

Oxidation behavior of amorphous metallic $\text{Ni}_3(\text{SbTe}_3)_2$ compound

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Received 15 June 2005; received in revised form 25 August 2005; accepted 2 September 2005

Available online 27 September 2005

Abstract

Amorphous $\text{Ni}_3(\text{SbTe}_3)_2$ compound was prepared from a metathesis between Zintl phase K_3SbTe_3 and NiBr_2 in solution and its oxidation behavior was investigated in the temperature range of 200–700 °C in air. To characterize the sample, thermogravimetry (TG), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDAX) analyses were performed and electrical conductivity was measured as a function of temperature in the range of 25–800 °C in air. The specimen showed a metallic conducting-like behavior below 585 °C while a semiconducting-like behavior above 585 °C. At a first oxidation step of $\text{Ni}_3(\text{SbTe}_3)_2$ below 500 °C, TeO_2 phase is formed. Above 500 °C, NiO phase is formed, then some NiO reacts with TeO_2 to form NiTeO_3 and NiSb_2O_6 is simultaneously formed. Above 700 °C, NiTeO_3 is further reacted with TeO_2 to form NiTe_2O_5 . Both NiTeO_3 and NiTe_2O_5 are decomposed above 774 °C.

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Keywords: A. Alloys; A. Amorphous materials; C. Thermogravimetric analysis (TGA); C. X-ray diffraction; D. Catalytic properties

1. Introduction

Metal chalcogenides are known to be suitable materials for optical data storage. We have reported the synthesis and characterization of a series of $\text{M}_3(\text{SbTe}_3)_2$ during the past 20 years. These ternary metal chalcogen compounds have been found to show a photomagnetic property at low temperatures [1–6]. M–Sb–Te compounds may possess potential applications as heterogeneous catalysts because it has been known that metal–metalloid alloys are active catalysts for the hydrogenation of carbon oxides [7–10]. In the previous paper [11], we reported amorphous $\text{Ni}_3(\text{SbTe}_3)_2$ compound to show catalytic activity for the partial oxidation of methane when it was treated in gaseous oxygen prior to the reaction. Its catalytic activity is considered to be due to active oxide phases formed by the O_2 -treatment, and thus the investigation of its oxidation at high temperatures may be helpful to understand its active sites for the methane activation. In this work, the oxidation behavior of amorphous $\text{Ni}_3(\text{SbTe}_3)_2$ was studied in the temperature range of 200–700 °C. To characterize the samples treated at various temperatures in gaseous oxygen, thermogravimetry (TG),

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X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDAX) analyses were performed and the electrical conductivity was measured in the temperature range of 25–800 °C in air.

2. Experimental

$\text{Ni}_3(\text{SbTe}_3)_2$ was prepared by the reaction of aqueous solutions of K_3SbTe_3 and NiBr_2 . The ternary Zintl phase K_3SbTe_3 prepared from a direct combination of the elements is soluble in polar solvents, such as ethyl alcohol and water by the reaction: $\text{K}_3\text{SbTe}_3(\text{s}) \rightarrow 3\text{K}^+ + \text{SbTe}_3^{3-}$, and the Zintl solution allows subsequent metathesis reaction with nickel salt to form amorphous material due to the transfer of electrons from the SbTe_3^{3-} anion to the nickel cation according to the reaction: $3\text{Ni}^{2+} + 2\text{SbTe}_3^{3-} \rightarrow \text{Ni}_3(\text{SbTe}_3)_2(\text{s})$. A stoichiometric quantity of K_3SbTe_3 aqueous solution was added slowly while stirring the NiBr_2 solution. A fine black precipitate was formed immediately, which was then separated by solution filtration, washed with deionized water and acetone, and dried under vacuum. All manipulations were carried out in an argon-filled glove-box because of the air sensitivity of the compounds. The experimental empirical formula of the resultant product determined by atomic absorption spectroscopy (AAS) was $\text{Ni}_{1.61}\text{Sb}_{1.00}\text{Te}_{3.59}$.

