The Preparation of Blue $CoAl_2O_4$ Powders by the Malonate Method: The Effect of the Amount of Malonic Acid Used, the Formation Pathway of $CoAl_2O_4$ Crystallites and the Characteristics of the Prepared Powders

Gong Yeol Lee, Kwang Hyun Ryu,[†] Hong Gun Kim,[‡] and Yoo Young Kim[§,*]

Korea Testing and Research Institute, Jeonju, Jeonbuk 561-481, Korea
[†]EN Chem, Goyang, Gyeonggi 410-314, Korea
[‡]Department of Mechanical and Automotive Engineering, Jeonju University, Jeonju, Jeonbuk 560-759, Korea
[§]Department of Nano and Advanced Materials Engineering, Jeonju University, Jeonju, Jeonbuk 560-759, Korea
[*]E-mail: yooykim@jj.ac.kr

A pathway for the formation of normal $CoAl_2O_4$ particles is suggested. The optimal amount of malonic acid was determined, and the characteristics of the obtained powders were investigated. Normal $CoAl_2O_4$ powders were prepared using solutions of malonic acid and metal nitrates. X-ray diffraction, Brunauer-Emmett-Teller (BET) and scanning electron microscope (SEM) measurements, as well as Fourier transform infrared (FTIR) and ultraviolet/visible (UV-Vis) spectroscopy were carried out. Normal $CoAl_2O_4$ crystallites were formed by a solid state reaction between Co_2AlO_4 and amorphous aluminum oxide. The optimal molar ratio of malonic acid to the nitrate anions present in the initial solution was found to be 0.30~0.35. The particles were composed of agglomerates of primary particles. The primary particles were 40 nm in size. This size was relatively constant regardless of the preparation temperature. However, the size of the agglomerated particles increased to 220 nm with increasing temperature.

Key Words: Normal $CoAl_2O_4$, Powder, Preparation, Malonic acid

Introduction

Normal cobalt aluminate ($CoAl_2O_4$) with a blue coloration plays an important role in many fields such as catalysts,[1,2] sensors[3] and pigments.[4] A variety of techniques are used to prepare $CoAl_2O_4$.[5-9] Combustion is one method of producing metal oxide by burning a fuel. The nitrate anion and citric acid of the organic acids are mainly used as the oxidant and a fuel, respectively.[6,7]

With combustion techniques, it is easy to prepare the precursor solution but the combustion process occurs violently and can be quite dangerous. Therefore, milder conditions are needed when preparing a metal oxide powder. In this aspect, it may be favorable to use malonic acid as a fuel for preparing normal $CoAl_2O_4$ powder.

The difference between the citrate method and the malonate method is as follows. The powder by the citrate method is generated by thermally decomposing a sol, whereas the powder by the malonate method is produced by a solidified precursor formed with the evaporation of water. The formation of a solidified precursor can lead to inhomogeneity in the distribution of the metal ions because the solubility of salts is different. Therefore, the amount of malonic acid affects the distribution of metal ions in the solidified precursor. Indeed, from the experimental results from this study, the contents of normal $CoAl_2O_4$ crystallites in the prepared powders differed according to the amount of malonic acid used. Therefore, the optimal amount of malonic acid in the production of metal oxide powder by the malonate method needs to be determined.

Crystallites of blue $CoAl_2O_4$ are generated at temperatures above 800 °C.[6] The oxide phases present in the powder obtained at less than 800 °C are cobalt oxide (Co_3O_4), cobalt cobalto-aluminate (Co_2AlO_4) and/or aluminum oxide (Al_2O_3). $CoAl_2O_4$ crystallites are formed by a solid state reaction between Co_3O_4 and Al_2O_3, and/or between Co_2AlO_4 and Al_2O_3. Therefore, the formation of Co_3O_4 and Co_2AlO_4 with the combustion of a solidified precursor leads to increase in the preparation temperature of blue $CoAl_2O_4$.

