Journal of Ceramic Processing Research. Vol. 13, No. 5, pp. 622~626 (2012)

J O U R N A L O F
Ceramic Processing Research

The synthesis and properties of bulk lanthanum phosphates obtained by hydrothermal hot pressing

Hiroaki Onoda* and Akinori Yoshida

Department of Informatics and Environmental Sciences, Faculty of Life and Environmental Sciences, Kyoto Prefectural University, 1-5, Shimogamo Nakaragi-cho, Sakyo-ku, Kyoto 606-8522, Japan

Bulk samples of lanthanum phosphates were synthesized in a hydrothermal hot pressing process. In this process, the pressing temperature, pressure, and the volume of water were varied to improve the density and various strengths. The strength of the bulk samples was estimated from drilling and ultrasonic treatments, and the residual ratio in hydrofluoric acid. Lanthanum phosphate formed the porous bulk samples with about 60% filling factor, which were calculated from the real and theoretical densities. By heating the lanthanum phosphate before the pressing, the maximum diameter became larger of the phosphate pellets without cracking. Lanthanum phosphate bulk samples gave a high residual ratio in hydrofluoric acid. The hydrothermal hot pressing process is a useful method to obtain the bulk samples of lanthanum phosphate.

Key words: Lanthanum phosphate, Hydrothermal hot pressing process, Drilling, Resistance against hydrofluoric acid.

Introduction

Phosphates have been widely used as ceramic materials, catalysts, adsorbents, fluorescent materials, dielectric substances, metal surface treatments, fertilizers, detergents, food additives, fuel cells, pigments, etc [1, 2]. In these phosphate materials, lanthanum phosphate is one of the important materials, which has a high melting point and a low solubility in acidic and basic solutions [3, 4].

For various applications, phosphates can be in the form of powders, bulk samples, or thin layers. Because phosphates decompose to oxide at high temperatures via loss of P_2O_5, it is difficult to obtain bulk samples of phosphate by standard sintering techniques. As a novel synthetic process, the hydrothermal hot pressing method has been studied [5-10]. In this method, mixtures of the starting powder and a small amount of water are sintered at relatively low temperatures, which usually leads to porous phosphate materials. The merit of this method is the low sintering temperature and porous bulk. However, although many porous phosphate bulk samples have often been formed in this hydrothermal hot pressing process, these bulk samples are physically too weak to use as a material. Therefore, it is necessary to improve the physical strength, which is related with the filling factor. This factor is calculated from the real and theoretical densities. Bulk samples with a high filling factor have a high physical strength. The strength against the mechanical processing is also important to form phosphate bulk samples. The bulk samples with a high density are hard, however these are sometimes fragile. The porous structure is relieved from the impacts by a mechanical treatment. Furthermore, these phosphate bulk samples are expected to have a high resistance to hydrofluoric acid in comparison with oxide materials.

In this study, lanthanum phosphates were prepared from lanthanum nitrate and phosphoric acid solutions, and treated in the hydrothermal hot pressing process. The lanthanum phosphate bulk samples were assessed from the density and filling factor, the machinable strength, the vibration strength, and the resistance against hydrofluoric acid.

Experimental

The 0.1 mol/l of lanthanum nitrate, $La(NO_3)_3$, solution was mixed with 0.1 mol/l of phosphoric acid solution in the molar ratio of La/P = 1/1. This ratio is settled from the chemical composition of lanthanum orthophosphate, $LaPO_4$. The precipitate was filtered off and dried in air. The precipitate obtained and its thermal product at 400 °C were estimated from XRD analyses and particle size distributions. The XRD patterns were recorded on a Rigaku Denki RINT 2000 X-Ray diffractometer using monochromated CuKα radiation. The particle size distributions of samples were measured with a laser diffraction/scattering particle size distribution HORIBA LA-910.

The mixtures of sample powder (1 g) and water (0-0.4 ml) were placed in a mold and mechanically pressed with a uniaxial pressure of 10 or 20 MPa for 1 h. Because the mold had a slight excess of space,

*Corresponding author:
Tel : 81-75-703-5653
Fax: 81-75-703-5653
E-mail: onoda@kpu.ac.jp

water could be volatilized in the sintering process. The filling factor was calculated from the density of the lanthanum phosphate bulk samples obtained and the ideal density of the crystallized rhabdophane-type lanthanum phosphate.

