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Analysis of the Refractive Indices of TiO_2, $TiOF_2$, and TiF_4: Concept of Optical Channel as a Guide To Understand and Design Optical Materials

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In an effort to gain insight into how optical properties of insulating materials are affected by a change in chemical composition, we investigated the dielectric functions of titanium dioxide, TiO_2, and its fluorine-substituted phases, $TiOF_2$ and TiF_4, by electron energy loss spectroscopy measurements and density functional theory electronic band structure calculations. The refractive indices of these compounds are found to be inversely proportional to their cell volumes per formula unit. This observation was explained by employing the concept of optical channels. Our study indicates that the light-scattering properties of insulating compounds can be controlled by modifying their cell volumes.

1. Introduction

The relationships between optical properties and chemical composition were recognized at an early age.[1] To some extent, these relationships remain mysterious because it is not fully understood how to design a material with a required opacity (i.e., the light-scattering power) and color strength (i.e., the light-absorbing capacity), which depend on the refractive indices n and the extinction coefficient k, respectively. It is therefore important to explore the factors governing the optical properties of materials and their refractive index in particular. In rationalizing and/or estimating refractive indices of closely related compounds, empirical relations have been widely used. Specifically, refractive indices are correlated with either band gaps (Moss relationship)[2] or mass densities (Gladstone−Dale relationship).[3] Although these relationships work satisfactorily for specific situations, there has been no simple rule with which to explain how structural and compositional changes might affect optical properties.

In describing the interaction of light with matter, one often employs oscillator models such as the Drude and Lorentz models.[4,5] However, a more precise description of this interaction requires a proper consideration of quantum mechanics. Density functional theory (DFT)[6,7] electronic band structure calculations and electron energy loss spectroscopy (EELS)[8] experiments enable one to determine the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ of a material, from which n and k are deduced.[9,10] These parameters are functions of the incident light energy $\hbar\omega$. The imaginary component $\epsilon_2(\omega)$ represents the absorption power of a material per unit volume at a given incident light energy. The zero-frequency limit of $n(\omega)$, commonly used as an indicator of the refractive

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index in the visible range for insulators, is related to the integration of the extinction coefficient $k(\omega)$ weighted by the inverse of the excitation energy, $1/\omega$. That is

$$n_0 \equiv n(0) = 1 + \frac{2}{\pi}\int_0^{+\infty}\frac{k(\omega)}{\omega}\,\mathrm{d}\omega \qquad (1)$$

The zero-frequency limit of the real component $\epsilon_1(\omega)$ is equal to n_0^2 and is related to the integration of $\epsilon_2(\omega)$ weighted by $1/\omega$

$$n_0^{\,2} = \epsilon_1(0) = 1 + \frac{2}{\pi}\int_0^{+\infty}\frac{\epsilon_2(\omega)}{\omega}\,\mathrm{d}\omega \qquad (2)$$

Consequently, as $k(\omega)$ or $\epsilon_2(\omega)$ becomes larger and as the optical gap becomes smaller, the refractive index becomes larger. On the basis of DFT calculations, we recently showed that the refractive indices n_0 of the seven allotropes of TiO_2 follow the Gladstone−Dale relationship, i.e., $n_0 \propto 1/V$, where V is the cell volume per formula unit (FU).[11] The refractive indices reported in the literature are commonly determined using the D lines of Na (i.e., ∼2.10 eV). The trends in the n values determined around $\hbar\omega \approx 2$ eV are well approximated by those of n_0 values.[11] For compounds having the same chemical composition, this study showed that the key parameter for controlling the refractive index is the total absorption power per unit volume $I(\epsilon_2)$, i.e., the integrated value of $\epsilon_2(\omega)$

$$I(\epsilon_2) = \int_0^{+\infty}\epsilon_2(\omega)\,\mathrm{d}\omega \qquad (3)$$

TiO_2 is widely used as a UV shield in different applications such as solar creams. However, although its bulk optical gap is well suited for UV absorption ($E_g \approx 3.1$ eV), it scatters visible light, leading to whitening of the surface or the volume to protect, because of its high refractive index ($n \approx 2.7$). An important industrial challenge is then to prepare colorless UV shield (second-generation UV shield) materials with $n < 2$ and $E_g \approx 3.1$ eV.