For the preparation of blue $CoAl_2O_4$ by the combustion technique, the combustion heat should be above 800 °C. as mentioned above. Cobalt malonate and aluminum nitrate decompose completely at 360[10] and 500 °C.[11] respectively. As the decomposition of the malonate anion in air is exothermic, the heat emitted by the combustion of the malonate might contribute to the formation of blue $CoAl_2O_4$. Therefore, it is essential to determine the formation pathway of $CoAl_2O_4$, in order to prepare the $CoAl_2O_4$ crystallites at lower temperatures using the malonte method.

In this study, powder X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and scanning electrom microscopy (SEM), and Fourier transform infrared (FTIR) and ultraviolet/visible (UV-Vis) spectroscopy were used to determine the optimal amount of malonic acid for the preparation of normal $CoAl_2O_4$ powder. In addition, the formation pathway of the $CoAl_2O_4$ crystallites was suggested, and the characteristics of the obtained powders were investigated.

Experimental

Preparation of sample powders. The N-CAO samples were prepared as followed. 0.05 moles of cobalt nitrate (Junsei, Japan) and a predetermined amount of malonic acid ($HOOCCH_2$

COOH: Junsei, Japan) according to the R value were dissolved in a solution containing 0.1 moles of aluminum nitrate (Samchun, Korea) in 20 g of distilled water. R is the malonic acid to nitrate molar ratio and ranged from 0.25 to 0.40. The solution was heated for 4 h at 350 °C and the obtained powder was heated to 700 °C. The resulting powder was ball-milled for 12 h with distilled water at room temperature and filtered. The filtered powder was dried for 24 h at 100 °C. The dried powder was roughly ground and heated for 12 and 4 h at 1000 and 1250 °C, respectively.

The C-CAO samples were obtained from the solutions used to dissolve a stoichiometric amount of basic cobalt carbonate (Samchun, Korea) and a predetermined amount of malonic acid in the aluminum nitrate solution. In order to eliminate carbon dioxide, the solutions containing the three compounds were left to stand for 24 h at room temperature. The forward processes were the same as the abovementioned processes.

Characterization of samples. The obtained samples were examined by X-ray powder diffraction using a MAC Science MXP[3] system equipped with a copper target (0.15418 nm). X-ray tube voltage and current were 40 kV and 10 mA. respectively. The diffraction patterns were recorded in the 28~70° range with a step-size of $2\theta = 0.05°$ and 0.5 sec/step. The area and intensity of the diffraction peak, which was recorded with a step-size of $2\theta = 0.006°$ and 0.5 sec/step, were obtained using the software included with the diffractometer. A constant mass was used in order to ignore the mass effect.

The FTIR spectra were obtained in air at room temperature over the range 400-2100 cm^{-1} using KBr disks on a JASCO FT/IR 5300 spectrometer. The resolution was 2 cm^{-1}. The UV-VIS spectra (Varian Cary 500 Scan spectrophotometer) were acquired using the diffuse reflectance technique in order to examine the local structure of Co^{2+} cation.

The surface areas of the samples were obtained using the BET technique on a Quantachrome Autosorb-1. The samples were degassed at 250 °C for 6 h. The SEM images were recorded on a Jeol JSM-840A instrument after coating the samples with platinum.

Results and Discussion

Determination of the suitable amount of malonic acid. Figure 1 shows the XRD patterns of the N-CAO samples obtained at 1250 °C. Although each pattern shows the characteristic peaks of the spinel structure, it cannot be concluded they are from the normal CoAl$_2$O$_4$ phase. This is because Co$_3$O$_4$ and Co$_2$AlO$_4$ have a spinel structure. Fortunately, the lattice parameter of CoAl$_2$O$_4$ (0.8104 nm, JCPDS 44-0160) is larger than those of Co$_3$O$_4$ (0.8084 nm, JCPDS 42-1476) and Co$_2$AlO$_4$ (0.8086 nm, JCPDS 38-0814). Based on the difference in lattice parameter between CoAl$_2$O$_4$ and Co$_2$AlO$_4$, the 2θ difference in the (440) peak between two compounds was 0.16° 2θ. The two peaks could be resolved (Fig. 2). The (440) peak due to the Co$_3$O$_4$ or Co$_2$AlO$_4$ phase was observed in the diffraction pattern of the N-CAO sample with R = 0.40. However, although not indicated in the patterns of the other samples, the contents of normal CoAl$_2$O$_4$ crystallites were different.