The machinable strength was estimated from the diameter of a drilled hole on the diameter of a 14 mm pellet. The vibration strength was estimated in the following method. 0.2 g of bulk samples was placed with 3 ml of water in a cell for an ultraviolet - visible (UV-Vis) spectrometer. The absorbance at 660 nm was measured before and after an ultrasonic treatment for 3 minutes. Furthermore, the resistance of materials was estimated using the following method. 0.2 g of bulk sample was allowed to stand in 100 ml of 5 wt% hydrofluoric acid for 1 day. Then, the solid was removed by filtration. The residual ratio of samples was calculated from the weight of the dried samples.

Results and discussion

Chemical composition and particle size of lanthanum phosphates

Figure 1 shows XRD patterns of samples with and without heating. Both samples had XRD peaks of rhabdophane-type lanthanum phosphate. By heating, the peak intensity became weak. Rhabdophane-type lanthanum phosphate lost the crystalline water and some parts of their structure were distorted by heating at over 250 °C [11]. Generally, the particle size has an influence on the formation of bulk materials from powders [12]. Figure 2 shows the particle size distribution of samples with and without heating. A large portion of the phosphate particles was from 1 to 10 μm in size in the sample without heating. The ratio of the particles larger than 10 μm increased by heating at 400 °C.

Density of lanthanum phosphate bulk samples

The density of the bulk samples is a fundamental and important property because it has a relationship with the physical strength. Figure 3 shows the density and filling factor of lanthanum phosphate bulk samples. The temperature had less influence on the density of lanthanum phosphate bulk samples (Fig. 3(I)). The filling factor was about 60% calculated from the ideal density of rhabdophane-type $LaPO_4$. This ratio is lower than that of the other phosphate bulk samples synthesized in the hydrothermal hot pressing process in

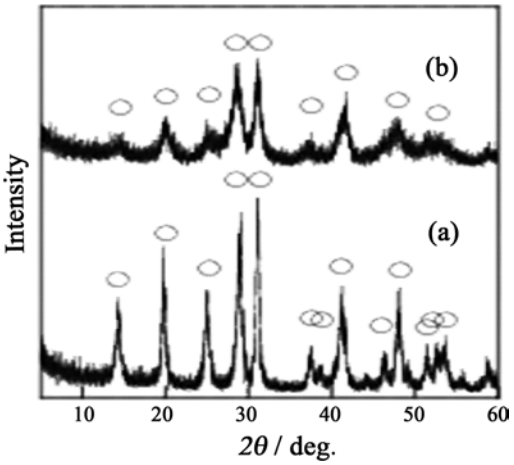

Fig. 1. XRD patterns of samples, (a) without heating, (b) heated at 400 °C, ○ ; rhabdophane-type $LaPO_4$.

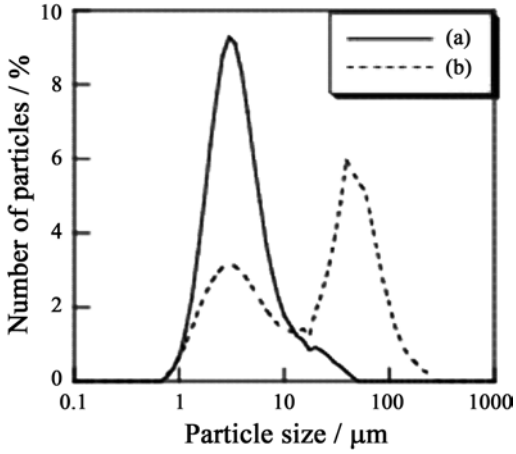

Fig. 2. Particle size distribution of samples, (a) without heating, (b) heated at 400 °C.