One way to reduce the extent of light scattering is to replace high-scattering elements with low-scattering ones, e.g., replacing high-scattering oxygen atoms with low-scattering fluorine atoms in TiO_2. The resulting compounds $TiOF_2$ and TiF_4 are made up of TiX_6 octahedra (X = O, F) as in the case of the seven allotropes of TiO_2. The replacement of one O atom by two F atoms increases the cell volume V per FU. Thus, the substitution of F for O should decrease the refractive index. However, the substitution increases the number of valence electrons per FU, which should increase the refractive index. To gain insight into the overall effect of a chemical substitution on optical properties, we examine in this work the optical properties of TiO_2, $TiOF_2$, and TiF_4. Our work is organized as follows: We describe our calculations of $\epsilon_2(\omega)$ and EELS measurements of $TiOF_2$ in section 2 and introduce the concept of optical channels in section 3. In section 4, we compare the experimental and theoretical $\epsilon_2(\omega)$ spectra of $TiOF_2$ and then show that the refractive indices of $TiOF_2$, TiF_4, and the seven TiO_2 allotropes are proportional to their $1/V$ values. The reason for the latter observation is discussed in section 5 using the concept of optical channels. Finally, important results of our study are summarized in section 6.

2. Electronic Structure Calculations and Electron Energy Loss Spectroscopy Measurements

2.1. Electronic Structure Calculations and Dielectric Function. First-principles DFT electronic band structure and optical property calculations were carried out on $TiOF_2$[12] and TiF_4[13] using the WIEN2k[14] code. In both cases, we employed the Perdew−Burke−Ernzerhof generalized-gradient[15] approximation for the exchange and correlation potential. As the crystal structure of $TiOF_2$ exhibits a cubic symmetry [SG (space group): $Pm\bar{3}m$] in which the O and F atoms randomly occupy the same site, three ordered model structures were generated from geometry optimization using the VASP[16] code with the projector augmented wave[17] potentials prior to the first-principles calculation of the imaginary part of the dielectric function. All model structures of $TiOF_2$ were derived from the ReO_3 structure. In model structures 1 and 2, the 1 × 1 × 1 unit cell is conserved but the F and O atoms are ordered: the O atoms are positioned axially in model structure 1 (SG: $P4/mmm$)[18] but in the equatorial plane in model structure 2 (SG: $P4/mmm$).[19] Model structure 3 corresponds to a random distribution of the F and O atoms in a 2 × 2 × 2 supercell (SG: $P1$).[20] The geometry optimizations (i.e., atomic positions and cell parameters) of these model structures give rise to cell parameters that are in good agreement with experiment (a slight overestimation of the cell parameters by less than 2%).

DFT calculations underestimate optical band gaps. There are several ways of correcting this deficiency,[21] the simplest one of

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(18) Optimized model structure 1 of $TiOF_2$ is as follows: $P4/mmm$; a = 3.9348 Å, c = 3.7143 Å; Ti = (0, $^1/_2$, 0), O = (0, 0, $^1/_2$), F = (0, $^1/_2$, 0).

(19) Optimized model structure 2 of $TiOF_2$ is as follows: $P4/mmm$; a = 7.6401 Å, c = 3.9179 Å; Ti = (0.761 40, 0.761 40, 0), O = (0, 0.745 28, 0), F1 = ($^1/_2$, 0.742 67, 0), F2 = (0.742 67, 0.742 67, $^1/_2$).

