

Microwave-assisted synthesis of nanocrystalline ZnWO₄ powders via a water-based citric acid complex precursor

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Nanocrystalline ZnWO₄ powders were successfully synthesized from a water-based citric acid complex precursor using microwave irradiation. The polymeric precursors were heat treated at temperatures from 300 to 600 °C for 3 h. Crystallization of the ZnWO₄ was detected at 400 °C and entirely completed at a temperature of 600 °C. The powders at 400 and 500 °C showed primarily a co-mixed morphology with spherical and silkworm-like forms. The powders at 500 °C had a relatively more homogeneous morphology, while the powders at 600 °C showed a relatively exaggerated growth including rectangular form. The average crystalline sizes were 18~25 nm, showing an ordinary tendency to increase with temperature from 400 to 600 °C.

Key words: Microwave-assisted synthesis, nanocrystalline powders, ZnWO₄, water-based citric acid complex precursor.

Introduction

ZnWO₄ has been suggested as a possible new material for MASER (microwave amplification by stimulated emission of radiation) [1], scintillator [2-4] and OHB (optical hole burning) lattice material [5], etc. It has the advantages of being less hygroscopic and much cheaper than Bi₄Ge₃O₁₂(BGO) which is a widely used scintillator material. Therefore, ZnWO₄ nano-sized powder of a high quality is required for these applications. ZnWO₄ has thus far been prepared by several different processes such as the Czochralski method [6], a solid-state reaction method [7], a reaction in aqueous solution followed by heating of the precipitate [8], heating of ZnO thin films with WO₃ vapor [9], a sol-gel reaction [10], and a hydrothermal reaction over an extensive period [11]. ZnWO₄ particles prepared by these processes are relatively large (grain size > 100 nm) with inhomogeneous morphologies. To obtain nano-sized powders, the conventional solid-state reaction methods have several problems, because WO₃ has a tendency to vaporize at high temperatures [12], non-homogeneous compounds might easily be formed during the solid-state reaction processing and the temperature for the solid state reaction is relatively high, just above 1000 °C for 24 h [7].

These problems could be solved by applying advanced wet chemical solution methods [13, 14]. A polymerized complex method such as a modified Pechini method [15], where several metal ions in a solution could be

first chelated to form metal complexes and then polymerized to form a gel, seems to be the most suitable among several chemical solution processes, because rigidly fixed cations are homogeneously dispersed in the polymer network and have few chances to segregate even during pyrolysis. This method has already been successfully used to prepare highly pure samples of various double oxides such as BaTiO₃ [16], Y₆WO₁₂ [17], mixed-cation oxides [18] and even for various superconductors [19] with multiple cationic compositions. However, in spite of the many advantages of the polymeric complex method, the weakness of the polymerized complex method is the difficulty of the effective removal of large amounts of organic substance. Based on this consideration, the citric acid complex method as another chemical solution process was tried for the synthesis of nanocrystalline ZnWO₄ powders. In this process, metal citrate complexes without a network structure are formed by using water instead of ethylene glycol.

Also, microwave irradiation as a heating method has found application and been developed for a number of systems in chemistry and ceramic processing [20-23]. Compared with the usual method, microwave synthesis has the advantages of very short reaction times, small particle sizes, narrow particle size distributions, and high purity. Jansen *et al.* [20] suggested that these advantages could be attributed to fast homogeneous nucleation and easy dissolution of the gel. In the study described here, we report the synthesis of nanocrystalline ZnWO₄ powders from a water-based citric acid complex precursor using microwave irradiation. The precursors and synthesized powders were evaluated in term of the crystallization process, thermal decomposition and morphology.

