)]^2.
$$

(2)

Here ε1(ω) and ε2(ω) are the real part and imaginary part of the dielectric constant. n(ω) and k(ω) = ε1(ω)/2ω are the
real component and imaginary component of the complex refraction, respectively. The parameters used to fit the experimental data are: $e_c = 3.2$, $\omega_p/2\pi = 0.10$ THz, $\gamma/2\pi = 0.25$ THz, $\omega_p/2\pi = 0.68$ THz, $\omega_\perp/2\pi = 1.45$ THz, and $\Gamma_\parallel/2\pi = 1.30$ THz. As shown in Fig. 1, the probed real and imaginary components of frequency-dependent dielectric constant, the power absorption and index of refraction of ZrF₄ agree quite well with the Drude-Lorentz model.

Having $\omega_p$ and $\gamma$, we can obtain the electron mobility $\mu_e = 1.12 \times 10^5$ cm²/V s through the formula: $\mu_e = e/(m' \gamma)$ when supposing the effective mass $m' = 1.0 m_0$. Then the zero-frequency resistivity is determined by $\rho = \gamma/(e_0 \omega_p^2) = 44.96 \ \Omega \ \text{cm}$.¹⁵

The frequency-dependent complex conductivity $\sigma(\omega)$ can be calculated by

$$\sigma(\omega) = \sigma_1(\omega) + i \sigma_2(\omega) = -i \omega \varepsilon_0 (\varepsilon(\omega) - \varepsilon_c).$$  (3)

Here $\sigma_1(\omega)$ and $\sigma_2(\omega)$ are the real part and imaginary part of the complex conductivity. Then we can easy obtain the real part of the conductivity as $\sigma_1(\omega) = \omega \varepsilon_0 \varepsilon_0(\varepsilon(\omega) - \varepsilon_c)$.

Figure 2 shows the measured absorption and the real part of complex conductivity of ZrC, ZrN, ZrO₂, and ZrF₄ over the frequency range from 0.1 to 2.0 THz. The observed experimental results are theoretically fit using the above described Drude-Lorentz model, shown as the solid line of Fig. 2. The dotted lines indicate that observed absorption peaks are shifted towards higher frequency from ZrC to ZrF₄. This characteristic is also corresponding to the shift in the conductivity. The power absorptions and the conductivity of ZrC, ZrN, and ZrO₂ present very similar shapes as that of ZrF₄ during the experimental frequency range.

In ionic crystalline solids, the atoms are bound in periodic arrays which propagate waves with constraints and behavior imposed by the dynamics of lattice motion. The interaction of a radiation field with the fundamental lattice vibrations generally results in the absorption of the electromagnetic wave due to the creation or annihilation of lattice vibrations.¹⁶ Optical absorption of ionic crystals in the far-IR region can be ascribed to the lattice vibration, which includes many modes induced by the interactions between the metal ion and the anion, as well as interaction between metal ions and between anions. For metal oxides, nitrides or sulfides,
the obvious far-IR THz absorptions usually come from the stretching vibration modes and flexural vibration modes of heavy atoms. As a result, the far-IR THz measurement provides the information about the lattice vibration of solid crystals.

As described above, for metal compounds, the stretching vibration and flexural vibration of heavy atoms cause the obvious far-IR absorption. Hence, here we consider that the vibration mode of heavy zirconium ion is dominant over the measured frequency region. The enhanced absorption can be ascribed to such visible vibration mode of zirconium ion. This is the reason that these four different zirconium compounds show the similar absorption characteristics during the measured frequency region. Furthermore, the distinctions among them can be seen and indicated as the dotted line. The enhanced peak of absorption is located in the frequency 0.92 THz, 1.05 THz, 1.40 THz, and 1.48 THz for ZrC, ZrN, ZrO₂, and ZrF₄, respectively. Accordingly, we denote that although the vibration mode of zirconium ion is dominant during the measured frequency region, at the same time the anion has a visible influence on it. The differences between them originate from the influence of anion. In the study of ionic crystals or ionic compounds, the radius of anion is an important parameter. The radius of anion for C⁴⁻, N³⁻, O²⁻, and F⁻ is 2.60 Å, 1.71 Å, 1.40 Å, and 1.36 Å. We notice in our measured absorption spectra that the enhanced peak is shifted toward higher frequency with reducing the radius of anion from C⁴⁻ to F⁻. This implies that the decrease in the radius of anion causes the frequency of vibration modes of zirconium ion shift towards a higher value. The similar shift feature was previously observed in the study of lattice far-IR absorption spectra of group II-VI compounds: ZnS, ZnSe, and ZnTe. The typical frequency of transverse optical phonon response was shifted from ZnTe (179 cm⁻¹) to ZnS (274 cm⁻¹) with the decrease in the radius of anion. However, in that case the mass of anion as an important factor has also to be taken into account besides the radius of anion, because in these class compounds the mass of anion has a remarkable change from Te²⁻ (atomic weight 127.60) to S²⁻ (atomic weight 32.07). The shift behavior is original from either the change of the mass of anions and the radius of anions. Strictly speaking, in our case both factors are contributing to the shift feature. But compared with the heavy zirconium ion (atomic weight 91.22), the mass of anion is smaller on the one hand, and the change in the mass of anion is also not very obvious from C⁴⁻ to F⁻ on the other. Hence, here we consider the obvious phonon resonance is dominated by the heavy zirconium ion and the shift feature is mainly governed by the variety in the radius of anion.

In conclusion, we have reported the measurements on the far-IR THz power absorption coefficient and index of refraction of several nearby zirconic compounds ZrC, ZrN, ZrO₂, and ZrF₄ by THz time-domain spectroscopy. The shift in the low-frequency vibrational spectra of different zirconium compounds samples are first observed. The recorded results are described well by a Drude-Lorentz model. The distinct characteristic and common features of their THz spectra could be identified as the signatures of vibration modes of ions. We explain that the variety in the radius of anion causes the shift characteristic in THz spectra of different zirconic compounds.

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8. Table of Periodic Properties of the Elements (Sargent-Welch, Sokie, IL, 1980).