(20) Optimized model structure 3 of $TiOF_2$ is as follows: $P1$; a = 7.7145 Å, b = 7.7176 Å, c = 7.7475 Å; $\alpha = \beta = 89.93$, $\gamma = 90.04°$; Ti1 = (0.526 98, 0.523 29, 0.500 40), Ti2 = (0.517 39, 0.480 77, 0.000 48), Ti3 = (0.025 44, 0.516 04, 0.487 34), Ti4 = (0.519 46, 0.001 81, 0.513 15), Ti5 = (0.043 23, 0.500 21, 0.013 28), Ti6 = (0.522 96, 0.005 72, 0.987 48), Ti7 = (0.044 48, 0.991 66, 0.499 95), Ti8 = (0.000 00, 0.000 00, 0.000 00), O1 = (0.523 50, 0.249 95, 0.001 33), O2 = (0.026 12, 0.500 40, 0.250 30), O3 = (0.775 24, 0.997 27, 0.001 87), O4 = (0.528 39, 0.747 70, 0.498 71), O5 = (0.025 36, 0.749 51, 0.500 47), O6 = (0.523 78, 0.000 30, 0.750 13), O7 = (0.274 94, 0.002 29, 0.498 89), O8 = (0.276 44, 0.500 75, 0.000 53), F1 = (0.529 29, 0.253 55, 0.495 49), F2 = (0.022 70, 0.249 22, 0.503 14), F3 = (0.024 76, 0.248 19, 0.995 01), F4 = (0.525 24, 0.747 92, 0.004 09), F5 = (0.025 31, 0.752 21, 0.993 34), F6 = (0.531 92, 0.499 66, 0.252 97), F7 = (0.524 64, 0.998 89, 0.250 07), F8 = (0.025 60, 0.005 51, 0.247 16), F9 = (0.529 85, 0.500 11, 0.748 26), F10 = (0.023 98, 0.497 40, 0.750 38), F11 = (0.025 31, 0.004 28, 0.752 34), F12 = (0.774 25, 0.490 09, 0.505 82), F13 = (0.777 32, 0.004 90, 0.496 11), F14 = (0.775 92, 0.503 91, 0.997 18), F15 = (0.278 79, 0.488 69, 0.505 93), F16 = (0.269 97, 0.994 52, 0.004 48).

Table 1. Cell Volume *V* per Formula Unit, Refractive Index *n*, and Total Absorption Power per Unit Volume $I(\epsilon_2)$ of $TiOF_2$, TiF_4, and Seven TiO_2 Allotropes

phase	V (Å^3)	n^a	n_0	$I(\epsilon_2)$
TiO_2 columbite	30.58	2.81	2.74	73.0
TiO_2 rutile	31.22	2.88 (2.87^b) [2.71^c]	2.78	71.9
TiO_2 brookite	32.17	2.73 [2.64^c]	2.67	69.6
TiO_2 anatase	34.06	2.63 [2.53^c]	2.57	65.2
TiO_2 ramsdellite	34.30	2.66	2.59	65.7
TiO_2 bronze	35.53	2.56	2.51	62.7
TiO_2 hollandite	38.26	2.50	2.45	58.7
$TiOF_2$ model 1	57.51	1.93 (1.98^b)	2.14	40.7
$TiOF_2$ model 2	57.17	2.01	2.02	40.5
$TiOF_2$ model 3	57.66	1.91	2.02	39.3
TiF_4	69.99	1.61	1.65	30.6

[a] Values calculated at 2.1 eV after using a proper scissors operator. [b] Values in parentheses are the EELS experimental *n* values determined at 2.1 eV. [c] Values in brackets are the experimental data.[27]

which is to use a scissors operator (SO), i.e., shifting the conduction bands rigidly with respect to the valence bands to obtain the correct band gap. We calculated n_0 without using an SO and the *n* values at 2.1 eV after using an appropriate SO. The values of the SO were adjusted to match the EELS data for TiO_2 (SO = 0.6 eV) and $TiOF_2$ (SO = 2.13, 0.83, and 1.53 eV for model structures 1−3, respectively). For TiF_4, we chose SO = 1.15 eV by matching the F 2p → Ti 3d peak positions of the $\epsilon_2(\omega)$ spectra of $TiOF_2$ and TiF_4. As can be seen from Table 1, the n_0 values exhibit a trend similar to that for the *n* values at 2.1 eV.