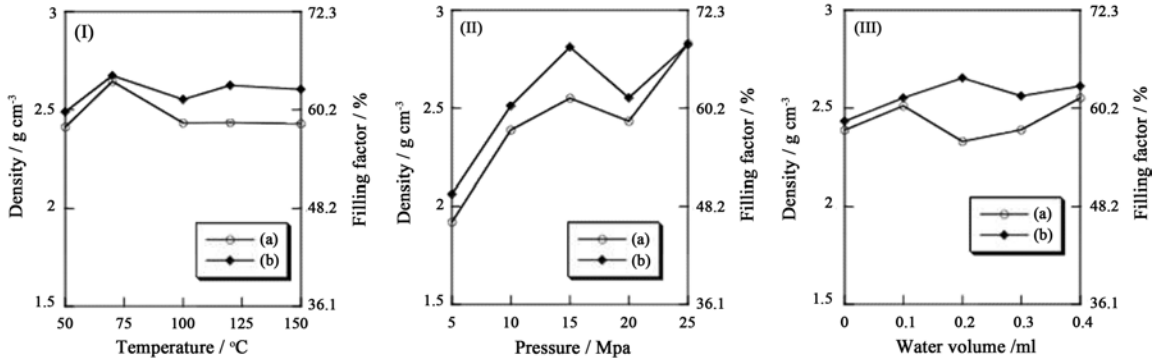

Fig. 3. Density and filling factor of bulk samples, (I) the influence of temperature, 20 MPa, (a) H_2O 0 ml, (b) 0.1 ml, (II) the influence of pressure, 100 °C, (a) H_2O 0 ml, (b) 0.1 ml, (III) the influence of solvent volume, 100 °C, (a) 10 MPa, (b) 20 MPa.

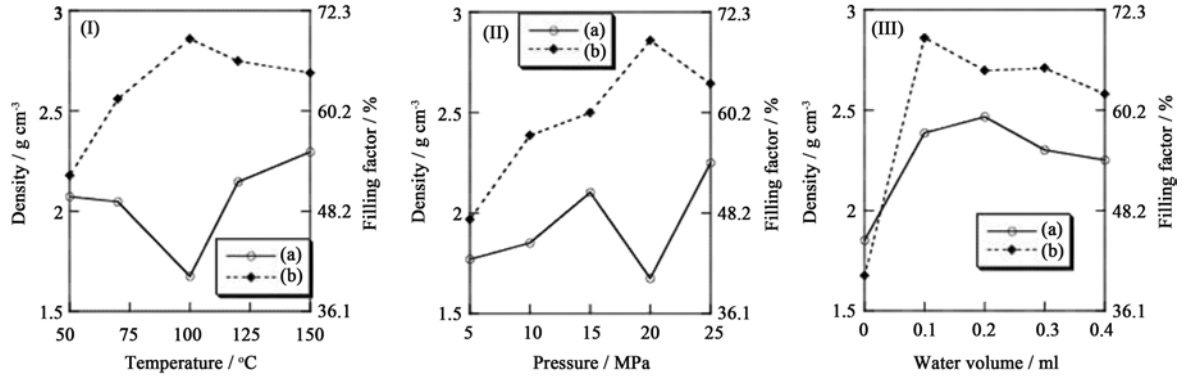

Fig. 4. Density and filling factor of bulk samples heated at 400 °C, (I) the influence of temperature, 20 MPa, (a) H_2O 0 ml, (b) 0.1 ml, (II) the influence of pressure, 100 °C, (a) H_2O 0 ml, (b) 0.1 ml, (III) the influence of solvent volume, 100 °C, (a) 10 MPa, (b) 20 MPa.

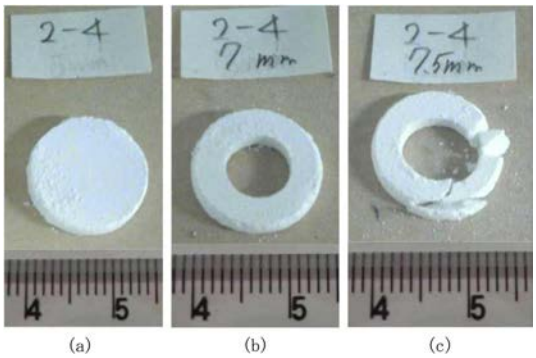

Fig. 5. Photographs of lanthanum phosphate bulk samples, (a) without mechanical treatment, (b) after 7.0 mm drilling, (c) after 7.5 mm drilling.

have about 0.5 molecular crystalline water [15]. By the addition of the crystalline water in the calculation, the filling factor increased up to about 70%, however, this ratio was still low. The phosphate bulk samples synthesized with 0.1 ml of water indicated a higher density than those synthesized without water (Fig. 3(I)(II)). With an increase of the pressure in the hydrothermal hot pressing process, the bulk density had a tendency to improve (Fig. 3(II)). The increase in the volume of the added water indicated a weak tendency to improve the density of bulk samples synthesized in the hydrothermal hot processing process (Fig. 3(III)).

