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Amorphous Cerium–Titanium Solid Solution Phosphate as a Novel Family of Band Gap Tunable Sunscreen Materials

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Exposure of the human body to sunlight to attain a tanned look has been fashionable in recent history. However, ultraviolet (UV) light in the sunshine rays can prove to be very harmful the human skin.[1] Consequently, many people fall victim to skin cancer, and sadly, almost all of these deaths could have been prevented. Compounds that can act as UV filters are typically synthetic organic chemicals but may also be inorganic in nature.[2] However, some of these organic UV filters have caused irritation on the skin of sensitive individuals and, therefore, may pose a safety problem when used at high concentrations.[3] However, very small amounts can sometimes penetrate the topmost layer of the skin and render the UV filter less effective. Chemically, some organic UV filters are not photostable.

In contrast to the organic compounds, ultrafine titanium oxide, zinc oxide, and recently cerium oxide have proven to be effective inorganic sunscreens and are widely utilized.[2,4,5] Although titanium oxide is the most popular inorganic sunscreen agent, it is also known that titanium oxide can also function as an excellent photocatalyst,[6] which may be harmful for the skin or affect other ingredients in the products, particularly sunscreen cosmetics. Zinc oxide is another widely utilized sunscreen agent, but it also possesses photo- and thermal catalytic properties.[7,8] Cerium oxide exhibits minimal photocatalysis, but facilitates the generation of reactive oxygen species upon slight heating, which is utilized in oxidation, combustion, and automotive exhaust cleaning catalysts.[9] It is therefore imperative that the surface of these inorganic compounds be coated with an inert substance to minimize the catalytic activities.[2] In addition, titanium oxide, when incorporated into sunscreen products, may cause the user's skin to look unnaturally white, due to the high refractive index (2.6–2.7).[4,10]

Herein, we demonstrate that a series of amorphous phosphates of $Ce_{1-x}Ti_xP_2O_7$ constitute promising candidates for advanced sunscreens: their broad-spectrum protection against ultraviolet radiation and chemical stability exceed those of the conventional sunscreens. Furthermore, by simply adjusting the composition, the

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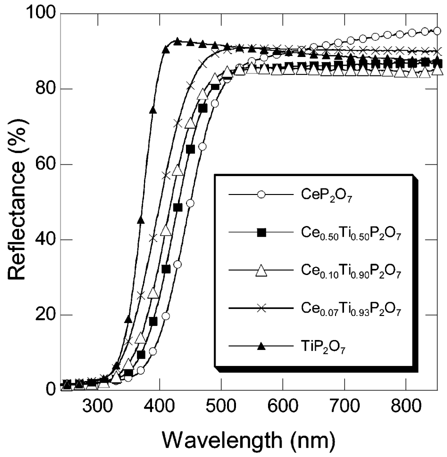

Figure 1. Optical reflectance spectra of the $Ce_{1-x}Ti_xP_2O_7$ sunscreens having various Ce/Ti ratios.

UV absorption edge of these phosphates can be carefully manipulated to absorb at the desired range, from UV-B (280−320 nm) to UV-A (320−400 nm). Metal phosphates, also known as a component of bones and teeth, have proven to be inert and safe, with no known side effects to the human body. Not only are these metal phosphates stable, but they are also very inert and do not possess the ability to catalyze the formation of active oxygen species, as seen in several other inorganic oxides.

The $Ce_{1-x}Ti_xP_2O_7$ phosphate nanoparticles were prepared easily by coprecipitation between a cerium and titanium sulfate mixed solution and a sodium pyrophosphate aqueous solution. The compositions of the samples were determined using an X-ray fluorescent spectrometer (Rigaku, ZEX-100e).

All samples were confirmed to be amorphous using X-ray powder diffraction analysis (Mac Science, M18XHF-SHA). Figure 1 shows UV−vis spectra of the $Ce_{1-x}Ti_xP_2O_7$ samples (Shimadzu, UV-2450; reference is $BaSO_4$; diffuse reflection mode). On these spectra, low reflectance means high absorption in the corresponding wavelength. The $Ce_{1-x}Ti_xP_2O_7$ can absorb UV light, almost completely, in which the UV cutoff (320−390 nm) depends on the Ce/Ti ratio. It was shown that the UV cutoff shifts to a longer wavelength as the Ce^{4+} content increases. When the composition was $Ce_{0.5}Ti_{0.5}P_2O_7$, the optical absorption behavior in the UV region under 400 nm was comparable to those of conventional ZnO, TiO_2, and CeO_2 sunscreens.

The optical energy gap (band gap) between the localized and exited states, or the localized states between the valence and conduction bands, E_{opt}, was determined using the Davis and Mott equation.[11,12] As listed in Table 1, the energy gap increases monotonically from 2.30 to 2.95 eV with increasing titanium content. Our data show that the $Ce_{1-x}Ti_xP_2O_7$ sunscreens effectively absorb in the UV-B to UV-A range, and furthermore, any band gap within the range can be readily tailored by proper adjustment of the Ce/Ti ratio.