2.2. Electron Energy Loss Spectroscopy. $TiOF_2$ samples were characterized by electron energy loss spectroscopy (EELS) measurements using a transmission electron microscope (TEM; Philips CM 30) with a LaB_6 gun. The TEM was operated at 100 kV and was coupled with a GATAN 666 spectrometer controlled by ELP3 software, which derives the optical constants of samples under investigation. The experimental procedure has been described elsewhere.[22−25] EELS experiments were not carried out for TiF_4 because the latter is highly sensitive to moisture.

3. Concept of Optical Channels

In general, n_0 increases with increasing $I(\epsilon_2)$. For the seven different allotropic forms of TiO_2, the total absorption power $I(\epsilon_2)V$ per FU is nearly constant, thereby explaining why the Gladstone−Dale relation works for these systems.[11] Although the refractive indices of allotropic phases are well described by the cell volume, there has been no simple rule that allows one to predict how a chemical substitution might influence refractive index. This is not surprising because chemical substitution influences the chemical bonding, the crystal structure, and the cell volume *V* simultaneously. To help simplify this multiple-parameter problem, we will introduce the concept of "optical channels". As described in section 1, calculations of optical properties are based on electronic band structures in which the electrons are viewed as completely delocalized. We define optical channels as chemical bonds associated with a chromophore. In compounds such as TiO_2, $TiOF_2$, and TiF_4 in which absorption in the visible range is related to charge-transfer excitation from the ligand p-block bands to the Ti d-block bands (in other words, from the anions O^{2-} and F^- to the cations Ti^{4+}), the optical channels are the Ti−O and Ti−F bonds. With this local view of light absorption, it is straightforward to consider two factors affecting optical properties, i.e., the chromophore and the volume. The chromophore effect depends on the efficiency of chemical bonds for light absorption (i.e., "channel quality"), the number of optical channels per FU (i.e., channel quantity), and the number of valence electrons per FU participating in excitation. The volume effect measures the density of the optical channels per FU. The quantity $I(\epsilon_2)$ reflects both the chromophore and volume effects, but the total absorption power, $I(\epsilon_2)V$, reflects only the chromophore effect. In this work, we show the utility of the concept of optical channels by studying the refractive indices of the titanium oxide fluorides $TiOF_2$ and TiF_4 on the basis of DFT electronic band structure calculations and EELS experiments. Such an approach can be useful in designing new-generation UV shields.

4. Effect of Fluorine Substitution on Refractive Index

The electronic band structures of TiO_2, $TiOF_2$, and TiF_4 exhibit similar features. The valence bands are composed largely of the 2p orbitals of O and/or F, and the conduction bands are composed largely of 3d orbitals of Ti. As expected, the F 2p-block bands lie somewhat lower in energy than the O 2p-block bands, but they do overlap in $TiOF_2$. The F and O 2s-block bands are well separated from the corresponding 2p-block bands (located approximately 15 eV below the top of the valence band). Thus, the O 2p → Ti 3d and/or F 2p → Ti 3d excitations are primarily responsible for the refractive indices of TiO_2, $TiOF_2$, and TiF_4. Consequently, 12, 18, and 24 valence electrons per FU are mainly responsible for the refractive indices of TiO_2, $TiOF_2$, and TiF_4, respectively. In addition, the contributions to the transition dipole moments associated with these excitations are significant only between the 3d orbitals of each Ti atom and the 2p orbitals of those oxygen/fluorine atoms forming the first coordination sphere. Therefore, the optical channels of these compounds are their Ti−O and Ti−F bonds.