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Experimentals

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}$), Junsei Chemical Co. LTD., Japan) and tungstic acid (H_2WO_4 , Acros Organics, USA), were used as sources of the metallic cations. De-ionized water (DW) and citric acid ($\text{HO}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})_2$, CA, Yukiri Pure Chemical Co, LTD., Japan) were used as solvent and chelating agent for the process. Figure 1 shows a schematic flow chart for the production of nanocrystalline ZnWO_4 powders by the citric acid complex method using microwave irradiation. The citrate solution was prepared by dissolving appropriate molar ratios of citric acid in de-ionized water (CA:DW molar ratio = 1:4). After complete homogenization of the citrate solution, zinc acetate dehydrate and tungstic acid were dissolved in the molar ratio of total chelate metal cations (TO) and citric acid (TO : CA molar ratio = 1 : 5). By keeping the solution at a temperature of 50°C for 30 minutes under constant stirring, the solution became a more viscous pale-yellow solution. A domestic microwave oven of 800 W power (Samsung Electronic Corp. Korea) was used for the reaction of the solution. The solution was placed in the microwave oven and the reaction was performed under ambient air for 30 minutes. The working cycle of the microwave oven was set between 30 s on and 30 s off. The solution became more viscous and changed its color from pale-yellow to brown. No visible precipitation was observed during the heating process. After this solution condensed, the brown product was converted into powder after grinding with a teflon bar. Thermal analysis was performed on this powder, hereinafter referred to as the 'precursor'. Heat-treatment of the precursor was performed at various temperatures from 300 to

600°C for 3 h.

The crystallization process of the polymeric precursor was evaluated by thermogravimetry-differential thermal analysis (TG-DTA, SETRAM, France), using a sample weight of about 24 mg and a heating rate of 10 Kminute^{-1} . The phase existing in the powders after heat-treatment was identified by ordinary X-ray diffraction (XRD, $\text{CuK}\alpha$, 40 kV, 30 mA, Rigaku, Japan) with a scan rate of $3^\circ/\text{minute}$. Fourier transform infrared spectroscopy (FT-IR, Model IR 550, Magna, Nicolet Company) was used for the interpretation of the thermal-decomposition behavior of the precursors and heat-treated powders in the frequency range from 400 to 4000 cm^{-1} . The FT-IR spectra were measured in KBr pellets. The average crystallite size of the heat-treated powders was calculated using the X-ray diffraction line broadening method through Scherrer's relationship [24]. The microstructure and surface morphology of the nanocrystalline powders were observed by scanning electron microscopy (SEM, JSM-35CF, JEOL) and transmission electron microscopy (TEM, JEM 2010, JEOL).

Results and Discussion

The crystallization process of the precursor was evaluated by TG-DTA with the results given in Fig. 2. In Fig. 2(a), with an increase of temperature, the weight loss occurs in the TG curve up to 600°C . Thereafter the weight remains constant, indicating that the decomposition of all the organic materials contained in the precursor together with their combustion and the crystallization of ZnWO_4 have been completed below 600°C . No significant plateau, corresponding to well-defined intermediate products, appeared in the heating process. The DTA curve in Fig. 2(b) shows three exothermic peaks which could be further classified into two types of physical process: (1) the left hand exothermic peak at 320°C corresponds to the initial decomposition of the precursor; and (2) the center exothermic peak at 365°C and (3) the right hand exothermic peak at 552°C correspond to the nucleation of the crystals and crystallization of ZnWO_4 . Below 365°C , the resultant powders were dark brown and porous in structure, denoting an amorphous phase. This was attributed to the presence of lot of carbon and ignitable organics. When the temperature was further increased above 400°C (just over 365°C , the center exothermic peak), crystal nuclei began to form, and consequently the primary crystallizing process has been completed accompanying the combustion of the residual carbon and ignitable organics.

Figure 3 shows XRD results for the phase identification of the powders heated for 3 h as a function of heating temperature. In Fig. 3(a), the powders at 300°C were amorphous without any crystallized phases. Above 400°C , in Fig. 3(b)~(d) the powders could be identified

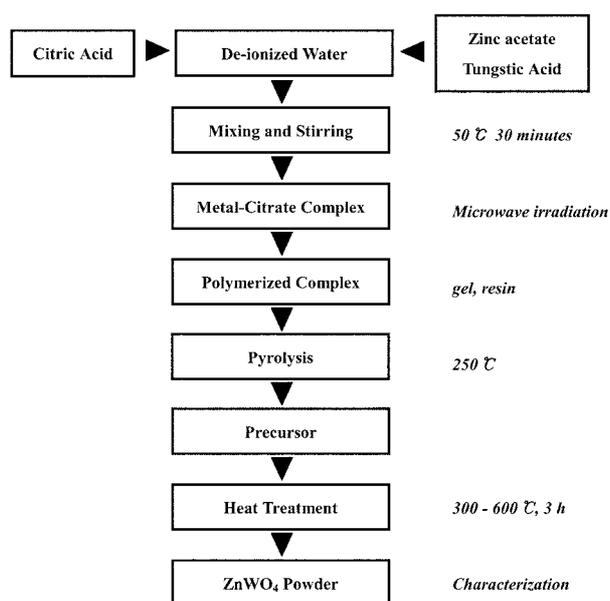


Fig. 1. Flow chart for synthesis of nanocrystalline ZnWO_4 powders from the water-based citric acid complex precursor using microwave irradiation.

