Journal of Alloys and Compounds 408–412 (2006) 1141–1144

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

New sunscreen materials based on amorphous cerium and titanium phosphate

Toshiyuki Masui [a], Hidekazu Hirai [a], Nobuhito Imanaka [a,*], Gin-ya Adachi [b]

[a] *Department of Applied Chemistry, Faculty of Engineering and Handai Frontier Research Center, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

[b] *Juri Institute for Environmental Science and Chemistry, College of Analytical Chemistry, 2-1-8 Temma, Kita-ku, Osaka 530-0043, Japan*

Received 30 July 2004; received in revised form 15 December 2004; accepted 15 December 2004

Abstract

Cerium–titanium pyrophosphates $Ce_{1-x}Ti_xP_2O_7$ (with $x = 0$, 0.50, and 1.0), which are novel phosphate materials developed as UV-shielding agents for use in cosmetics, were characterized by X-ray diffraction, X-ray fluorescent analysis, UV–vis reflectance, and Raman spectroscopy. Since the optical reflectance shifted to lower wavelengths by the crystallization of the phosphates and the stabilization of the amorphous state of the cerium–titanium pyrophosphates was carried out by doping niobium (Nb). Raman spectroscopic study of the phosphate showed that P—O—P bending and stretching modes decreased with the loading of Nb, accompanying with the formation of Nb—O stretching mode. Therefore, the increase in the amount of the non-bridging oxygen in the amorphous phosphate should be the reason for the inhibition of the crystallization. This stabilization is a significant improvement, which enables to apply these amorphous phosphates not only to cosmetics and paints, but also plastics and films.

Keywords: Cerium phosphate; Titanium phosphate; Amorphous; UV-shielding; Sunscreen; Stabilization

1. Introduction

It has been well known that ultraviolet (UV) rays in sunshine are very harmful to the human skin and deteriorates some organic materials, and many sunscreen materials for UV-shielding have been developed using synthetic organic and inorganic chemicals [1]. However, the organic sunscreens may pose a safety problem when they are used at high concentrations, because it has been suggested that some of the organic UV absorbers cause irritation on the skin of sensitive individuals and demonstrate estrogenic activities [2,3]. In contrast to the organic compounds, ultrafine titanium oxide, zinc oxide, and cerium oxide have been applied as effective inorganic sunscreens [4–6]. Titanium oxide and zinc oxide are popular inorganic sunscreen agents. However, the former is also known as an excellent photocatalyst that may be harmful for the skin, and sometimes affects other ingredients in the products. The latter has a photo-induced dissolution problem to form Zn^{2+} ions [7,8]. Although cerium oxide exhibits minimal photocatalysis, it has high catalytic activities for oxidation of organic compounds, as applied in oxidation, combustion, and automotive exhaust cleaning catalysts [9]. Therefore, it is imperative to cover the surface of these inorganic compounds with an inert substance to avoid the catalytic activities.

In order to solve the problems described above, we have demonstrated that a series of amorphous cerium–titanium pyrophosphates ($Ce_{1-x}Ti_xP_2O_7$; $x = 0$–1) is a promising candidate for advanced sunscreens [10]. Because metal phosphates are well known as components of bones and teeth, the present amorphous $Ce_{1-x}Ti_xP_2O_7$ samples are stable and inert. Furthermore, the UV absorption edge of these phosphates can be tunable to absorb at the desired range from UV-B (280–320 nm) to UV-A (320–400 nm) by simply adjusting the composition. Here, it is significantly important

---

* Corresponding author. Tel.: +81 6 6879 7352; fax: +81 6 6879 7354.
E-mail address: imanaka@chem.eng.osaka-u.ac.jp (N. Imanaka).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.136

to stabilize the amorphous state in order to maintain the UV-ray shielding effect steadily, because these materials utilized their amorphous features that make it possible to tune the absorption edge maintaining cerium ions in the tetravalent state. However, systematic studies on the thermal behavior of the amorphous $Ce_{1-x}Ti_xP_2O_7$ have not been reported, except for CeP_2O_7 [11,12], and there is no report on the stabilization of the amorphous state. In this study, therefore, we aim to characterize and enhancement the thermal stability of the amorphous $Ce_{1-x}Ti_xP_2O_7$ by doping niobium as a stabilizer, because niobium ions have the same positive charge (5+) as phosphorous and can form amorphous phosphate easily [13].