Figure 4 shows the density and filling factor of the bulk samples prepared from lanthanum phosphate heated at 400 °C as a pretreatment. The presence of water had a significant influence on the density in Figure 4 (I) and (II). Because of the crystalline water, lanthanum phosphate without heating as a pretreatment had a smaller difference at the density of the bulk samples synthesized in the hydrothermal hot pressing process. Lanthanum phosphate heated at 400 °C lost the crystalline water, the added water in the pressing process improved the density of the bulk samples. In these results of lanthanum phosphate heated at 400 °C, the higher temperature produced a higher density of bulk samples (Fig. 4(I)). The density of bulk samples

Table 1. Maximum diameter of drilled hole in lanthanum phosphate pellets without cracking, (I) Temperature dependence, 20 MPa, (II) Pressure, 100 °C, (III) Volume of water, 100 °C.

(I) Water volume	Temperature / °C				
/ml	50	70	100	120	150
0	6.0	4.5	4.0	x	x
0.1	6.0	x	x	x	x
(II) Water volume	Pressure / MPa				
/ml	5	10	15	20	25
0	5.5	4.0	x	4.0	x
0.1	4.0	4.5	x	x	x
(III) Pressure	Solvent volume / ml				
/MPa	0	0.1	0.2	0.3	0.4
10	4.0	4.5	5.0	x	x
20	4.0	x	x	4.0	5.0

improved with an increase of the pressure in the pressing process (Fig. 4(II)). The 0.1 ml of the added water indicated a high density. On the other hand, the density became low with a increase of the added water over 0.2 ml (Fig. 4(III)). A greater volume of the added water produced more porous phosphate bulk samples.

Drilling properties of lanthanum phosphate bulk samples

As well as the physical strength of bulk samples, the change of the bulk shape is important for use as a material [16]. Inorganic materials are generally strong against a physical stress, however easy to crack by a mechanical treatment. Therefore, the strength against a mechanical treatment was studied with a drilling process. Figure 5 shows the photographs of bulk samples with and without the drilling treatment. The bulk samples had a diameter of 14 mm. The diameter of the drill was increased from 4.0 mm at a rate of 0.5 mm for each test. The maximum diameter was recorded on the phosphate bulk samples without the cracking.

Table 2. Maximum diameter of drilled hole in lanthanum phosphate pellets without cracking (pretreatment; 400 °C, 1 h), (I) Temperature dependence, 20 MPa, (II) Pressure, 100 °C, (III) Volume of water, 100 °C.

(I) Water volume	Temperature / °C				
/ml	50	70	100	120	150
0	7.5	4.0	4.0	6.0	5.5
0.1	x	6.0	x	x	5.0
(II) Water volume	Pressure / MPa				
/ml	5	10	15	20	25
0	4.0	5.0	7.0	7.0	6.5
0.1	4.5	7.0	4.0	x	x
(III) Pressure	Solvent volume / ml				
/MPa	0	0.1	0.2	0.3	0.4
10	5.0	7.0	5.0	4.5	x
20	7.0	x	5.0	4.5	4.0

Table 1 shows the maximum diameter of lanthanum phosphate bulk samples without cracking. The mark, x, means no record, that is the cracking of bulk samples by the 4.0 mm drill. Cracking took place of many bulk samples synthesized from lanthanum phosphate without heating as a pretreatment. Bulk samples synthesized at 50 °C and 20 MPa were drilled with a hole with 6.0 mm in a diameter. Other samples indicated a diameter smaller than 5.5 mm before cracking. The lanthanum phosphate bulk samples without the pretreatment were easy to destroy by drilling.

Table 2 shows the result on bulk samples synthesized from lanthanum phosphate heated at 400 °C as a pretreatment. The number of bulk samples that were cracked by the 4.0 mm drill decreased in comparison with the bulk samples without a pretreatment. Many conditions indicated a diameter larger than 6.0 mm. A hole greater than 7.0 mm was obtained on some bulk samples whose diameter was 14 mm. Heating at 400 °C before the pressing process was effective in obtaining strong bulk samples against the drilling treatment. The pressing temperature, pressure, and the volume of water did not have a clear influence on the strength of bulks against the drilling.

