ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2012, Vol. 57, No. 1, pp. 72–78. © Pleiades Publishing, Ltd., 2012. Original Russian Text © O.I. Gyrdasova, V.N. Krasil'nikov, E.V. Shalaeva, M.V. Kuznetsov, A.P. Tyutyunnik, 2012, published in Zhurnal Neorganicheskoi Khimii, 2012, Vol. 57, No. 1, pp. 78–85.

PHYSICAL METHODS OF INVESTIGATION

Synthesis and Structure of Quasi-One-Dimensional Zinc Oxide Doped with Manganese

O. I. Gyrdasova, V. N. Krasil'nikov, E. V. Shalaeva, M. V. Kuznetsov, and A. P. Tyutyunnik

Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences, ul. Pervomaiskaya 91, Yekaterinburg, 620219 Russia Pacaived December 10, 2010

Received December 10, 2010

Abstract—Nanotubes of manganese-doped zinc oxide $Zn_{1-x}Mn_xO$ ($0 \le x \le 0.2$) were synthesized by heating the $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ precursor in air at 500°C. The precursor with extended crystals was synthesized by a solvothermal method based on heat treatment of a mixture of $Zn_{1-x}Mn_x(HCOO)_2 \cdot 2H_2O$ with an ethylene glycol excess at 100–130°C. The tubular morphology of $Zn_{1-x}Mn_xO$ particles was identified by transmission electron microscopy. Tubular quasi-one-dimensional particles were shown to have a nanodispersed polycrystalline structure, the size of separate crystallites being from 5 to 20 nm. X-ray photoelectron spectroscopy suggested that the manganese distribution on the outer surface layer of $Zn_{1-x}Mn_xO$ nanotubes is nonuniform.

DOI: 10.1134/S0036023612010111

Zinc oxide is a multifunctional semiconductor and, therefore, is in the center of attention of researchers in various fields of science [1-6]. In last years, studies of this oxide have been intensified with the aim of creating sensors, room-temperature ferromagnents, and photocatalysts of oxidation of toxic organic compounds and detoxification of water and air contaminated by pathogenic bacteria, as well as sunlight water splitting cells [7-11]. The photocatalytic properties of ZnO are dictated by its electronic structure, in particular, by the existence of the band gap of appropriate width (3.37 eV) [6]. The photocatalytic activity of ZnO can be enhanced by tailoring its electronic state energies and extending the spectral sensitivity range toward long wavelengths. Such an effect can be achieved, for example, by doping zinc oxide with d metals [12–14]. On the other hand, the $Zn_{1-x}M_xO$ solid solutions (M = Mn, Fe, Co, Ni, Cu) are room-temperature ferromagnets, which allows one to classify them with diluted magnetic semiconductors [15-17]. A task of prime interest is to synthesize low-size doped zinc oxide in the quasi-one-dimensional (1D) state since such structures have a developed effective surface and often exhibit anisotropy of the useful functional properties [18, 19]

The present work was aimed at studying the formation conditions low-size manganese-doped zinc oxide $(Zn_{1-x}Mn_xO)$ with a tubular structure of aggregates, as well as at determining the microstructure of these aggregates. The doped oxide samples were synthesized by an original precursor method in which the precursor was the formate glycolate $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ with needle or fibrous crystals [20].

EXPERIMENTAL

synthesis of the $Zn_{1-x}Mn_x(HCOO)$ The $(OCH_2CH_2O)_{1/2}$ precursor (x = 0 - 0.3) was based on the solvothermal interaction of the $Zn_{1-x}Mn_x$ $(HCOO)_2 \cdot 2H_2O$ formate with excess ethylene glycol, which was thus used simultaneously as a reagent and solvent [20]. For the reasons described below, the synthesis temperature did not exceed 130°C. The resulting formate glycolate crystals were separated from the mother liquor by vacuum filtration, washed with acetone, dried at 50°C for 1 h, and placed for storage into weighing bottles with ground stoppers. The $Zn_{1-x}Mn_x(HCOO)_2 \cdot 2H_2O$ formate used in the synthesis, was prepared by treating a mixtures of stoichiometric amounts of ZnO (special purity grade) and $MnCO_3$ (pure for analysis) with formic acid (pure for analysis).