In general, the intensity and area of a spectroscopic peak

reflects the concentration of the substance responsible. Figure 3 shows the (311) peaks, the maximum peaks, of the N-CAO samples obtained at 1250 °C. The (311) peak of the N-CAO
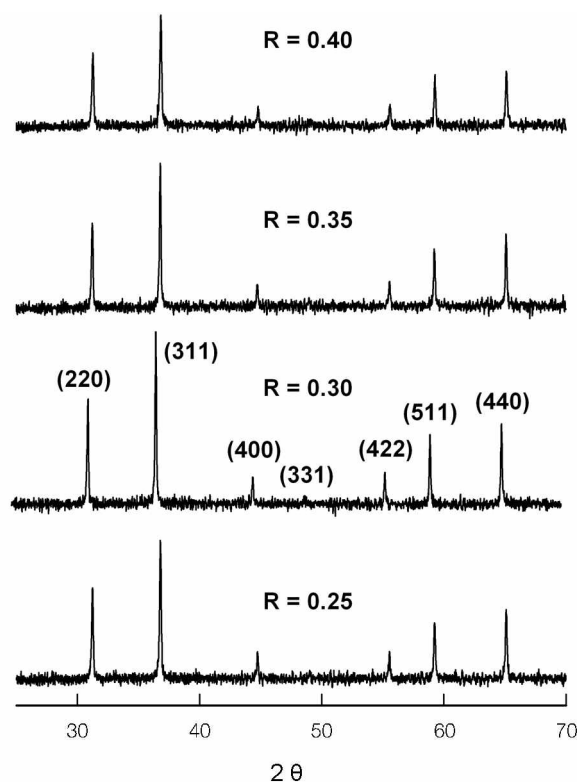

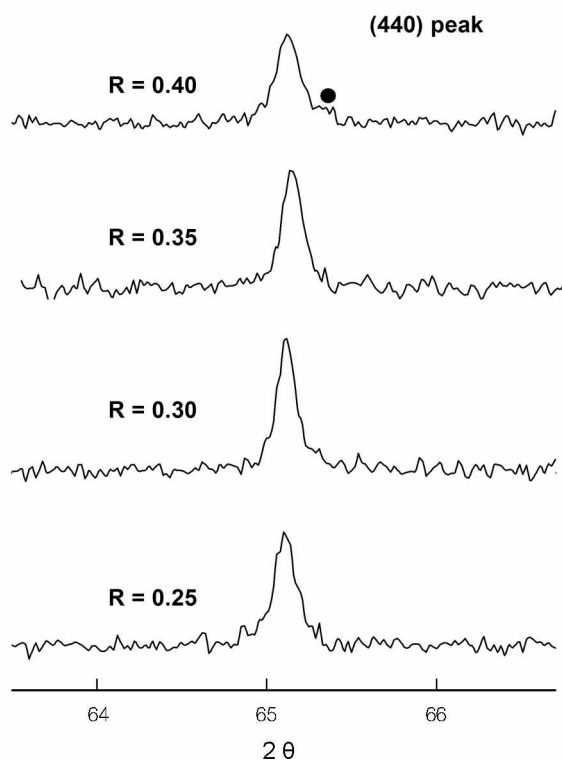**Figure 1.** XRD patterns of the N-CAO samples obtained at 1250 °C.