XRD analysis was performed for the samples treated at various temperatures in a flow of dry air for 1 h. TG analysis was carried out for the samples at a heating rate of 20 °C/min in the temperature range of 25–900 °C in flows of both air and argon gas. SEM analysis was performed for the samples to investigate the morphological change with the heating temperature. EDAX analysis was performed for the samples to investigate the chemical composition. Electrical conductivity was measured as a function of temperature in the range of 25–800 °C in air by means of the four-probe method. To measure the electrical conductivity, the pellet with a diameter of 12 mm and a thickness of about 3 mm was connected to the Pt probes using nickel paste and then inserted into the quartz sample container which was placed in an electrical furnace to control the temperature.

3. Results and discussion

Fig. 1 presents the TG curves of $\text{Ni}_3(\text{SbTe}_3)_2$ measured at a heating rate of 20 °C/min in flows of both Ar and air (20 cm³/min). In Fig. 1, small weight loss is observed in the temperature range of 25–488 °C in a flow of Ar and of 25–285 °C in a flow of air, which is due to the vaporization of residual solvent molecules. In a flow of air, a weight gain is observed in the temperature range of 285–508 °C and then a small weight loss is observed in the temperature range of 508–573 °C. Beyond 573 °C, a weight gain occurs again up to 774 °C and a large weight loss begins at 774 °C. The uptake in weight is larger in dry air than in argon gas, which means that a lot of gaseous oxygen is chemisorbed on the surface, leading to an oxidation of sample. To provide more information on the oxidation of $\text{Ni}_3(\text{SbTe}_3)_2$, TG analysis of Sb and Te elements was performed. Fig. 2 presents the TG curves of Sb and Te elements measured in flows of both Ar and air in the temperature range of 25–800 °C. In a flow of Ar, a weight loss of Te begins at 450 °C, which corresponds to the melting point of Te at 1 atm. The vapor pressure of Te element is known to be 1 and 10 Torr at 520 and 633 °C, respectively. When Te is vaporized above 450 °C, the weight will be decreased as shown in Fig. 2. Accordingly, a weight loss above 488 °C in Fig. 1(A) is believed to be due to the vaporization of Te. In Fig. 1(B), the weight of $\text{Ni}_3(\text{SbTe}_3)_2$ increases in the temperature range of 285–774 °C in a flow of air. Fig. 3 presents the TG curves of the samples treated at 200, 300, 400, 500 and 600 °C for 1 h in a flow of air, in which the samples treated at 200 and 300 °C show a small weight gain at 285 °C, indicating the samples to be oxidized. The TG data of the samples treated below 500 °C show a weight loss at a temperature below 560 °C, but the TG data of the sample treated at 600 °C show a weight loss at about 780 °C, implying that rather stable metal oxides are produced on the sample when $\text{Ni}_3(\text{SbTe}_3)_2$ is treated in air above 600 °C. The cause of the weight decrease above 780 °C is mainly the evaporation of tellurium.

Fig. 4 presents the X-ray diffraction patterns of the samples. The samples treated at 200 and 400 °C in air show the presence of TeO_2 as a XRD detectable phase. The sample treated at 500 °C in air shows no crystalline peak as shown in Fig. 4(C), indicating the sample to be amorphous phase. Because TeO_2 is easily combined with other metal oxides to form glasses [12], the sample treated at 500 °C in air is considered to be metal tellurium oxide glasses. The sample treated at 600 °C in air shows the presence of NiO , NiTeO_3 , NiSb_2O_6 and Ni_3Te_2 phases as presented in Fig. 4(D).