The phase analysis of the samples was performed on a POLAM S-112 polarization microscope in the transmission mode and by X-ray diffraction. The X-ray powder diffraction patterns were recorded at room temperature on a STADI-P automated diffractometer equipped with mini-PSD (Cu K_{α} radiation, transmission geometry, scan step $\Delta 2\theta = \tilde{0}.02^{\circ}, 2\theta =$ $2^{\circ}-120^{\circ}$). Polycrystalline silicon was used as the internal reference (a = 5.43075(5) Å). Possible impurity phases were identified with the use of the PDF2 ICDD database (Release 2009). Thermogravimetric analysis was carried out on a Q-1500D derivatograph on heating in air at a rate of 10 K/min. The IR spectra of powders were recorded on a Perkin-Elmer Spectrum One spectrophotometer in the range $400-4000 \text{ cm}^{-1}$. The shape and size of particles in the samples were determined by scanning electron microscopy (SEM) on JEM-200CX and Philips-CM30 microscopes. For electron microscopy studies, the powders were dispersed in isobutyl alcohol and as such were applied to a supporting copper grid with deposited carbon coating. The diffraction constant of a microscope was determined on an aluminum film obtained by vacuum thermal deposition onto a NaCl single crystal.

The zinc and manganese in the samples were quantified by atomic adsorption spectroscopy on a Perkin-Elmer instrument and by inductively coupled plasma atomic emission spectroscopy on a JY-48 spectrometer. The BET surface area was estimated by the lowtemperature nitrogen adsorption method on a Micromeritics TriStar 3000 automated analyzer. The chemical composition of the surface and the valence state of manganese in the $Zn_{1-x}Mn_xO$ structure were determined by X-ray photoelectron spectroscopy. Measurements were carried out on a ESCALAB MK spectrometer with nonmonochromatic Mg K_{α} radiation (1253.6 eV). In the course of XPS measurements, the residual pressure was maintained at a level of 10^{-8} Pa. Sample charging due to photoelectron emission was taken into account using the C1s peak of natural hydrocarbon contaminations ($E_{\rm b}$ C1s = 284.5 eV).

RESULTS AND DISCUSSION

The interaction of the $Zn_{1-x}Mn_x(HCOO)_2 \cdot 2H_2O$ formate with ethylene glycol is temperature dependent and occurs in three stages in the temperature range $50-180^{\circ}C$:

$$Zn_{1-x}Mn_{x}(HCOO)_{2} \cdot 2H_{2}O + HOCH_{2}CH_{2}OH \qquad (1)$$

$$= Zn_{1-x}Mn_{x}(HCOO)_{2}(HOCH_{2}CH_{2}OH) + 2H_{2}O\uparrow,$$

$$Zn_{1-x}Mn_{x}(HCOO)_{2}(HOCH_{2}CH_{2}OH)$$

$$= Zn_{1-x}Mn_{x}(HCOO)(OCH_{2}CH_{2}O)_{1/2} \qquad (2)$$

$$+ 1/2 HOCH_{2}CH_{2}OH + HCOOH\uparrow,$$

$$Zn_{1-x}Mn_{x}(HCOO)(OCH_{2}CH_{2}O)_{1/2} + 1/2 HOCH_{2}CH_{2}OH \qquad (3)$$

$$= Zn_{1-x}Mn_{x}(OCH_{2}CH_{2}O) + HCOOH\uparrow.$$

The first step at about 50°C involves the formation of the $Zn_{1-x}Mn_x(HCOO)_2(HOCH_2CH_2OH)$ solvate as a result of substitution of one ethylene glycol molecule for two water molecules in the formate. The crystals of this compound have a platy habit and low birefringence. When heated above 100°C, the solvate is dissolved in ethylene glycol to form a homogeneous solution, and then fibrous or needle-shaped $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ formate glycolate crystals precipitate, which have a pronounced tendency for longitudinal intergrowth with an increase in the degree of substitution of manganese for zinc. It is worth noting that an indispensable condition in the synthesis of $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ is maintenance of a temperature regime since, above



Fig. 1. IR spectra of the (1) $Zn_{0.9}Mn_{0.1}(HCOO)(OCH_2CH_2O)_{1/2}$ formate glycolate and (2) $Zn_{0.9}Mn_{0.1}(OCH_2CH_2O)$ glycolate.

>130°C, $Zn_{1-x}Mn_x(OCH_2CH_2O)$ glycolate crystals form as distorted octahedra.