Vibration strength of lanthanum phosphate bulk samples

The strength against vibration is also important for a bulk material. Figure 6 shows the vibration strength of lanthanum phosphate bulk samples. Bulk samples

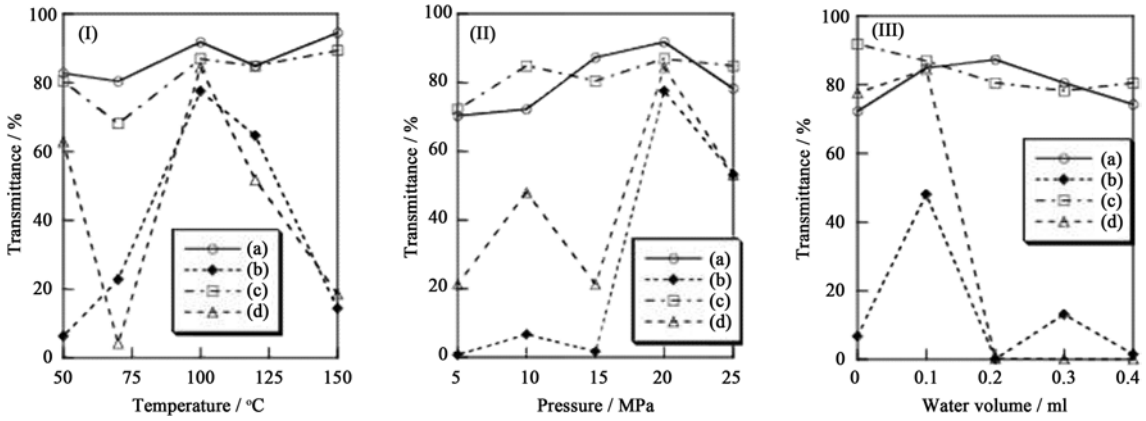

Fig. 6. Vibration strength of bulk samples, (I) the influence of temperature, 20 MPa, (a) H_2O 0 ml, before, (b) 0 ml, after, (c) 0.1 ml, before, (d) 0.1 ml, after, (II) the influence of pressure, 100 °C, (a) H_2O 0 ml, before, (b) 0 ml, after, (c) 0.1 ml, before, (d) 0.1 ml, after, (III) the influence of solvent volume, 100 °C, (a) 10 MPa, before, (b) 10 MPa, after, (c) 20 MPa, before, (d) 20 MPa, after.

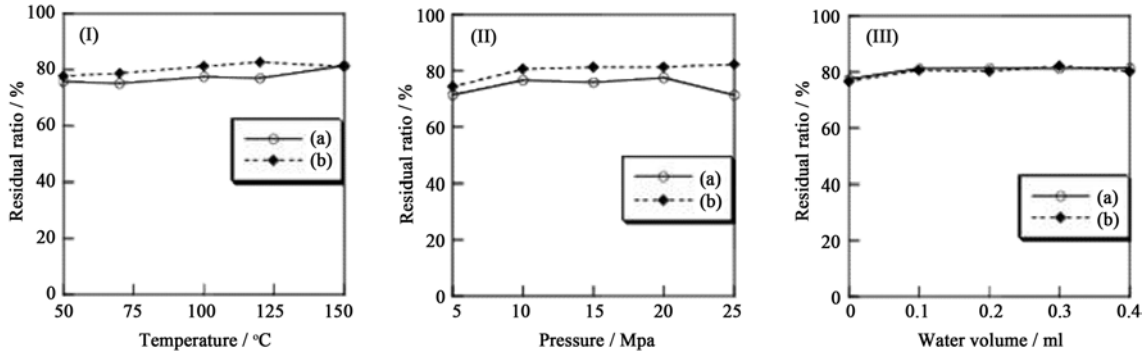

Fig. 7. Residual ratios of bulk samples to hydrofluoric acid, (I) the influence of temperature, 20 MPa, (a) H_2O 0 ml, (b) 0.1 ml, (II) the influence of pressure, 100 °C, (a) H_2O 0 ml, (b) 0.1 ml, (III) the influence of solvent volume, 100 °C, (a) 10 MPa, (b) 20 MPa.

indicated about 85% in transmittance before the vibration. A small part of bulk samples was dispersed into the water when a bulk sample was sunk. With a vibration for 3 minutes, the transmittance became lower in all the bulk samples. When the bulk samples were strong against the vibration, the transmittance of the water with the bulk samples indicated no decrease. Some of the lanthanum phosphate bulk samples indicated over 40% in transmittance. These bulk samples had a higher strength against the vibration than the others. The tendency of the transmittance was not well defined from the pressing temperature, pressure, and the volume of water. A relationship between this vibration strength and the density was not observed in these lanthanum phosphate bulk samples. Furthermore, in the case of samples heated at 400 °C as a pretreatment, bulk samples also showed a decrease in the transmittance by the vibration, without a relationship with the pressing temperature, pressure, and the volume of water.