Fig. 5(A) presents the SEM photograph of amorphous $\text{Ni}_3(\text{SbTe}_3)_2$. Fig. 5(B) presents the $\text{Ni}_3(\text{SbTe}_3)_2$ treated at 400 °C in air, showing a rod-shaped crystallite. From the EDAX result, the rod-shaped crystallite was found to be TeO_2

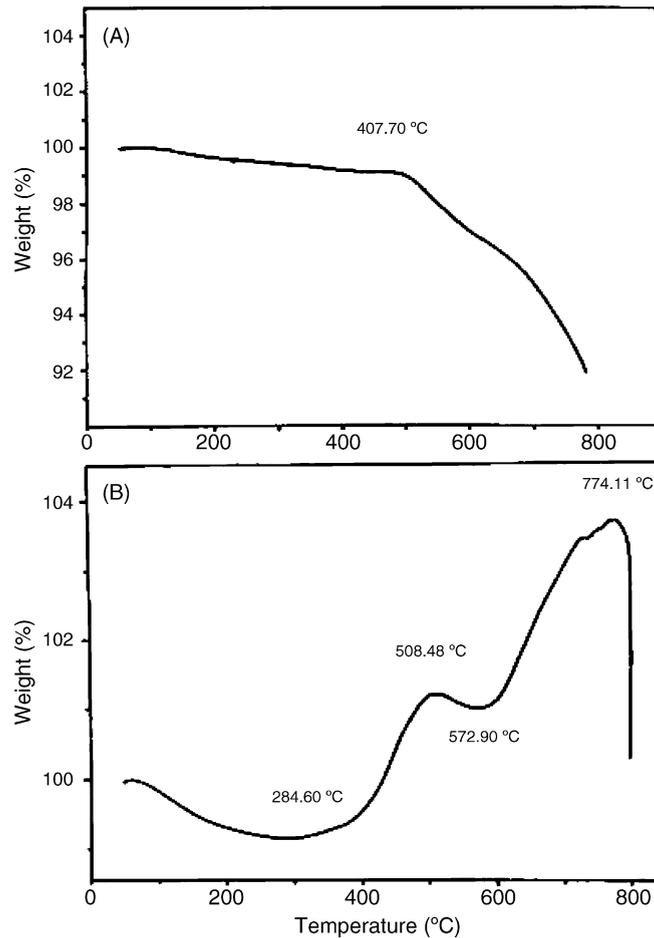


Fig. 1. TG curves of amorphous $\text{Ni}_3(\text{SbTe}_3)_2$ in flows of (A) Ar and (B) air.

phase, which was identified by XRD as shown in Fig. 4(B). Fig. 5(D) presents the SEM photograph of the sample treated at 600 °C, showing a microcrystallite, which was found to be NiTeO_3 by EDAX analysis.

The electrical conductivity of amorphous $\text{Ni}_3(\text{SbTe}_3)_2$ was measured with increasing the temperature at a heating rate of 5 °C/min in the range of 25–800 °C in air. Fig. 6 shows the plot of log conductivity versus temperature (°C), in

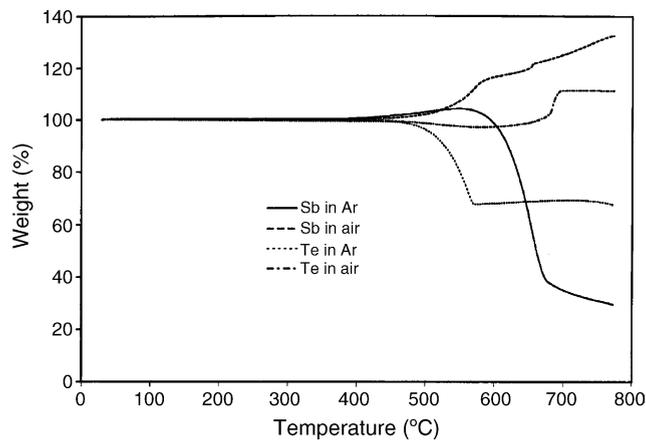


Fig. 2. TG curves of Sb and Te in flows of Ar and air.