 $Zn_{1-x}Mn_x$ (HCOO) The IR spectra of $(OCH_2CH_2O)_{1/2}$ samples with x = 0.0, 0.05, 0.10, 0.20,and 0.30 are identical, which is evidence that this compound is a substitutional solid solution with manganese atoms substituted for zinc atoms in the $Zn(HCOO)(OCH_2CH_2O)_{1/2}$ structure. Analogous solid solutions have been obtained on the basis of Fe²⁺, Co²⁺, Ni²⁺, and Cu⁺ cations [20]. The IR spectra of $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ can be represented as a superposition of the HCOO⁻ and $OCH_2CH_2O^{2-}$ anions coordinated to a metal ion. The asymmetric and symmetric vibrations of the carboxyl group (COO) of the formate ion [21] are responsible for two strong absorption bands at 1572 and 1360 $\rm cm^{-1}$, respectively. The C-O bond vibrations in the $OCH_2CH_2O^{2-}$ ion coordinated to zinc and manganese give rise to two strong bands at 1082 and 1041 cm⁻¹, analogous to those observed in the spectrum of liquid ethylene glycol (1087 and 1043 cm^{-1}) [22]. The twisting vibrations of C-C bonds correspond to strong bands at 898 and 870 cm⁻¹ shifted toward higher frequencies from the bands in the spectrum of liquid ethylene glycol (883 and 862 cm^{-1}). Figure 1 shows for comparison the IR spectra of the $Zn_{0.90}Mn_{0.10}(HCOO)(OCH_2CH_2O)_{1/2}$ formate glycolate and $Zn_{0.90}Mn_{0.10}(OCH_2CH_2O)$ glycolate. The major difference between these IR spectra is the



Fig. 3. X-ray powder diffraction patterns of the $Zn_{1-x}Mn_xO$ solid solutions obtained in air at 450°C: (1) x = 0.01, (2) x = 0.1, and (3) x = 0.3.

absence of the bands corresponding to formate ion vibrations in the spectrum of the glycolate; all observed bands correspond to vibrations of the OCH₂CH₂O²⁻ anion and M–O bonds. The absorption bands corresponding to C–O bond vibrations (1070 and 1046 cm⁻¹) are noticeably shifted toward each other as compared with their positions in the spectra of $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ and liquid ethylene glycol. The C–C vibration frequencies are shifted to 898 and 881 cm⁻¹. Thus, the vibrational spectroscopy data are consistent with the notion that $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ and $Zn_{1-x}Mn_x(OCH_2CH_2O)$ are substitutional solid solutions with manganese substitution for zinc in the structures of zinc formate glycolate and zinc glycolate.

The thermal decomposition of $Zn_{1-x}Mn_x(HCOO)$ $(OCH_2CH_2O)_{1/2}$ in air occurs in two steps in the temperature ranges ~270-340 and 340-460°C (Fig. 2), which corresponds to the presence of two types of anions in the structure and to the successive decomposition of the formate and glycolate groups with removal of the decomposition products. The experdetermined weight loss of the imentally $Zn_{0.90}Mn_{0.10}(HCOO)(OCH_2CH_2O)_{1/2}$ sample on heating at a rate of 2.5 K/min to 500° C is 37.94 wt %, which is close to the theoretical weight loss 38 wt % calculated under the assumption that the initial salt converts to the $Zn_{0.90}Mn_{0.10}O$ oxide. The powders of the $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ thermolysis products have large BET surface areas: in particular, it is $38-54 \text{ m}^2/\text{g}$ for the $Zn_{1-x}Mn_xO$ series (x = 0-0.2).

The X-ray powder diffraction patterns of samples obtained by annealing the precursor in air at 500°C points to the formation of $Zn_{1-x}Mn_xO$ solid solutions with a wurtzite structure (Fig. 3). The changes in the unit cell parameters of $Zn_{1-x}Mn_xO$ with an increase in the degree of doping with manganese are presented in the table. According to powder X-ray diffraction, the $Zn_{0.70}Mn_{0.3}$ (HCOO)(OCH₂CH₂O)_{1/2} thermolysis product is not single-phase (table) since its X-ray powder diffraction pattern shows, in addition to the peaks of the $Zn_{1-x}Mn_xO$ solid solution (a = 3.2556 Å, b = 5.241 Å, space group $P6_3mc$), peaks of an impurity phase of the tentative composition $Mn_{3-y}Zn_yO_4$ with a spinel structure (a = 8.373 Å, space group Fd3m).