Figure 1 presents $n(\omega)$ and $k(\omega)$ plots for $TiOF_2$, deduced from EELS measurements and calculated for model structure 1, as a function of the incident photon energy. The EELS and DFT data are in good agreement, as was also found for the rutile TiO_2 phase. The main features of the $\epsilon_2(\omega)$ spectra of TiO_2 and TiF_4 (associated with the O 2p → Ti 3d and F 2p → Ti 3d transitions, respectively) can be recognized from the $\epsilon_2(\omega)$ spectrum of $TiOF_2$ (Figure 2). The calculated *n* value of 1.93 is in excellent agreement with the experimental value deduced from our EELS measurements. The three different model structures of $TiOF_2$ lead essentially to the same value of refractive index, that is, the F/O disorder does not significantly affect the refractive index (Table 1). The *n* value decreases steadily from rutile TiO_2 (2.9) to $TiOF_2$ (1.9)

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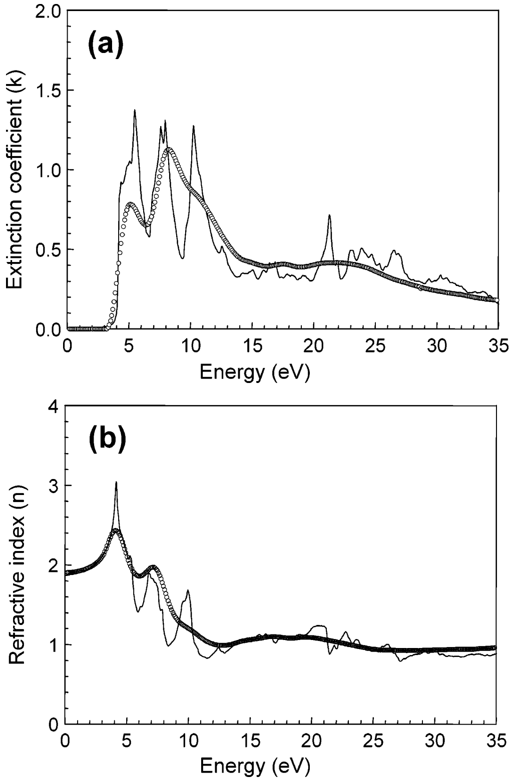

Figure 1. Comparison of the optical properties of $TiOF_2$ determined from EELS experiments (open circles) and electronic band structure calculations using structure model 1 (solid curves): (a) refractive index *n* and (b) extinction coefficient *k* as functions of the energy of the incident light.

and to TiF_4 (1.6) (Table 1). This decrease in *n* is related to the corresponding decrease in the $I(\epsilon_2)$ value from 71.9 to 40.7 to 30.6 (Figure 2, Table 1). Thus, the decrease in *n* is correlated with a lowering of the total absorption capability when one O is substituted by two F atoms.

For $TiOF_2$, TiF_4, and the seven TiO_2 allotropic phases, the refractive index *n* varies linearly with the total absorption capability per unit volume $I(\epsilon_2)$ (Figure 3a) and also with the reciprocal volume $1/V$ (Figure 3b). The latter observation indicates that the trends in the refractive indices are well described by the cell volumes per FU. It is important to understand the origin and meaning of this observation. The cell volume *V* per FU increases steadily from TiO_2 to $TiOF_2$ to TiF_4 (Table 1). In the case of the seven TiO_2 allotropes, $I(\epsilon_2)V$ is nearly constant. This indicates that the structural changes in the seven TiO_2 allotropes affect mainly their cell volumes but not their chromophores. This is understandable because the natures of the Ti−O bonds, and hence the absorption power of the Ti−O bonds, are similar in the TiO_2 allotropes. It is surprising that the $I(\epsilon_2)V$ term is also nearly constant for TiO_2, $TiOF_2$, and TiF_4 although the Ti−O and Ti−F bonds should exhibit considerably different absorption capabilities. The probable reason for this observation is discussed in the next section.