2. Experimental

Amorphous $Ce_{1-x}Ti_xP_2O_7$ (with $x = 0, 0.50$, and 1.0) were prepared by the co-precipitation method [10–12]. Cerium sulfate tetrahydrate and titanium sulfate were dissolved in deionized water in the stoichiometric ratio, adjusting the total cation concentration to be 0.1 mol dm^{-3}. Each solution was dropped into a 0.1 mol dm^{-3} of sodium pyrophosphate aqueous solution. Stabilization of the amorphous state was achieved by substituting phosphorus ion with niobium ion in the above amorphous phosphates in the ratio of 40 mol%. An ethanol solution containing niobium chloride (0.05 mol dm^{-3}) was also prepared. The cerium–titanium sulfate solution and the stoichiometric sodium pyrophosphate aqueous solution were simultaneously dropped into the ethanol solution. The resulting precipitates were separated by centrifuging, successively washed with deionized water for five times, and dried in an oven at 353 K for 24 h.

The composition of the samples was confirmed by an X-ray fluorescent spectrometer (Rigaku ZEX-100e). The X-ray powder diffraction data were obtained by an X-ray diffractmeter (Rigaku Multiflex) with Cu Kα radiation. The samples were also characterized by UV–vis (Shimadzu, UV-2450, reference is $BaSO_4$, diffuse reflection mode) and Raman spectroscopy (Kaiser Optical Systems, HoloProbe).

3. Results and discussion

X-ray powder diffraction patterns of as-prepared and calcined $Ce_{1-x}Ti_xP_2O_7$ (with $x = 0, 0.50$, and 1.0) samples are shown in Fig. 1. It clearly shows that all the as-prepared samples are amorphous and these CeP_2O_7, $Ce_{0.5}Ti_{0.5}P_2O_7$, and TiP_2O_7 amorphous phases were maintained up to 723, 873, and 623 K, respectively. Fig. 2 depicts the optical reflectance spectra of these phosphates before (as-prepared) and after the calcination at 673 K. The reflectance profiles shifted to lower wavelengths after the heating, which means UV-ray absorption efficiency decreased. The degree of the decrease in UV absorption was not so high for CeP_2O_7 and $Ce_{0.5}Ti_{0.5}P_2O_7$, while it was particularly remarkable for TiP_2O_7, because only the amorphous TiP_2O_7 crystallizes at even 673 K among CeP_2O_7, $Ce_{0.5}Ti_{0.5}P_2O_7$, and TiP_2O_7. Therefore, the crystallization of these amorphous phases affected their optical reflection spectra critically.

The decrease in the UV absorption efficiency of the CeP_2O_7 and $Ce_{0.5}Ti_{0.5}P_2O_7$ samples can be attributed to the reduction of cerium ion from tetravalent to trivalent state upon heating, because the optical absorption in the long-wavelength ultraviolet region in these samples are mainly caused by the $O_{2p}{}^{2-} \rightarrow Ce_{4f}{}^{4+}$ charge transfer transition. In fact, it has been previously evidenced that cerium orthophosphate, $CePO_4$ (Ce^{3+}), was partially produced by the crystallization of the amorphous CeP_2O_7 [11,12].

On the contrary, in the case of amorphous TiP_2O_7, the UV-ray absorption is caused by the $O_{2p}{}^{2-} \rightarrow Ti_{3d}{}^{4+}$ charge transfer transition, because there is no cerium ion in the sample. From the X-ray diffraction patterns shown in Fig. 1, the formation of crystalline $Ti_4P_6O_{23}$ (Ti^{4+}) phase was observed. Since 3d electron shell is easily affected by the crystal field, it is reasonable to assign the optical absorption change to the