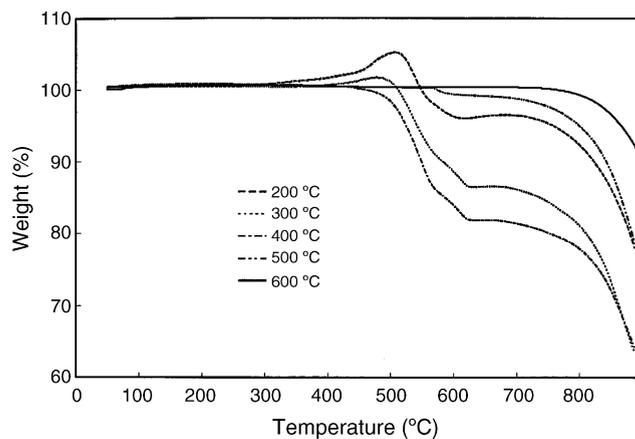


Fig. 3. TG curves of $\text{Ni}_3(\text{SbTe}_3)_2$ treated at various temperatures in air for 1 h.

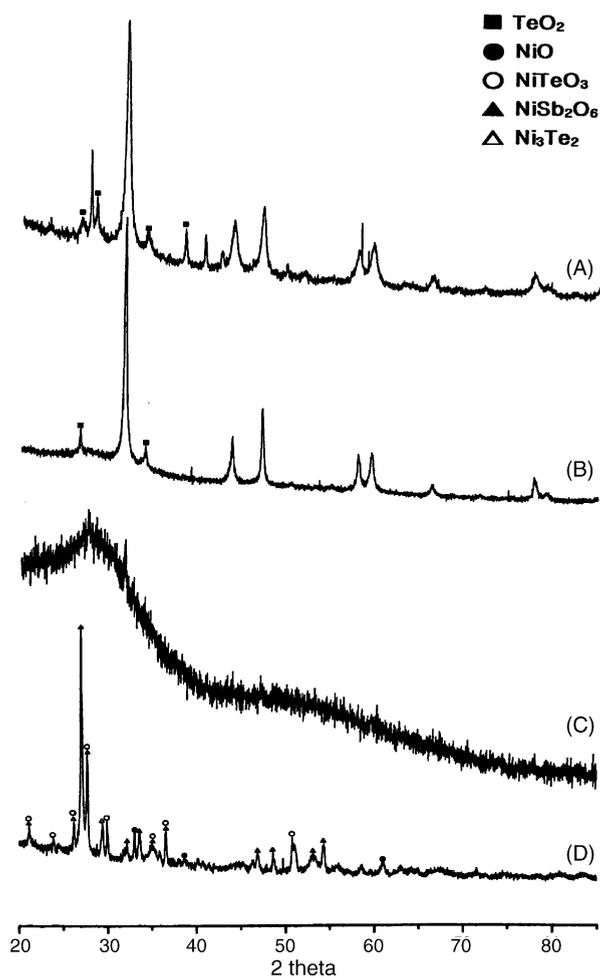


Fig. 4. X-ray diffraction patterns of $\text{Ni}_3(\text{SbTe}_3)_2$ samples treated at (A) 200 °C, (B) 400 °C, (C) 500 °C and (D) 600 °C in air for 1 h.