Figures 4a and 4b show typical SEM images demonstrating the morphology and particle size of the $Zn_{0.9}Mn_{0.1}(HCOO)(OCH_2CH_2O)_{1/2}$ precursor and the product of its thermolysis, the $Zn_{0.9}Mn_{0.1}O$ oxide, exposed to 500°C in air for 2 h. The shape of precursor crystals is inherited by the oxide aggregates; however, these aggregates have a loose structure since they are composed of smaller extended particles, which easily separate from each other upon sonication. According to TEM, these particles are tubes with a cross section on the order of 150 nm. The quasi-one-dimensional tubular structure of $Zn_{1-x}Mn_xO$ samples obtained by thermolysis of $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ is demonstrated by bright-field TEM images (Figs. 5a and 5b), which show a characteristic change in the diffraction contrast along the line of projection of the cross section of a quasi-one-dimensional tubular aggregate (Figs. 5b and 5d). In addition, quasi-onedimensional particles with the tube (or rod)-into-tube morphology were revealed (Figs. 5c and 5d). Electron diffraction patterns obtained for separate quasi-onedimensional particles show a system of continuous Debye rings, which corresponds to a nanodispersed polycrystalline structure of $Zn_{1-x}Mn_xO$, which have no preferable orientation (texture) of crystallites. The sizes of separate $Zn_{1-x}Mn_xO$ crystallites constituting tubular quasi-one-dimensional aggregates were estimated from the dark-field TEM images obtained in the (100)/(002)/(101) diffraction reflections of the

| | $Zn_{1-x}Mn_xO$ | | | |
|---------------------------|-----------------|-----------|-----------|----------|
| Unit cell parameters | x = 0.01 | x = 0.1 | x = 0.3 | |
| | $P6_3mc$ | $P6_3mc$ | $P6_3mc$ | Fd3m |
| a, Å | 3.2497(3) | 3.2501(3) | 3.2556(9) | 8.373(1) |
| <i>c</i> , Å | 5.2082(5) | 5.2102(5) | 5.241(1) | |
| <i>V</i> , Å ³ | 47.633 | 47.663 | 48.107 | 587.007 |
| <i>d</i> , nm | 32.72 | 19.74 | 10.00 | 11.01 |

Unit cell parameters of $Zn_{1-x}Mn_xO$ solid solutions and the size (d) of their crystallites as a function of the degree of doping with manganese

ZnO-ICDD: *a* = 3.249 Å, *c* = 5.206 Å.

wurtzite phase. The size of individual crystallites varies from 5 to 20 nm and, hence, the walls of the tubular quasi-one-dimensional aggregates can consist of one to several crystallite layers.

According to dark-field TEM images, the polycrystalline structure of quasi-one-dimensional oxides is a low-porosity and highly continuous one. This is supported by the fact that well-formed intercrystallite boundaries, including small-angle ones, with off-orientation angles between crystallites of no more than 5° are observed (Fig. 6b, inset). As a result, for most quasi-one-dimensional $Zn_{1-x}Mn_xO$ oxides synthesized by the precursor method in this work, heating under beam (in situ in an electron microscope) is accompanied by recrystalization with grain coarsening and intercrystallite boundary perfection (Fig. 6c) and, often, by destruction of quasi-one-dimensional aggregates into separate crystalline oxide particles.

The nanodispersed polycrystalline structure of quasi-one-dimensional $Zn_{1-x}Mn_xO$ oxide detected by TEM should account for high specific surface area values, which is consistent with those obtained in this work ($S_{sp} \sim 38-54 \text{ m}^2/\text{g}$). Taking into account that the structure of intercrystallite boundaries in quasi-one-dimensional aggregates is of low porosity and that the thickness of the walls in one-dimensional tubular

quasi-one-dimensional oxides are several crystallites, we can state that the high surface areas of the oxide samples should be mainly determined by the developed surface of nanodispersed quasi-one-dimensional aggregates. This conclusion is consistent well with the specific surface areas estimated using the suggested model of the structure of nanodispersed quasi-onedimensional $Zn_{1-x}Mn_xO$ oxides with average crystallite size of 15 nm. A typical TEM image of the quasione-dimensional $Zn_{1-x}Mn_xO$ surface is shown in Fig. 6d. The mechanism of formation of tubular quasi-onedimensional oxides in thermolysis of quasi-onedimensional precursors is currently unknown. We may assume that the formation and growth of oxide crystallites in the course of thermolysis occur in the matrix of the precursor structure, and the tubular morphology is either inherent in the initial precursor state or its intermediate form in thermolysis and is inherited the oxide.