The origin of the optical energy gap in these amorphous phosphates is due to the charge-transfer excitation of electrons.[13] The monotonic shift of the absorption

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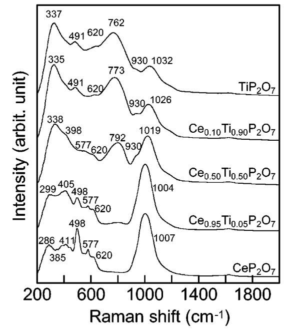

Figure 2. Raman spectra of the $Ce_{1-x}Ti_xP_2O_7$ powders.

Table 1. Variation of Optical Energy Gap and Catalysis Indices with Composition

sample	E_{opt} (eV)	$I_{ca.}$(thermal)	$I_{ca.}$(photo)
CeP_2O_7	2.30	5.10	0.22
$Ce_{0.95}Ti_{0.05}P_2O_7$	2.37	2.75	0.00
$Ce_{0.50}Ti_{0.50}P_2O_7$	2.40	3.67	0.10
$Ce_{0.10}Ti_{0.90}P_2O_7$	2.48	0.00	0.00
$Ce_{0.07}Ti_{0.93}P_2O_7$	2.55	0.13	0.45
$Ce_{0.05}Ti_{0.95}P_2O_7$	2.70	0.00	0.13
TiP_2O_7	2.95	0.01	0.07
CeO_2	3.10	19.9	0.99
TiO_2 (rutile)	3.00	4.22	2.76
ZnO	3.20	11.4	0.94

edges as a function of the Ce/Ti ratio can be attributed to the changes in the bonding state of the phosphates that takes place in the amorphous substance. This feature was confirmed using Raman spectra measurements (Kaiser Optical Systems, HoloProbe) as shown in Figure 2. An increase in the titanium content resulted in systematic changes in the Raman spectra; in particular, it is important to note the increase in the relative intensity of the peaks around 340, 770, and 930 cm^{-1} and a concomitant decrease in that of the peak around 1000 cm^{-1}. The increase of the former three peaks is attributable to the formation of P−O−P bending, symmetric stretching, and asymmetric stretching modes of the pyrophosphate structure, respectively, and the decrease of the latter peak is attributable to the disappearance of symmetric P−O stretching vibrations of the PO_3 and PO_4 sites.[14] As a result, increase in the titanium content progressively induces the formation of bridging oxygen that is based on pyrophosphate species, which increases the E_{opt} value of phosphate materials.[13] Therefore, the band gap energies of $Ce_{1-x}Ti_xP_2O_7$ increase with titanium content.

Characterizations of several other properties of the $Ce_{1-x}Ti_xP_2O_7$ particles were carried out to estimate their aptitude as sunscreens. Catalytic activities for the thermal oxidation of organic material were determined using the conductometric determination method.[15] In addition to thermal oxidation at 403 K, photocatalytic activities were also estimated using light irradiation for 9 h with a solar simulator (Kansai Kagaku Kikai, XES-502S). The normalized catalysis indices, $I_{ca.}$(thermal) and $I_{ca.}$(photo),[16−18] are also summarized in Table 1.

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Smaller values for $I_{ca.}$ indicate lower catalytic activity. Conventional materials such as TiO_2 (rutile), ZnO, and CeO_2 exhibited thermal or photocatalysis, whereas the $Ce_{1-x}Ti_xP_2O_7$ materials exhibited neither thermal nor photocatalytic activities, thus indicating that these metal phosphates are very inert toward oxidation of organic materials.

Textural and physical properties of $Ce_{1-x}Ti_xP_2O_7$ were also characterized. The particles consisted of weakly agglomerated primary particles with 15−30-nm diameters. Such particle sizes are suitable for avoiding the undesirable whitening effect.[10] In addition, the refractive indices of cerium and titanium phosphates lie between 1.6 and 2.0.[19,20] These properties are also favorable for the metal phosphate compounds to meet the demand for inorganic sunscreens that show high transparency in the visible region.[2]

The use of inorganic sunscreens in personal care products with UV protection is growing rapidly. Although the inorganic sunscreens can be formulated with or without a combination of organic sunscreens, products that contain inorganic sunscreens exclusively will increase due to the lower stability and higher toxicity of organics. The use of amorphous $Ce_{1-x}Ti_xP_2O_7$ phosphates can provide us with effective, safe, and desirable UV protection without surface coatings to depress either thermal or photocatalysis, which has not been realized by the conventional materials.

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Supporting Information Available: Detailed synthesis and characterization procedure of the $Ce_{1-x}Ti_xP_2O_7$ and results of X-ray diffraction, comparison of the UV−vis spectrum with the conventional materials such as TiO_2, ZnO, and CeO_2, and TEM photograph at $x = 0.5$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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