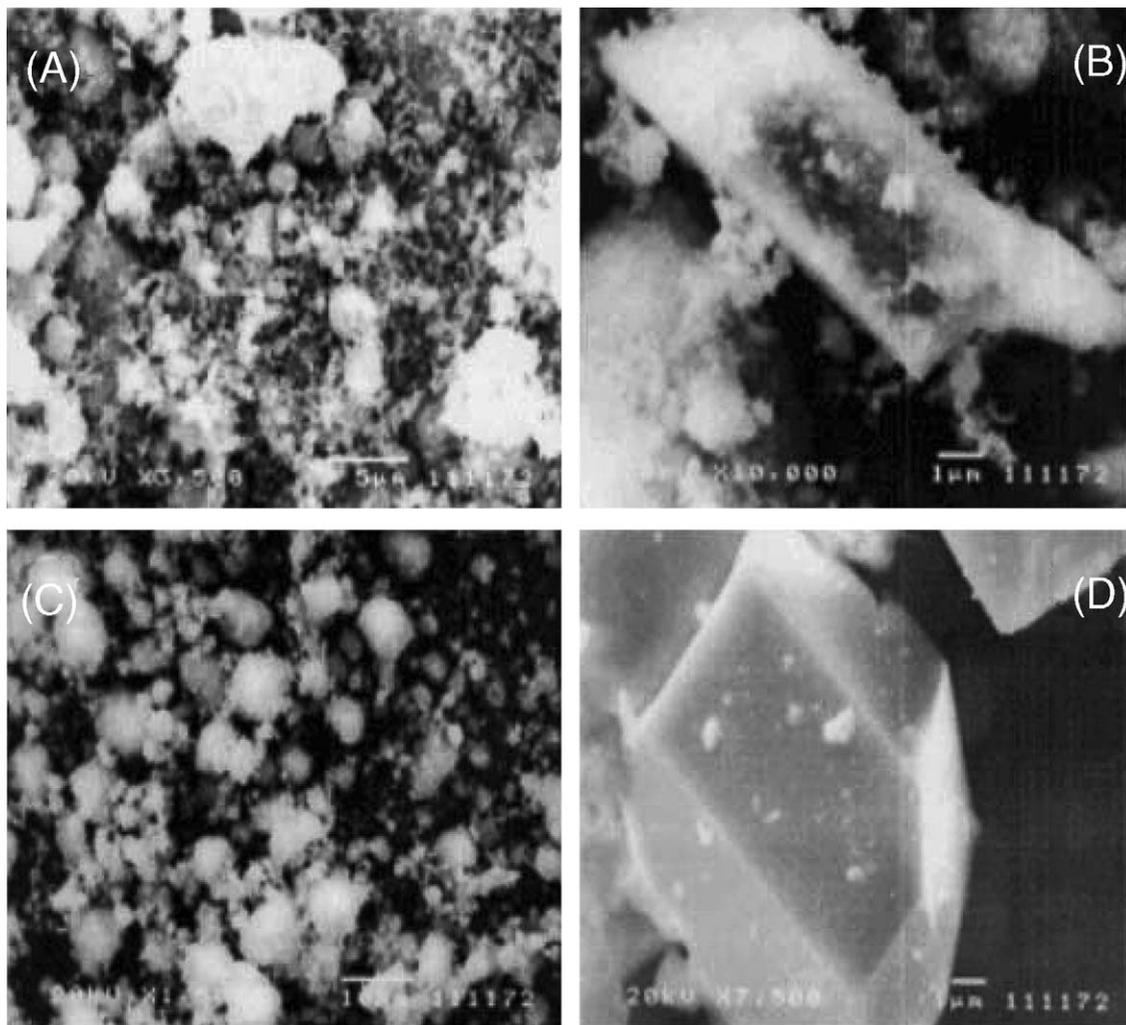


Fig. 5. SEM photographs of (A) $\text{Ni}_3(\text{SbTe}_3)_2$ and $\text{Ni}_3(\text{SbTe}_3)_2$ samples treated at (B) 400 °C, (C) 500 °C and (D) 600 °C in air for 1 h.

which the electrical conductivity decreases with increasing temperature up to 585 °C, while above 585 °C the electrical conductivity increases with increasing temperature. The result indicates the electrical conductivity of the specimen to be changed from a metallic conducting-like behavior to a semiconducting-like behavior at 585 °C. According to the TG data in Fig. 1(B), a small weight gain is observed in the temperature range of 285–400 °C, indicating the oxidation of the specimen to begin at 285 °C. The weight is steeply increased in the temperature range of 400–508 °C. Considered the electrical conductivity data in conjunction with the TG result, in the temperature range of 400–585 °C the specimen seems to be decomposed and simultaneously oxidized to form a mixture, which is amorphous as shown in the XRD result of Fig. 4(C).