Figure 2. The (440) peaks of the N-CAO samples obtained at 1250 °C. The dot (●) represents the impurity phase.

The Preparation of Blue CoAl₂O₄ Powders by the Malonate Method

Bull. Korean Chem. Soc. **2009**. Vol. 30, No. 2   375

sample with $R = 0.30$ showed the highest intensity and widest area. The ratios of the intensities and areas of the other peaks were calculated based on the intensity and area of this peak. Figure 4 shows the calculation results. The N-CAO and the C-CAO series have a maximum at $R = 0.30$ and 0.35, respectively. This suggests that the optimal amount of malonic acid corresponds to a R value ranging from 0.30 to 0.35, and also suggests that the presence of an amorphous phase in all of samples except the N-CAO sample obtained at 1250 °C with $R = 0.30$. Identification of the amorphous substance will help determine the pathway for the formation of $CoAl_2O_4$.

Formation pathway of $CoAl_2O_4$. Figure 5 shows the XRD patterns of the N-CAO samples obtained at 1250, 1000 and 700 °C from a solution with $R = 0.30$. The three patterns contain the characteristic peaks of the spinel structure. However, the spectroscopic characteristics of the N-CAO sample obtained at 700 °C were clearly different from those of the other two samples.

Figures 6 and 7 show the FTIR and UV-Vis reflectance spectra of the above three samples, respectively. The FTIR spectra in Figure 6(a) and (b) show the characteristic bands due to normal $CoAl_2O_4$ at below 800 cm^{-1}.[6,8] The absorption band at 666 cm^{-1} was assigned to the Al-O stretching vibration of the AlO_6 octahedra and the bands at 511 and 556 cm^{-1} were attributed to the Co-O stretching vibration of the CoO_4 tetra-

hedra.[12] However, the characteristic bands for $CoAl_2O_4$ were not observed in the FTIR spectrum of Fig 6(c).

Figure 7(a) and (b) show three absorption bands in the UV-Vis reflectance spectra due to spin-allowed transitions of Co^{2+} ions in tetrahedral or octahedral coordination[6] at 500~700 nm, whereas the spectrum in Fig. 7(c) does not show these bands. The major phase in the sample obtained at 1000 °C was normal $CoAl_2O_4$ whereas, from Fig. 5, the sample prepared at 700 °C contained the Co_3O_4 and/or Co_2AlO_4 crystallites as the major phase. Therefore, the amorphous material is a polymorph of aluminum oxide. The main problem is which compound the peaks in the diffraction pattern of the sample at 700 °C refer to.

The sample obtained at 700 °C had a slightly dark green color. The coloration of a mixture of black Co_3O_4 with white Al_2O_3 is grey. If the sample at 700 °C contains a mixture of Co_3O_4 and Al_2O_3, the content of the normal $CoAl_2O_4$ crystallites in a sample obtained from it at 1000 °C would be very small. The $CoAl_2O_4$ crystallites by a solid state reaction of the parent oxides are produced at above 1200 °C. As a result, the

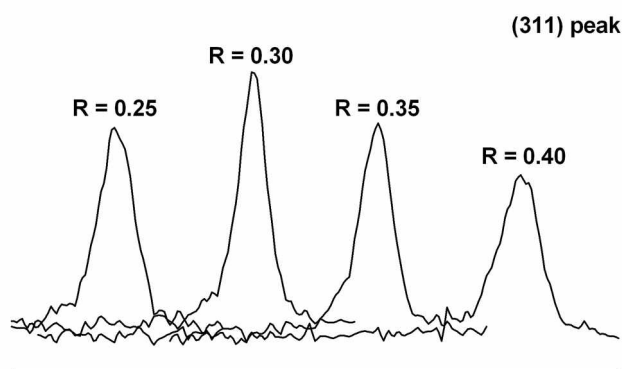**Figure 5.** XRD patterns of the N-CAO samples obtained at 1250, 1000 and 700 °C from the solution with $R = 0.30$.