5. Total Absorption Power and Optical Channel

The fact that the total absorption power per FU is nearly constant for the TiO_2, $TiOF_2$, and TiF_4 phases implies that one Ti−O optical channel is optically equivalent to two Ti−F

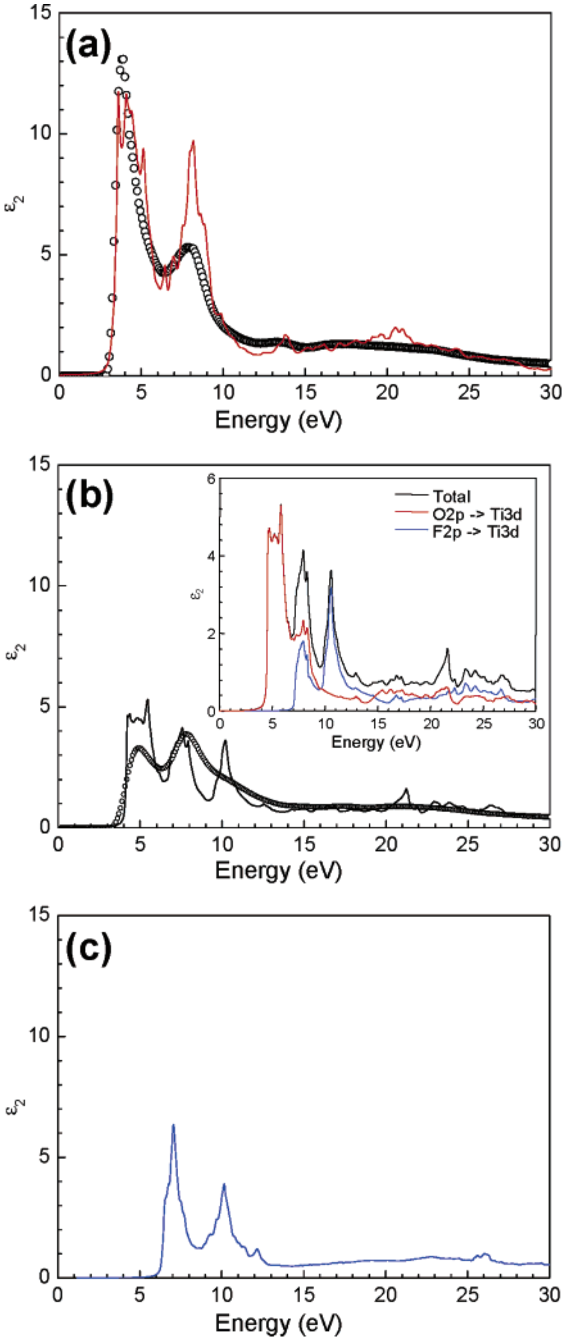

Figure 2. Isotropic imaginary part ϵ_2 of the dielectric function as a function of the energy of the incident light: (a) rutile TiO_2, (b) $TiOF_2$ (for the structure model 1), (c) TiF_4. The open circles correspond to the experimental ϵ_2 values from EELS measurements, and the solid curves to the theoretical ϵ_2 values predicted from electronic band structure calculations. The inset in b shows the contributions of the O 2p → Ti 3d and F 2p → Ti 3d transitions to ϵ_2.

optical channels. The valence electrons of F are more strongly bound to the nucleus than are those of O. Thus, the extent of covalent interaction is stronger in the Ti−O bond than in the Ti−F bond, so that the extent of overlap between the Ti 3d and ligand 2p orbitals is stronger in the Ti−O bond. Consequently, each Ti−F optical channel contributes less to the optical absorption than does each Ti−O optical channel. Thus, on going from TiO_2 to $TiOF_2$ to TiF_4, the quality of the optical channel decreases. However, on going from TiO_2 to $TiOF_2$ to TiF_4, the number of valence electrons