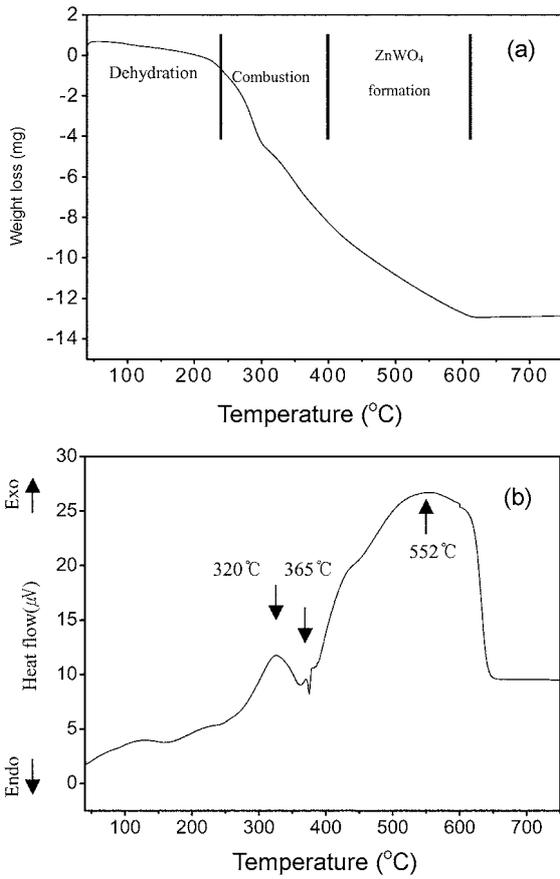


Fig. 2. (a) TGA curves and (b) DTA curves of the precursor in flowing air.

as the $ZnWO_4$ phase. At 500°C in Fig. 3(c), unreacted WO_3 phase was observed and it seemed to be a phase additional to the $ZnWO_4$ phase. For a higher heating temperature, at 600°C in Fig. 3(d), the WO_3 peaks disappeared and the $ZnWO_4$ peaks had higher intensity. It is noted that only the $ZnWO_4$ single phase could be observed at 600°C.

Figure 4(a)~(e) shows the FT-IR spectra for the

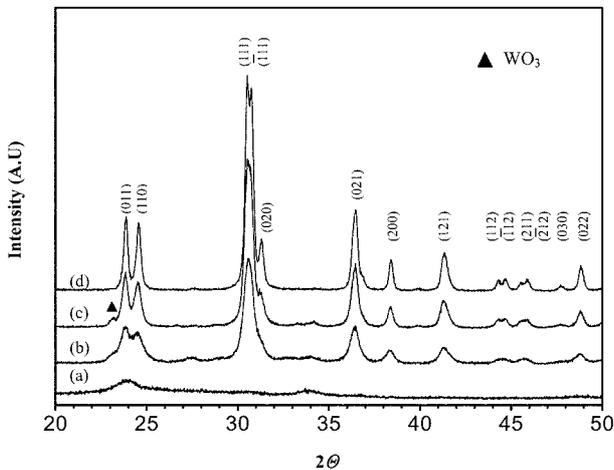


Fig. 3. XRD patterns of the powders heat-treated at (a) 300, (b) 400, (c) 500 and (d) 600°C for 3 h.

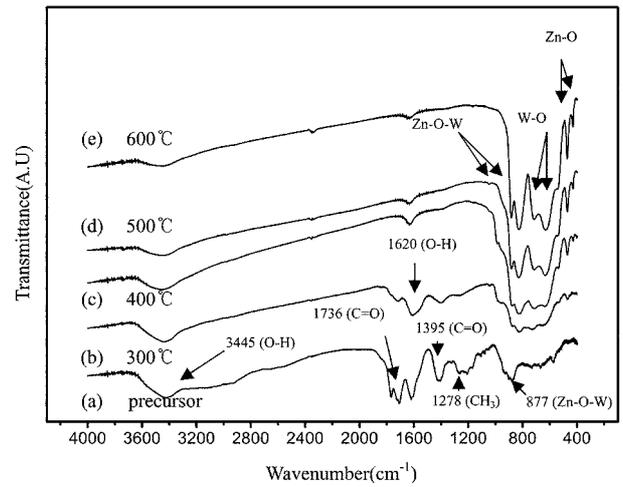


Fig. 4. FT-IR spectra of the (a) precursor and powders heat-treated at (b) 300, (c) 400, (d) 500 and (e) 600°C for 3 h.