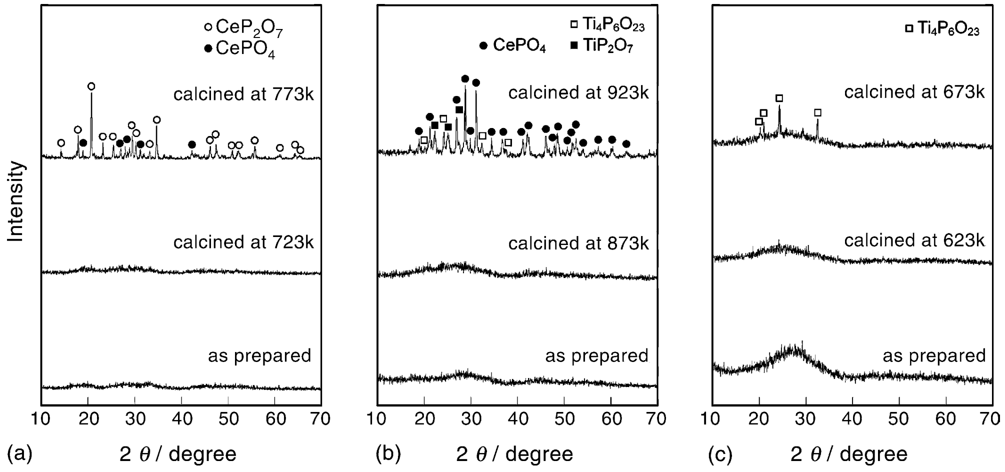

Fig. 1. X-ray powder diffraction patterns of the as-prepared and calcined $Ce_{1-x}Ti_xP_2O_7$ samples: (a) $x = 0$, (b) $x = 0.50$, and (c) $x = 1.0$.

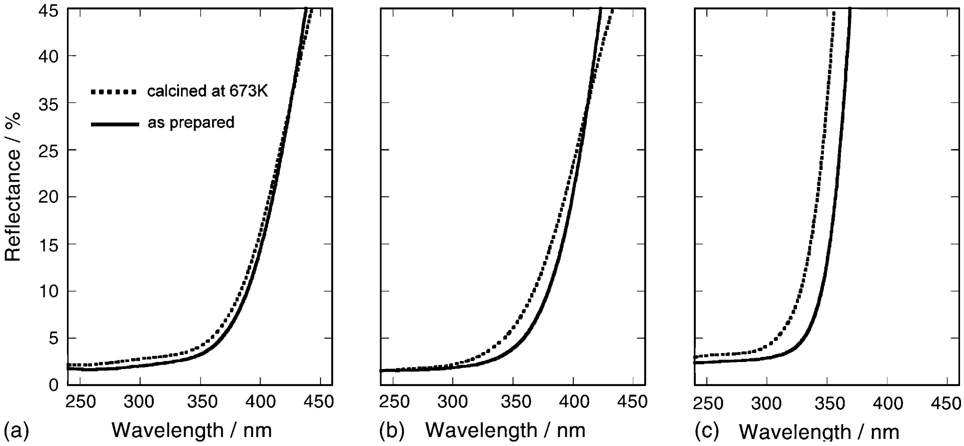

Fig. 2. Calcination temperature dependence for optical reflectance spectra of the $Ce_{1-x}Ti_xP_2O_7$ samples: (a) $x = 0$, (b) $x = 0.50$, and (c) $x = 1.0$.

variation of coordination state of the Ti^{4+} ion accompanying with the crystallization.

It is not preferable for the amorphous $Ce_{1-x}Ti_xP_2O_7$ materials to crystallize at low temperatures, considering the application of them to plastics and films. However, the amorphous state is stabilized by the addition of niobium ion as a stabilizer, which substitutes a part of the phosphorous ion sites in the amorphous phosphates.

Fig. 3 depicts the composition dependence of the crystallization temperatures of $Ce_{1-x}Ti_xP_2O_7$ and $Ce_{1-x}Ti_x(P_{0.6}Nb_{0.4})_2O_7$ ($x = 0$, 0.5, and 1.0), confirmed by the X-ray powder diffraction results. Comparing the samples with and without Nb in the phosphates, the stabilization of amorphous phase by the Nb doping is the most effective in TiP_2O_7 in which the amorphous state was maintained up to 973 K. This temperature is higher by 300 K than that of the sample without Nb doping. Indeed, the optical reflectance of the $Ti(P_{0.6}Nb_{0.4})_2O_7$ calcined at 873 K almost corresponds to that of the as-prepared one (Fig. 4), because the amorphous $Ti(P_{0.6}Nb_{0.4})_2O_7$ does not crystallize at this temperature.