In general, metal tellurides are known to be readily oxygenated in the presence of gaseous oxygen and the present result is similar to those for other metal tellurides [10,13,14]. According to the study on the oxidation of nickel tellurium compounds [15], NiO is produced in the first stage of oxidation, various nickel tellurium oxides are slowly formed above 450 °C, and the metal oxides decompose above 900 °C, leaving NiO as the final solid product. However, the present samples treated at 200, 300 and 400 °C revealed the existence of TeO_2 phase and NiO phase was not observed as shown in Fig. 4. Namely, TeO_2 phase is formed in the first stage of oxidation of $\text{Ni}_3(\text{SbTe}_3)_2$ according to the reaction: $\text{Ni}_3\text{Sb}_2\text{Te}_6 + x\text{O}_2 \rightarrow x\text{TeO}_2 + \text{Ni}_3\text{Sb}_2\text{Te}_{6-x}$. The sample treated at 600 °C did not show the presence of TeO_2 phase, but showed the presence of NiO phase as in Fig. 4(C).

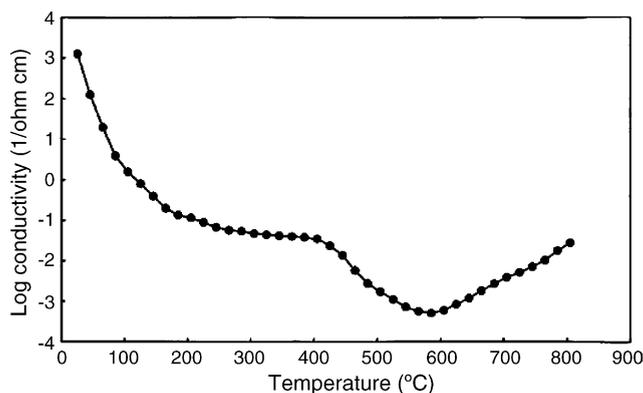


Fig. 6. Electrical conductivity of $\text{Ni}_3(\text{SbTe}_3)_2$ as a function of temperature in the temperature range of 25–800 °C at atmospheric pressure.

The TG curve in Fig. 1(B) indicates that the sample is largely oxidized in the temperature range of 573–774 °C. The XRD result of the sample treated at 600 °C exhibits the presence of NiO, NiTeO₃ and NiSb₂O₆ phases as shown in Fig. 4(D). The NiTeO₃ can be formed by the reaction of NiO and TeO₂: $\text{NiO} + \text{TeO}_2 \rightarrow \text{NiTeO}_3$. A small weight loss (about 0.2%) in the temperature range of 508–573 °C seems to be due to the decomposition of some TeO₂ uncombined with nickel oxide. The presence of NiSb₂O₆ suggests that some NiO reacts with Sb₂O₅ to form NiSb₂O₆ above 600 °C: $\text{NiO} + \text{Sb}_2\text{O}_5 \rightarrow \text{NiSb}_2\text{O}_6$. On the other hand, the XRD pattern of the sample treated at 700 °C showed the existence of NiTe₂O₅ as well as NiO, NiTeO₃ and NiSb₂O₆ phases, suggesting that NiTeO₃ can be further reacted with TeO₂ to form NiTe₂O₅: $\text{NiTeO}_3 + \text{TeO}_2 \rightarrow \text{NiTe}_2\text{O}_5$. According to the TG data in Fig. 1(B), a large weight loss begins at 774 °C, which is believed to be due to the decomposition of NiTeO₃ and NiTe₂O₅. Namely, the nickel tellurium oxides are considered to be decomposed into TeO₂ and NiO above 774 °C. The TeO₂ can be subsequently decomposed, resulted in a rapid weight loss as shown in Fig. 1(B).