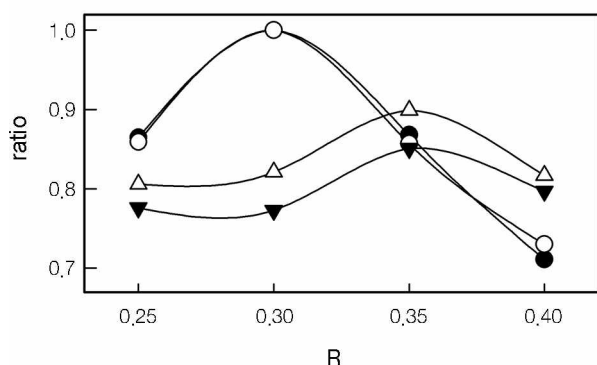**Figure 3.** The (311) peaks of the N-CAO samples obtained at 1250 °C.

Figure 4. The calculated ratios of the intensity and area for the (311) peaks based on the intensity and area of the (311) peak of the N-CAO sample with $R = 0.30$. The circle and the triangle represent the N-CAO and the C-CAO samples, respectively. The open and the filled symbols represent the intensity and the area ratios, respectively.
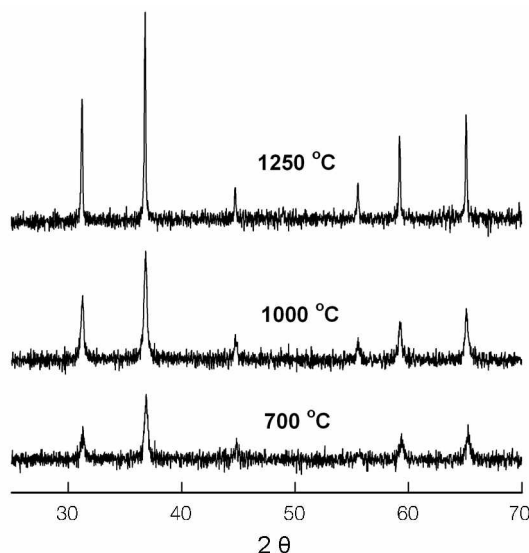

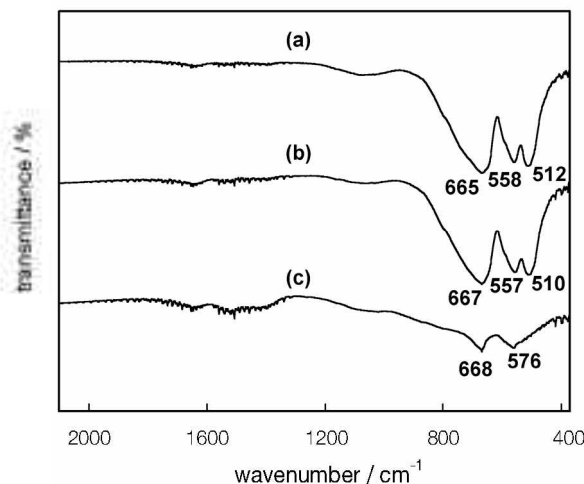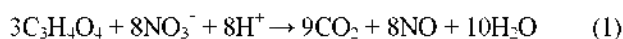**Figure 6.** FTIR spectra of the N-CAO samples obtained at 1250 (a), 1000 (b) and 700 (c) °C from the solution with $R = 0.30$.

CoAl₂O₄ crystallites in this study were formed by a solid state reaction from a mixture of Co₂AlO₄ and amorphous Al₂O₃ at high preparation temperature.

Effect of the amount of malonic acid used on the obtained powder. CoAl₂O₄ crystallites are generated from a mixture of Co₂AlO₄ crystallites and amorphous Al₂O₃, as mentioned above. One of two Co ions in a single formular unit of Co₂AlO₄ has a trivalent state. This Co ion needs to be reduced to the divalent state to form normal CoAl₂O₄. The combustion of malonic acid becomes more reductive with increasing amounts. Nevertheless, the change of the content of CoAl₂O₄ crystallites in the final product does not follow this trend. (Refer to Fig. 4.)