The manganese on the surface of the doped $Zn_{1-x}Mn_xO$ oxide was quantified by means of XPS. The general XPS spectrum of the $Zn_{1-x}Mn_xO$ surface (not shown in this work) shows bands due to Mn, Zn, O, and C electronic states, as well as the peaks of different Auger transitions. To estimate the metal ratio (Mn/Zn) on the $Zn_{1-x}Mn_xO$ surface, it is reasonable to use either the strongest Mn2p and Zn2p lines of



Fig. 4. SEM images of (a) $Zn_{0.9}Mn_{0.1}(HCOO)(OCH_2CH_2O)_{1/2}$ and (b) the product of its thermolysis at 500°C in air.

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 57 No. 1 2012



Fig. 5. (a–c) Bright-field TEM images and microdiffraction patterns (insets) of quasi-one-dimensional $Zn_{1-x}Mn_xO$ oxides: (a, b) with tubular morphology, (c) with tube-into-tube morphology, (d) schematic calculated change in the transmitted radiation along the cross section as a function of the quasi-one-dimensional oxide morphology: (1) tube and (2) tube into tube.



Fig. 6. (a) Electron diffraction pattern and (b, c) dark-field TEM images of individual tubular quasi-one-dimensional $Zn_{1-x}Mn_xO$ structures. (a) The Debye rings were indexed to fit the wurtzite structure. (b) Polycrystalline structure with small-angle intercrystallite boundaries (inset) of initial tubular quasi-one-dimensional $Zn_{1-x}Mn_xO$ oxides; (c) the recrystallized quasi-one-dimensional structure after in situ irradiation in a microscope; (d) bright-field TEM image of the surface of tubular quasi-one-dimensional $Zn_{1-x}Mn_xO$ oxides.



Fig. 7. X-ray photoelectron spectra of core levels (a) Zn2p, (b) Mn2p, (c) Mn3p and Zn3p, and (d) O1s.

these metals or the neighboring Mn3p and Zn3p peaks (Fig. 7). In the first case, the kinetic energy of Mn and Zn photoelectrons is ~600 and ~200 eV, respectively; At such energy, the depth of analysis is limited by 2-3 nm of the surface layer. In the case of manganese and zinc 3pphotoelectrons, the kinetic energy exceeds 1100 eV, and the depth of analysis increases to ~5 nm. The Mn/Zn ratio on the $Zn_{1-x}Mn_xO$ structures estimated from the 2p metal bands is ~3, whereas the estimates made from the 3p manganese and zinc bands give ~1.3. Inasmuch as in the former case, the XPS sensitivity to the surface is higher, we can suggest that (1) the surface layers of the $Zn_{1-x}Mn_xO$ structures are significantly enriched in manganese, and (2) the Mn/Zn ratio on the surface is close to 3. This is consistent with X-ray powder diffraction evidence of the existence of the impurity phase $Mn_{3-\nu}Zn_{\nu}O_{4}$ and can reflect the segregation of spinel to the surface of the $Zn_{1-x}Mn_xO$ fibers. The formation of individual manganese oxide structures, most likely Mn₂O₃ or Mn₃O₄, on the surface also cannot be ruled out. The thickness of the modified layer is a few nanometers. These surface structures are unreliably identified by other methods but can have a significant effect, for example, on the photocatalytic properties of the material.

Figure 7 shows the XPS spectra of the Zn2p and Mn2p core states, the 3p and 3s states of these metals, and O1s of the oxygen of the $Zn_{1-x}Mn_xO$ fiber surface. The O1s spectrum is composed of two bands at 529.4 and 531.7 eV (Fig. 7). The major band at 529.4 eV is due to the oxides: the host $Zn_{1-x}Mn_xO$ structure and the surface layer phases, which we identify as