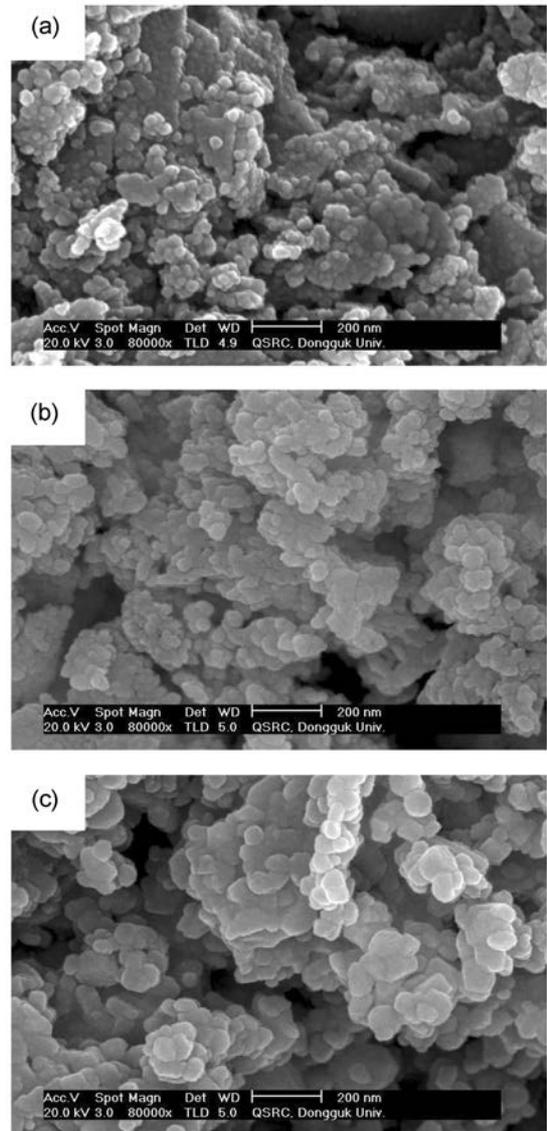


Fig. 5. Scanning electron micrographs of nanocrystalline $ZnWO_4$ powders heat-treated at (a) 400, (b) 500 and (c) 600°C for 3 h.