An increase in the amount of malonic acid leads to the formation of its Co salts. The produced salts will be isolated in a solidified precursor. The isolated salts form Co₃O₄ crystallites by the intramolecular decomposition.[13] Therefore, the normal CoAl₂O₄ powder prepared at lower temperature contains the parent oxides as the impurity. This claim is supported by the results for the C-CAO samples from Fig. 4. Most of malonic acid added to the initial solutions of the C-CAO series was present as malonate and hydrogenmalonate anions. The content of CoAl₂O₄ crystallites in the N-CAO sample with R = 0.30 was smaller than that in the C-CAO sample with R = 0.35.

On the other hand, a decrease in the amount of malonic acid promotes a more oxidative atmosphere. As a matter of course, the formation of Co₃O₄ crystallites is easier. Therefore, there is an optimal R value; 0.30~0.35. This is because the nitrate (NO₃⁻) anion reduces to nitrogen oxide (NO) or nitrogen dioxide (NO₂). All the NO₃⁻ anions present in the initial solution are reduced completely to nitrogen oxide or nitrogen dioxide at a malonic acid to NO₃⁻ molar ratio of 0.375 or 0.125 according to the respective equations below:

$$3C_3H_4O_4 + 8NO_3^- + 8H^+ \rightarrow 9CO_2 + 8NO + 10H_2O \tag{1}$$

$$C_3H_4O_4 + 8NO_3^- + 8H^- \rightarrow 3CO_2 + 8NO_2 + 6H_2O \tag{2}$$

Under the condition that R > 0.375, malonic acid may lead to incomplete combustion whereas the parent oxides will
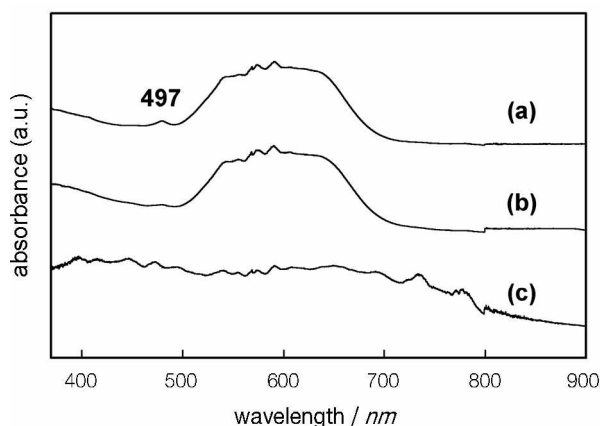
Figure 7. UV-Vis reflectance spectra of the N-CAO samples obtained at 1250 (a), 1000 (b) and 700 (c) °C from the solution with R = 0.30. The band at 497 nm is due to the spin-forbidden transition of Co²⁺ ion.
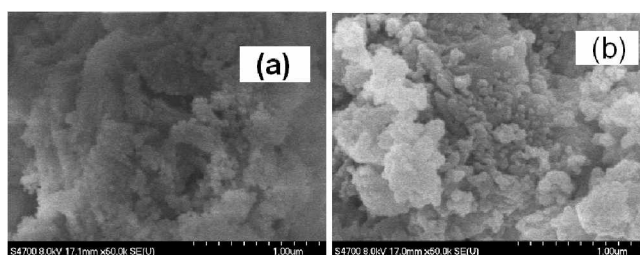
Figure 8. SEM images of the samples obtained at 1000 (a) and 1250 (b) °C from the solution with R = 0.30.

remain in the product when R < 0.125. The nitrate salts produce the oxides. The maximum and minimum limits of R in this study were determined to be < 0.375 and > 0.125, respectively. From experimental observations, a brown NO₂ gas evolved after heating the initial solutions to 350 °C.