Resistance against hydrofluoric acid

The chemical strength is also important for a material. Figure 7 shows the residual ratio of lanthanum phosphate bulk samples with hydrofluoric acid. The residual ratio was about 80% in spite of the change in the pressing conditions. In the same conditions, silicon dioxide was perfectly dissolved in hydrofluoric acid. Lanthanum phosphate bulk samples had a high resistance against hydrofluoric acid. Bulk samples synthesized from lanthanum phosphate heated at 400 °C as a pretreatment gave similar results in this residual ratio. This resistance against hydrofluoric acid strongly depended on the chemical composition of the bulk sample and less on the pressing conditions in the hydrothermal hot pressing process.

Conclusions

Lanthanum phosphate bulk samples were synthesized by a hydrothermal hot pressing process. The bulk samples obtained had about 60% as a filling factor. Because of the crystalline water, lanthanum phosphate without heating as a pretreatment had a smaller difference in the density of the bulk samples synthesized in the hydrothermal hot pressing process. The lanthanum phosphate bulk samples without a pretreatment were easy to destroy by drilling. Heating at 400 °C before the pressing process was effective to obtain the strong bulk samples against the drilling process. A relationship between the vibration strength and the density was not observed in these lanthanum phosphate bulk samples. Lanthanum phosphate bulk samples had a high resistance against hydrofluoric acid.

References

1. H. Onoda, H. Nariai, A. Moriwaki, H. Maki, and I. Motooka, J. Mater. Chem. 12 [6] (2002) 1754-1760.
2. H. Onoda, T. Ohta, J. Tamaki, and K. Kojima, Appl. Catal. A 288 [1-2] (2005) 98-103.
3. H. Onoda, K. Taniguchi, and I. Tanaka, Microp. Mesop. Mater. 109 (2008) 193-198.
4. H. Onoda, K. Tange, and I. Tanaka, J. Mater. Sci. 43 [16] (2008) 5483-5488.
5. M. Takimura, H. Nagata, Y. Yamasaki, T. Suzuki, Y. Ikuhara, and A. Nakahira, J. Ceram. Soc. Jpn. 114 (6) (2006) 554-557.
6. A. Nakahira, M. Takimura, and Y. Yamasaki, J. Non-Cryst. Solid 353 (2007) 4203-4207.
7. Z. Matamoros-Veloza, K. Yanagisawa, J. C. Rendon-Angeles, S. Oishi, and M. A. Cisneros-Guerrero, Solid State Ionics 172 [1-4] (2004) 597-600.
8. T. Onoki, K. Hosoi, and T. Hashida, Scrip. Mater. 52 [8] (2005) 767-770.
9. S. Katsuyama, A. Kishida, and M. Ito J. All. Comp. 414 [1-2] (2006) 215-220.
10. T. Onoki, K. Hosoi, T. Hashida, Y. Tanabe, T. Watanabe, E. Yasuda, and M. Yoshimura Mater. Sci. Eng. C 28 [2] (2008) 207-212.
11. H. Onoda, H. Nariai, H. Maki, and I. Motooka, Mater. Chem. Phys. 73 [1] (2002) 19-23.
12. H. Onoda, K. Okumoto, A. Nakahira, and I. Tanaka, Mater. 2 (2009) 1-9.
13. H. Onoda, R. Sakai, A. Nakahira, and I. Tanaka, Inorg. Mater. 45 [9] (2009) 1048-1052.
14. H. Onoda, Y. Inagaki, A. Kuwabara, N. Kitamura, K. Amezawa, A. Nakahira, and I. Tanaka, Phosphorus Res. Bull. 23 (2009) 20-24.
15. M. Tsuhako, S. Ikeuchi, T. Matsuo, I. Motooka, and M. Kobayashi, Bull. Chem. Soc. Jpn 52 [4] (1979) 1034-1040.
16. W. Min, D. Miyahara, K. Yokoi, T. Yamaguchi, K. Daimon, Y. Hikichi, T. Matsubara, and T. Ota Mater. Res. Bull. 36 [5-6] (2001) 939-945.