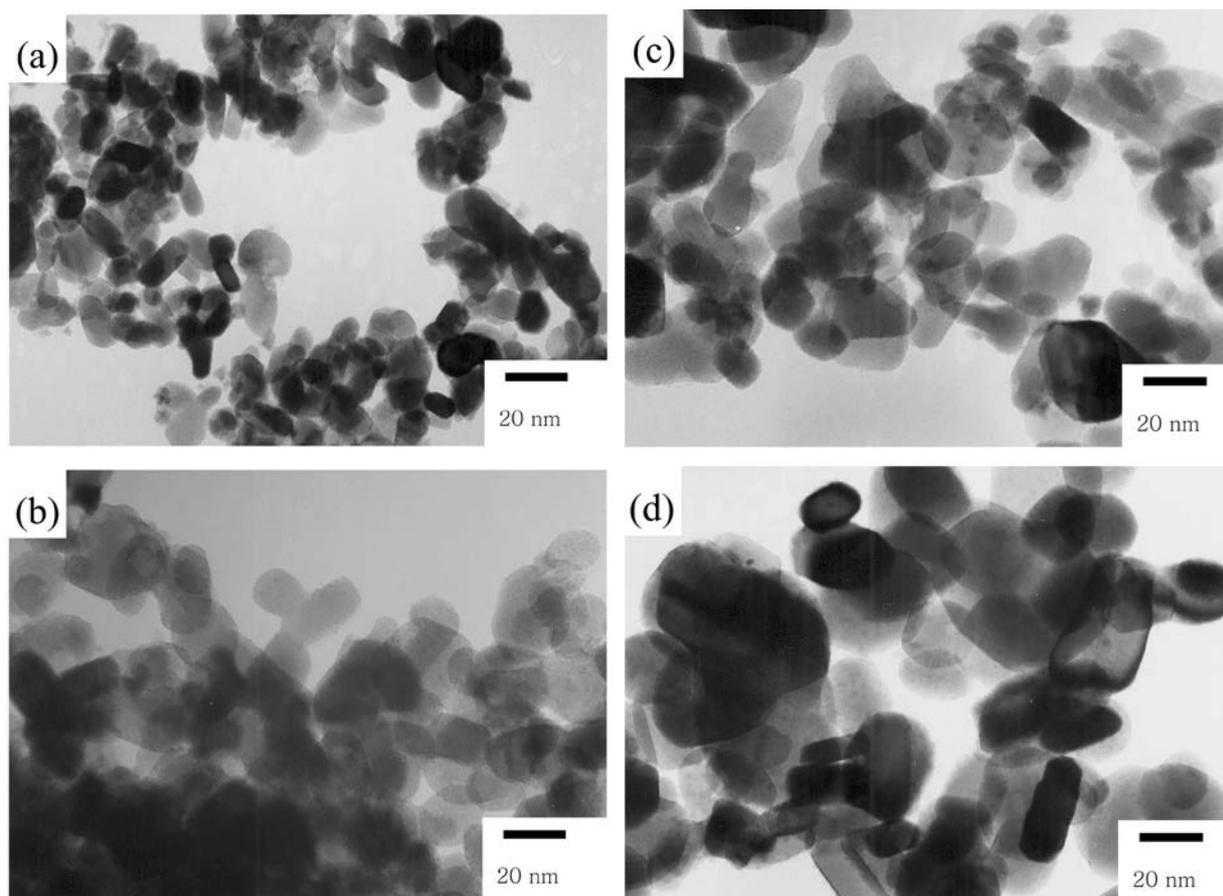


Fig. 6. Transmission electron micrographs of nanocrystalline ZnWO₄ powders heat-treated at (a) 300, (b) 400, (c) 500 and (d) 600 °C for 3 h.

precursor and powders heated at 300~600 °C. For the precursor (Fig. 4(a)), the bands at 1620, 3445 cm⁻¹ (O-H stretching modes), 1736, 1395 cm⁻¹ (carboxyl group stretching modes), 1278 cm⁻¹ (CH₃) and absorption bands near 877 cm⁻¹ (W-O-Zn stretching mode) seem to define the relatively dehydrated (ZnW)-citrate complex. Heat-treatment at 300 °C in Fig. 4(b) leads to a significant change in its infrared spectra. A decrease of the bands at 1736, 1395 and 1620 cm⁻¹ is produced, while the band at 1278 cm⁻¹ disappears. At 400 °C in Fig. 4(c), the bands of the carbonyl group disappear, while new absorption bands appear between 400 and 900 cm⁻¹. In Fig. 4(c)~(e), the bending and stretching vibrations of Zn-O (473, 532 cm⁻¹), W-O (633, 710 cm⁻¹) and Zn-O-W bond (834, 877 cm⁻¹) could be identified and associated to the synthesized ZnWO₄.

Figure 5 shows SEM results of ZnWO₄ prepared at (a) 400, (b) 500 and (c) 600 °C for 3 h. Fig. 5(a) and (b) show spherical particles with an average size of 20~30 nm. Fig. 5(c) shows elongated particles of around 40~50 nm which are agglomerates, being composed of many crystals. Fig. 6 shows TEM images of the ZnWO₄ nanocrystallines heat-treated at (a) 300, (b) 400, (c) 500 and (d) 600 °C for 3 h. The powders at 400 and 500 °C

Table 1. Average crystallite size of nanocrystalline ZnWO₄ powders as a function of heating temperature

Temperature (°C)	Average crystallite size (nm)
300	18
400	20
500	23
600	25

in Fig. 6(a) and (b) show primarily a co-mixed morphology with spherical and silkworm-like forms. The particles at 500 °C in Fig. 6(c) have a relatively more homogeneous morphology. The powders at 600 °C in Fig. 6(d) show relatively exaggerated growth including rectangular habits. Table 1 shows the average crystallite sizes for the heat-treated powders calculated by the XRD line broadening method [24]. The calculated average crystallite sizes were 18, 20, 23 and 25 nm for the heat-treated powders at (a) 300, (b) 400, (c) 500 and (d) 600 °C, respectively. These correspond to the SEM and TEM observations in Fig. 5 and Fig. 6 showing an ordinary tendency to increase with temperature from 400 to 600 °C.