In order to identify the reason for the stabilization of the amorphous state of TiP_2O_7 by niobium doping, the changes in the bonding state of the amorphous substance were discussed using Raman spectra as shown in Fig. 5. By the doping of niobium ion into the amorphous TiP_2O_7, the relative Raman intensity at 337 and 762 cm^{-1} corresponding to P–O–P bending and symmetric stretching modes decreased [14], while the Nb–O stretching mode at 645 cm^{-1} increased [13,15,16]. Therefore, the increase in the intensity of this Nb–O band corresponds to the promotion of non-bridging oxygen species in the samples. Because the presence of the bridging oxygen facilitates crystallization in phosphate grasses [17], it

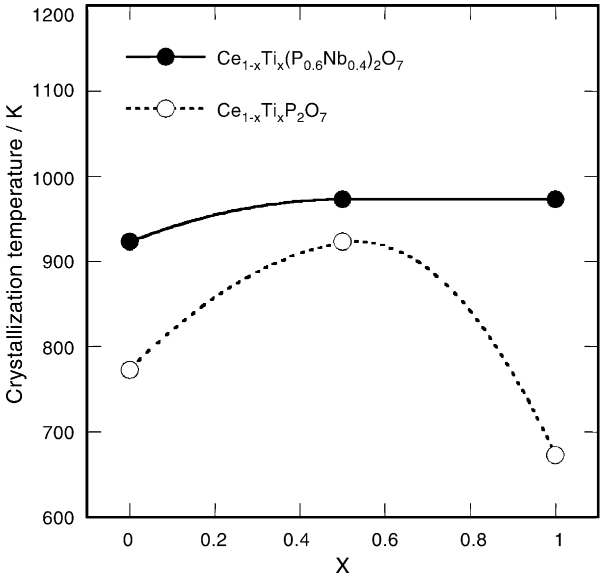

Fig. 3. Compositional dependence of crystallization temperatures of $Ce_{1-x}Ti_xP_2O_7$ and $Ce_{1-x}Ti_x(P_{0.6}Nb_{0.4})_2O_7$ ($x = 0$, 0.5, and 1.0).

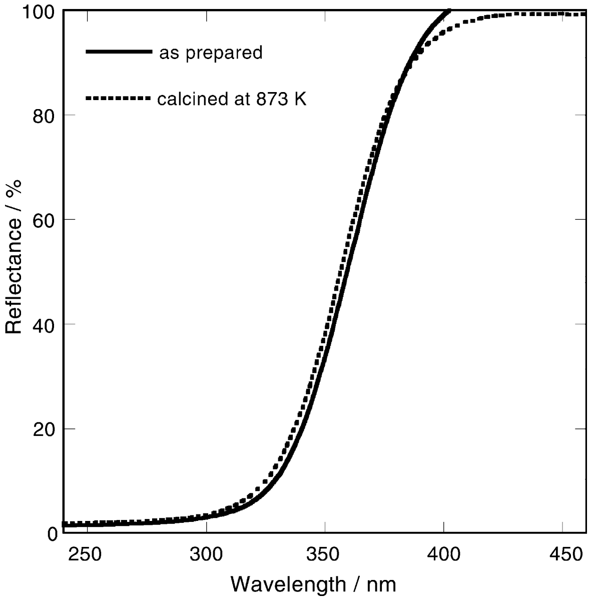

Fig. 4. Optical reflectance spectra of the amorphous $Ti(P_{0.6}Nb_{0.4})_2O_7$: (a) as-prepared and (b) after the calcination at 873 K.

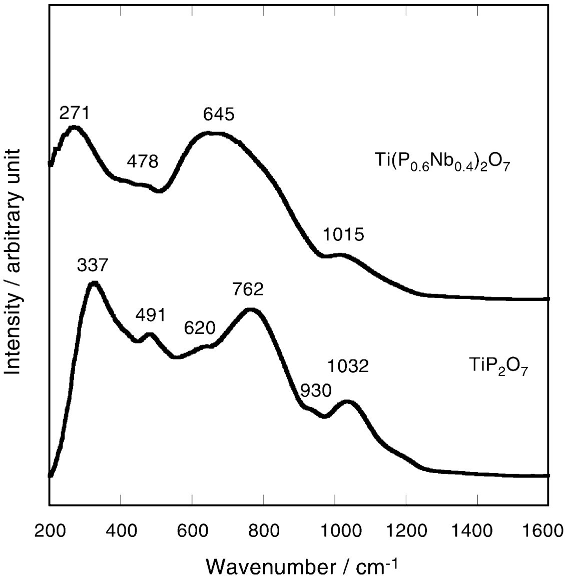

Fig. 5. Raman spectra of the amorphous (a) TiP_2O_7 and (b) $Ti(P_{0.6}Nb_{0.4})_2O_7$ samples.

is concluded that the stabilization of the amorphous state is attributable to the breaking of bridging oxygen in the P–O–P bond in the pyrophosphate structure and simultaneous formation of the non-bridging oxygen in the Nb–O bond.