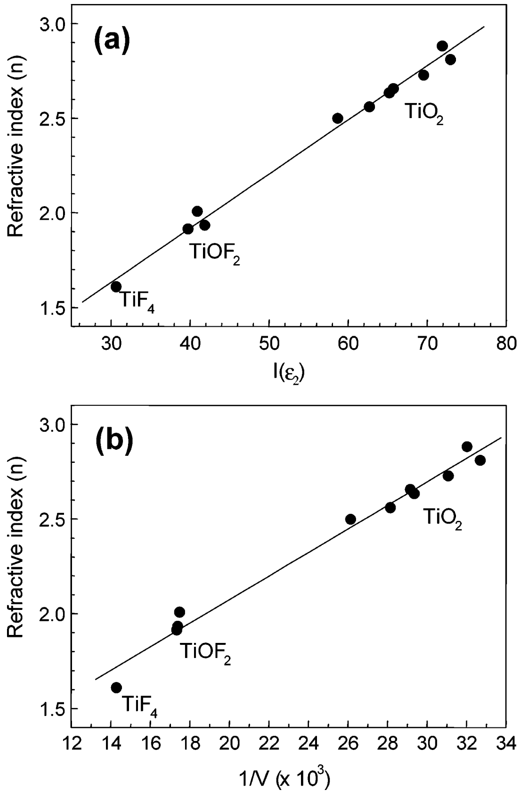

Figure 3. Refractive indices of TiO_2, $TiOF_2$, and TiF_4 as functions of (a) $I(\epsilon_2)$ and (b) $1/V$.

participating in the optical excitation increases (i.e., 12, 18, and 24 per FU, respectively). The total number of optical channels per FU is the same in TiO_2, $TiOF_2$, and TiF_4; i.e., each Ti has six Ti−O channels in TiO_2, two Ti−O and four Ti−F channels in $TiOF_2$, and six Ti−F channels in TiF_4. As already mentioned, it is expected that one Ti−O channel is equivalent to two Ti−F channels in efficiency. Effectively, therefore, each Ti has six Ti−O channels in TiO_2, four Ti−O channels in $TiOF_2$, and three Ti−O channels in TiF_4. Thus, the numbers of channels in TiO_2, $TiOF_2$, and TiF_4 have the ratio 6:4:3, whereas the numbers of their valence electrons participating in the excitation have the ratio 12:18:24. That is, the decrease in the efficiency for electrons to be excited from the ligand to the Ti atoms is compensated by the increase in the number of valence electrons that can be excited. As a consequence, the total absorption capability per FU, i.e., $I(\epsilon_2)V$, remains constant in TiO_2, $TiOF_2$, and TiF_4.

It is of interest to note that the variation in the optical properties of a series of compounds can be described in terms of their total absorption capability per FU, i.e., $I(\epsilon_2)V$, which deals with only the chomophore effect. The scattering property of a material arises from the oscillating dynamic deformation of its electron density induced by an applied electric field. The *n* value becomes larger as the electron density distribution can be more easily distorted (i.e., is more polarizable). From the viewpoint of quantum mechanics, any deformation of a ground-state electron density requires the mixing of excited-state wave functions into the ground-state wave function (in a sense, by electronic excitations). Consequently, the greater the absorption probability, the higher the refractive index becomes.

6. Concluding Remarks

In summary, the total absorption capability per FU, $I(\epsilon_2)V$, is nearly constant for $TiOF_2$, TiF_4, and the seven allotropes of TiO_2 because the effect of decreasing the quality of the optical channel is counterbalanced by the effect of increasing the number of valence electrons participating in the optical excitation. Because the refractive index *n* increases with increasing $I(\epsilon_2)$, it follows that $n \propto 1/V$ for all of these systems. Such a linear relationship was unexpected because the substitution of F for O induces dramatic changes in the structure and nature of the chemical bond. The concept of optical channels readily clarifies this seemingly unusual observation by separating the effect of the chromophore from the effect of the volume. Note that, in the optical channels consisting of the Ti−O and Ti−F bonds, the ligands O and F belong to the same row of the periodic table. For the refractive indices of ZnQ and CdQ (Q = O, S, Se, Te), in which the ligands Q of the optical channels (the Zn−Q and Cd−Q bonds) belong to different rows of the periodic table, the values of the total absorption capability $I(\epsilon_2)V$ are not constant but increase steadily as Q changes from O to S to Se to Te.[26] Finally, we note that, on going from rutile TiO_2 to $TiOF_2$, the scattering properties is reduced by about 30%, without significantly changing the optical band gap. This observation implies that improved UV shields can be prepared by controlling the “chromophore” volume.

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