Conclusions

Nanocrystalline ZnWO₄ powders were successfully synthesized from a water-based citric acid complex precursor using microwave irradiation. Crystallization of ZnWO₄ was detected at 400 °C and entirely completed at a temperature of 600 °C. Bending and stretching vibrations of Zn-O, W-O and Zn-O-W bond were identified and associated to the synthesized ZnWO₄ above 400 °C. The powders at 400 and 500 °C showed primarily a co-mixed morphology with spherical and silkworm-like forms. The powders at 500 °C had a relatively more homogeneous morphology, while the powders at 600 °C showed relatively exaggerated growth including rectangular form. The average crystalline sizes were 18~25 nm showing an ordinary tendency to increase with the temperatures from 400 to 600 °C.

References

1. L.G. Van Uitert and S. Preziosi, *J. Appl. Phys.* 33 (1962) 2908-2909.
2. T. Oi, K. Takagi, and T. Fukuzawa, *Appl. Phys. Letts.* 36[4] (1980) 278-280.
3. I. Foeldvari, A. Peter, S. Keszthelyi-landori, R. Capelletti, I. Cravero, and F. Schmidt, *J. Crystal Growth* 79 (1986) 714-718.
4. P.F. Schofield, K.S. Knight, and G. Cressey, *J. Mat. Sci.* 31 (1996) 2873-2877.
5. A. Caprez, P. Meyer, P. Mikhail, and J. Hulliger, *Mat. Res. Bull.* 32[8] (1997) 1045-1049.
6. J.C. Brice and P.A.C. Whiffin, *Br. J. Appl. Phys.* 18 (1967) 581-584.
7. A.R. Phani, M. passacantando, L. Lozzi, and S. Santucci, *J. Mat. Sci.* 35 (2000) 4879-4883.
8. A. Kuzmin and J. Purans, *Raditt. Meas.* 33 (2001) 583-586.
9. A. Henglein, and Ber. Bunsenges, *Phy. Chem.* 78 (1974) 1078-1083.
10. M. Bonanni, L. Spanhel, M. Lerch, E. Fuglein, and G. Muller, *Chem. Mater.* 10 (1998) 304-307.
11. F.-S. Wen, X. Zhao, H. Huo, J.-S. Chen, E.-S. Lin, and J.H. Zhang, *Mater. Lett.* 55 (2002) 152-156.
12. K. Kuribayashi, M. Yoshimura, T. Ohta, and T. Sata, *Bull. Chem. Soc. Jpn.* 50[11] (1977) 2932-2934.
13. N.G. Eror and H.U. Anderson, *Mater. Res. Soc. Symp. Proc.* 73 (1986) 571-576.
14. M. Kakihana, *J. Sol-Gel Sci. Technol.* 6 (1996) 7-12.
15. M.P. Pechini, U.S. Pat. No. 3330697, July 11, 1967.
16. S. Kumar, G.L. Messing, and W.B. White, *J. Am. Ceram. Soc.* 76 (1993) 617-620.
17. M. Yoshimura, J. Ma, and M. Kakihana, *J. Am. Ceram. Soc.* 81 (1998) 2721-2724.
18. P.A. Lessing, *Am. Ceram. Soc. Bulletin* 68[5] (1989) 1002-1009.
19. M. Kakihara, M. Yoshimura, H. Mazaki, H. Yasuoka, and L. Borjesson, *J. Appl. Phys.* 71 (1992) 3904-3910.
20. C. Jansen, A. Arafat, A.K. Barakat, H. Van Bekkum, in: M.L. Occelli, H. Robson (Eds.), *Synthesis of Microporous Materials*, vol. 1, Van Nostrand Reinhold, New York, (1992) 507-508.
21. I. Gimus, K. Hoffmann, F. Marlow, and J. Caro, *Microporous Mater.* 2 (1994) 537-539.
22. X.C. Xu, W.S. Yang, J. Liu, and L.W. Lin, *Adv. Mater.* 3 (2000) 195-198.
23. K.J. Rao, B. Vaidhyanathan, M. Gaguli, and P.A. Ramakrishnan, *Chem. Mater.* 11 (1999) 882-887.
24. K.-N.P. Kumar, K. Keizer, and A.J. Burggraaf, *J. Mater. Chem.* 3 (1993) 1141-1149.