As shown in Fig. 6, a semiconducting-like behavior above 585 °C may originate from metal oxide networks, such as NiO, NiTeO₃, NiSb₂O₆ and NiTe₂O₅. The activation energy calculated from the slope of \ln conductivity versus $1000/T$ plot in the temperature range of 700–800 °C was about 0.9 eV and this value is in the range of 0.78–1.07 eV measured by other investigators for NiO [16], which enables us to consider that the semiconducting behavior above 585 °C arises from NiO phase. The XRD signal intensity of NiO for the sample treated at 700 °C was stronger than that for the sample treated at 600 °C, while the XRD signal intensity of NiTeO₃ for the sample treated at 700 °C was less than that for the sample treated at 600 °C. The result suggests that some NiTeO₃ is decomposed at higher temperatures, leaving NiO on the surface. When NiO particles are either making contact among themselves or are separated by very small gaps, the charge carriers can migrate from one aggregate to a neighboring one through hopping.

Consequently, in the oxidation of $\text{Ni}_3(\text{SbTe}_3)_2$, TeO₂ phase is formed as a first oxidation step below 500 °C, NiO is formed above 500 °C, then some NiO reacts with TeO₂ to form NiTeO₃, and NiSb₂O₆ is simultaneously formed with the formation of NiTeO₃. Above 700 °C, NiTeO₃ further reacts with TeO₂ to form NiTe₂O₅. Both NiTeO₃ and NiTe₂O₅ are decomposed above 774 °C, leaving NiO on the sample as the final product.

Acknowledgement

This paper was supported by Konkuk University in 2003.

References

- [1] R.C. Haushalter, C.J. O'Connor, J.P. Haushalter, A.M. Umarji, G.K. Shenoy, *Angew. Chem.* 97 (1984) 147.
- [2] R.C. Haushalter, C.J. O'Connor, A.M. Umarji, G.K. Shenoy, C.K. Saw, *Solid State Commun.* 49 (1984) 929.
- [3] C.J. O'Connor, J.F. Noonan, *J. Phys. Chem. Solids* 48 (1987) 303.
- [4] J.W. Foise, R.C. Haushalter, C.J. O'Connor, *Solid State Commun.* 63 (1987) 349.
- [5] J.H. Zhang, A.J. van Duynveldt, J.A. Mydosh, J.W. Foise, J. O'Connor, *Inorg. Chim. Acta* 162 (1989) 5.
- [6] J.-S. Jung, L. Ren, C.J. O'Connor, *J. Mater. Chem.* 2 (1992) 829.

- [7] A. Yokohama, H. Komiyama, H. Inoue, T. Masumoto, H. Kimura, *J. Catal.* 68 (1981) 355.
- [8] H. Habazaki, M. Yamasaki, B.-P. Zhang, A. Kawashima, S. Kohno, T. Takai, K. Hashimoto, *Appl. Catal. A* 172 (1998) 131.
- [9] G. Kisfaludi, K. Lazar, Z. Schay, L. Guzzi, Cs. Fetzter, A. Lovas, G. Konczos, *Appl. Surf. Sci.* 24 (1985) 225.
- [10] J.I. Kong, J.-S. Jung, J.-G. Choi, S.H. Lee, *Appl. Catal. A* 204 (2000) 241.
- [11] S.H. Lee, J.-S. Jung, J.-U. Joo, N.-S. Myung, J.H. Jun, J.-G. Choi, *Appl. Catal. A* 237 (2002) 91.
- [12] B.V.R. Chowdari, P. Pramoda Kumari, *J. Phys. Chem. Solids* 58 (1997) 515.
- [13] P. Arun, A.G. Vedeshwar, *Mater. Res. Bull.* 34 (1999) 203.
- [14] S.B. Elvy, P.A. Williams, A.N. Buckley, *Surf. Interface Anal.* 24 (1996) 641.
- [15] J.G. Desmaison, M. Billy, W.W. Smeltzer, in: J. Wood, O. Lindqvist, C. Helgesson, N.-G. Vannerberg (Eds.), *Reactivity of Solids*, Plenum Press, New York, 1977.
- [16] J.D. Mackenzie, in: N.M. Tallan (Ed.), *Electrical Conductivity in Ceramics and Glass*, Marcel Dekker, New York, 1983 (Chapter 8).