 $Mn_{3-\nu}Zn_{\nu}O_{4}$ or $Mn_{2}O_{3}$ ($Mn_{3}O_{4}$). For the undoped zinc oxide, the O1s band position was determined at $530.3 \pm 0.3 \text{ eV}$ [23, 24]. It is hardly expectable that the substitution of manganese for some zinc atoms in the ZnO lattice will lead to a significant change in the charge state of oxygen and, hence, to a considerable shift of the O1s bands. Therefore, the binding energy of the O1s level at 529.4 eV for the compound under consideration is most likely due to the surface phases based on manganese oxide. The O1s band in the spectra of MnO, Mn₂O₃, and MnO₂ oxides was reported to be at 529.6 eV for the first two oxides and at 529.9 eV for the last one with the scatter of ± 0.3 eV. The O1s binding energy in the $Mn_{3-\nu}Zn_{\nu}O_4$ cubic spin is unknown; however, it is expected that it will be within 529–530 eV. An extra high-energy component of the OH⁻ spectrum (at 531.7 eV) can be due to either OH groups sorbed on the oxide surface or deficient zinc oxide structures [23]. The Mn2p spectrum can be represented by a $2p_{3/2}$ and $2p_{1/2}$ doublet at 641.3 and 652.8 eV, respectively (Fig. 7). From the viewpoint of the energy position and multiplet spitting, the spectrum corresponds to the Mn²⁺ or Mn³⁺ state. The manganese valence can be determined more accurately from the splitting of the Mn3s states [24]; however, this band is partially overlapped by stronger Zn3p bands and cannot be interpreted correctly.

Thus, our study showed that doped zinc oxide nanotubes can be synthesized by a precursor method. As a rule, the thermolysis of the precursor is a pseudomorphous process; i.e., the particles of the nascent oxide inherit the shape of the precursor crystals. Thermal decomposition of the $Zn_{1-x}Mn_x(HCOO)(OCH_2CH_2O)_{1/2}$ precursor fibers of needles leads to $Zn_{1-x}Mn_xO$ oxide as tubular quasi-one-dimensional aggregates with a nanodispersed polycrystalline structure. A specific feature of these quasi-one-dimensional aggregates is a nonuniform distribution of manganese in their surface layer 2–3 nm thick.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 09-03-00252-a).

REFERENCES

- S. A. Wolf, D. D. Awschalom, R. A. Buhrman, et al., Science 294, 1488 (2001).
- S. Thota, T. Dutta, and J. Kumar, J. Phys.: Condens. Matter 18, 2473 (2006).
- 3. T. Dietl, H. Ohno, F. Matsukura, et al., Science **287**, 1019 (2000).
- 4. P. Sharma, A. Gupta, K. V. Rao, et al., Nat. Mater. 2, 673 (2003).
- 5. W. Yan, Z. Sun, Q. Liu, et al., Appl. Phys. Lett. **90**, 242509 (2007).
- K. Byrappa, A. K. Subramani, S. Ananda, et al., Bull. Mater. Sci. 29, 433 (2006).
- X. Ren, D. Han, D. Chen, and F. Tang, Mater. Res. Bull. 42, 807 (2007).
- A. J. Attia, S. H. Kadhim, and F. H. Hussein, Eur. J. Chem. 5, 219 (2008).

- 9. J. Zheng, Z. -Y. Jiang, Q. Kuang, et al., J. Solid State Chem. **182**, 115 (2009).
- 10. S. Ekambaram, Y. Iikubo, and A. Kudo, J. Alloys Comp. **433**, 237 (2007).
- 11. B. Yang, A. Kumar, N. Upia, et al., J. Raman Spectrosc. 41, 88 (2010).
- 12. S. Lee, D. Y. Kim, and Y. Shon, Appl. Phys. Lett. 89, 022120 (2006).
- 13. K. Wilke and H. D. Breuer, Z. Phys. Chem. 213, 135 (1999).
- 14. C. J. Cong and K. L. Zhang, Phys. Stat. Solidi (B) **243** (12), 2764 (2006).
- 15. A. B. Mahmoud, H. J. von Bardeleben, J. L. Cantin, et al., Phys. Rev. B 74, 115203.
- Q. Xiao, J. Zhang, C. Xiao, and X. Tan, Mater. Sci. Eng. (B) 142, 121 (2007).
- 17. Y. Wang and M. Li, Mater. Lett. 60, 266 (2006).
- J. Xie, P. Li, W. Yanji, and Y. Wei, Phys. Stat. Solidi A 205, 1560 (2008).
- 19. D. Wang, R. Yu, Y. Chen, et al., Solid State Ionics 172, 101 (2004).
- 20. O. I. Gyrdasova, V. N. Krasil'nikov, E. V. Shalaeva, et al., Dokl. Chem. **434** (1), 211 (2010).
- 21. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Interscience, New York, 1986).
- 22. H. Matsuura and T. Miyazawa, Bull. Chem. Soc. Jpn. **40**, 85 (1967).
- 23. M. Chen, X. Wang, Y. H. Yu, et al., Appl. Surf. Sci. **158**, 134 (2000).
- 24. D. Briggs and M. P. Seah, *Practical Surface Analysis* (Wiley, New York, 1993).