Particle size of samples obtained. The specific surface areas of the N-CAO samples with R = 0.30 at 1000 and 1250 °C are 22.8 and 6.27 m²/g. Under the assumption that the particle shape is cubic, the average particle size was calculated to be 59.6 and 217 nm, respectively, using the surface area measured and the theoretical density (4.416 g/cm³) of CoAl₂O₄.

In addition, the average particle size was estimated using the Scherrer equation from the full width at half maximum (FWHM) of the diffracted peak as follows:

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta} \tag{3}$$

where K is a constant (normally equal to 0.89), λ is the wavelength of the incident X-ray radiation (0.15418 nm in this study) and β_{hkl} is the FWHM in radians. The value, θ is half of 2θ, the position of the reflection in radians, from which the β_{hkl} is taken. The FWHM values of the (311) peak for the two samples was 0.21°. The average particle size estimated from this FWHM value by equation (3) was 39.5 nm. This size is smaller than that determined using the BET technique. This suggests that growth occurs through aggregation between the primary particles proceeds with increasing preparation temperature rather than by crystal growth. Figure 8 indicated no grain growth had occurred.

Conclusions

Normal CoAl₂O₄ crystallites were produced by a solid state reaction of Co₂AlO₄ crystallites and amorphous Al₂O₃. The amount of malonic acid used was found to influence the content of CoAl₂O₄ crystallites in the final product. The optimal malonic acid to nitrate molar ratio in the initial solution was found to be 0.30~0.35.

The particles of the sample powders consisted of agglomerates of primary particles. The size of the primary particles was approximately 40 nm and was constant regardless of the preparation temperature. The average size of the agglomerated particles obtained at 1000 °C and 1250 °C was 60 and 220 nm, respectively. Therefore, particle growth proceeded by agglomeration with a rate that increases with increasing temperature rather than by crystal growth.

References

1. Liotta, L. F.; Pantaleo, G.; Di Carlo, G.; Marci, G.; Deganello, G. *Appl. Catal. B* **2004**, *52*, 1.
2. Ji, L.; Tang, S.; Zeng, H. C.; Lin, J.; Tan, K. L. *Appl. Catal. A* **2001**, *207*, 247.
3. Vijaya, J. J.; Kennedy, L. J.; Sekaran, G.; Jevaraj, B.; Nagaraja, K. S. *Sensors and Actuators B* **2007**, *123*, 211.
4. Melo, D. M. A.; Cunha, J. D.; Fernandes, J. D. G.; Bernardi, M. I.; Melo, M. A. F.; Martinelli, A. E. *Mater. Res. Bull.* **2003**, *38*, 1559.
5. Bolt, P. H.; Habraken, F. H. P. M.; Geust, J. W. *J. Solid State Chem.* **1998**, *135*, 59.
6. Zayat, M.; Levy, D. *Chem. Mater.* **2000**, *12*, 2763.
7. Cho, W. S.; Kakihana, M. *J. Alloys and Compounds* **1999**, *287*, 87.
8. Ouahdi, N.; Guillemet, S.; Demai, J. J.; Durand, B.; Er Rakho, L.; Moussa, R.; Samdi, A. *Mater. Lett.* **2005**, *59*, 334.
9. Wang, C.; Bai, X.; Liu, S.; Liu, L. *J. Mater. Sci.* **2004**, *39*, 6191.
10. Ghosh, S.; Ray, S. K.; Ray, P. K.; Banerjee, T. K. *J. Indian Chem. Soc.* **1984**, *61*, 850.
11. Pacewska, B.; Keshr, M. *Thermochim. Acta* **2002**, *385*, 73.
12. Allen, G. C.; Paul, M. *Applied Spectroscopy* **1995**, *49*, 451.
13. Galwey, A. K.; Jamieson, D. M.; Le Van, M.; Berro, C. *Thermochim. Acta* **1974**, *10*, 161.