In the case of CeP_2O_7 and $Ce_{0.5}Ti_{0.5}P_2O_7$, the effect of the Nb doping was not as remarkable as that observed in TiP_2O_7, because the initial amount of the P–O–P bond in the former two compounds is relatively smaller than that of the latter [10]. However, the crystallization temperatures of CeP_2O_7 and $Ce_{0.5}Ti_{0.5}P_2O_7$ increased up to 923 and 973 K after the Nb doping, respectively, which corresponded to the increase of the peak intensity at 645 cm^{-1} in their Raman spectra. The thermal stability of the amorphous state in these samples can satisfy the demand in the applications for UV-shielding plastics and films, which are sometimes heated (maximum 673 K) in their production process.

4. Conclusions

This work deals with a thermal stability of the UV-ray absorption characteristics based on amorphous state of the $Ce_{1-x}Ti_xP_2O_7$ phosphates. The results of optical reflectance analysis suggest that shielding effect for the UV-ray decreased with crystallization of them, because of reduction of cerium ion from tetravalent to trivalent state or variation of the coordination state around titanium ion. However, it becomes possible to stabilize the amorphous state and to maintain the UV-ray shielding characteristics by acting on the bonding state of oxygen in the phosphate anion, that is, by partially substituting phosphorous site with niobium ion in the amorphous phosphates.

Acknowledgements

The authors sincerely thank Dr. Kuniaki Murase and Prof. Dr. Yasuhiro Awakura (Kyoto University) for their assistance with the Raman spectra measurements. The present work was supported by a Grant-in-Aid for Scientific Research No. 16750173 from The Ministry of Education, Science, Sports and Culture. This work was also partially supported by the Industrial Technology Research Grant Program in 02 (Project No. 02A27004c) and the Nanotechnology Materials Program—Nanotechnology Particle Project from the New Energy and Industrial Technology Development Organization (NEDO) based on funds provided by the Ministry of Economy, Trade and Industry, Japan (METI).

References

[1] N.J. Lowe, N.A. Shaath, M.A. Pathak (Eds.), Sunscreens—Development, Evaluation, and Regulatory Aspects, second ed., Marcel Dekker, New York, 1997.
[2] M.S. Reisch, Chem. Eng. News 79 (2001) 25.
[3] M. Schlumpf, L. Berger, B. Cotton, M. Conscience-Egli, S. Durrer, I. Fleischmann, V. Haller, K. Maerkel, W. Lichtensteiger, SOFW J. 127 (2001) 10.
[4] G.P. Dransfield, Radiat. Prot. Dosim. 91 (2000) 271.
[5] S. Yabe, T. Sato, J. Solid State Chem. 171 (2003) 7.
[6] T. Masui, H. Hirai, Roy Hamada, N. Imanaka, G. Adachi, T. Sakata, H. Mori, J. Mater. Chem. 13 (2003) 622.
[7] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[8] J.M. Herrmann, C. Guillard, P. Pichat, Catal. Today 17 (1993) 7.
[9] A. Trovarelli (Ed.), Catalysis by Ceria and Related Materials, Imperial College Press, London, 2002.
[10] N. Imanaka, T. Masui, H. Hirai, G. Adachi, Chem. Mater. 15 (2003) 2289.
[11] T. Masui, H. Hirai, N. Imanaka, G. Adachi, Phys. Status Solidi (a) 198 (2003) 364.
[12] H. Hirai, T. Masui, N. Imanaka, G. Adachi, J. Alloys Compd. 374 (2004) 84.
[13] J.C.G. Da Silva, S. Folgueras-Domíngues, A.C.B. Dos Santos, J. Mater. Sci. Lett. 18 (1999) 197.
[14] R.K. Brow, D.R. Tallant, W.L. Waren, Phys. Chem. Glasses 38 (1997) 300.
[15] G.T. Stranford, R.A. Condrate, J. Mater. Sci. Lett. 3 (1984) 303.
[16] E.B. De Araujo, J.A.C. De Paiva, J.A. Freitas Jr., A.S.B. Sombra, J. Phys. Chem. Solids 59 (1998) 689.
[17] A. Hayashi, K. Tadanaga, M. Tatsumisago, T. Minami, Y. Miura, J. Ceram. Soc. Jpn. 107 (1999) 510.