

FORMATION OF LANTHANUM HYDROXIDE NANOSTRUCTURES: EFFECT OF NaOH AND KOH SOLVENTS

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Abstract Lanthanum hydroxide (La(OH)₃) nanostructures, including elliptical nanoparticles, octahedral rods and irregular nanoparticles were prepared chemically in NaOH and KOH solutions with 10 M concentration. The obtained powders were characterized with XRD, SEM, TEM and DTA. Crystallinities, morphologies and thermal behavior of the obtained nanostructure powders were investigated under the influence of above mentioned solvents. The effect of chemical's temperature was also determined in one of the solvents (i.e. NaOH). The formation of growth in nanostructure mechanism under the influence of alkali solutions (i.e., KOH and NaOH) have been discussed considerably in this paper.

Keywords Lanthanum Hydroxide, Nanostructure, Chemical Processing

چکیده در این تحقیق نانوساختارهای هیدروکسید لانتانیم (La(OH)₃) به صورت نانوذرات بیضی شکل، میله های هشت وجهی و نانوذرات بی شکل در حضور حلال های NaOH و KOH با غلظت ۱۰ مولار، به صورت شیمیایی بدست آمدند. پودر های بدست آمده توسط آنالیزهای XRD، SEM، TEM و DTA مورد بررسی قرار گرفتند. اثر نوع حلال به کار رفته بر میزان کریستالی شدن، شکل ذرات و رفتار حرارتی پودرهای بدست آمده، مورد ارزیابی قرار گرفت. همچنین در حلال NaOH، اثر دمای فرایند بر نانوساختار پودرها بررسی گردید. مکانیزم پیشنهادی تشکیل این نانوساختارهای یک بعدی تحت اثر دو حلال قلیایی مذکور عنوان گردیده و مورد بحث و بررسی قرار گرفته است.

1. INTRODUCTION

The synthesis and characterization of one-dimensional (1D) nanostructure materials has become one of the most exciting research areas from the time of carbon nanotubes discovery [1-3], due to their novel properties and applications in nanoscience and nanotechnology [4,5].

Various nanoscale materials have been prepared previously among which, rare earth compounds are interesting due to their fascinating catalytic [6], photonic, optoelectronic [7] and magnetic [8]

properties, which originate from their 4f orbital electrons [9]. These materials are promising candidates for up-conversion phosphors (UCPs) [10], catalysts [11] and time resolved fluorescence labels for biological detection [12], which their 1D nanostructures is a step toward the advancement of novel nanoscale devices [13]. Lanthanum hydroxide (La(OH)₃) and oxide (La₂O₃) are rare novel earth compounds which have so far been fabricated with various morphologies such as nanopowders [8,14], nanotubes [13], nanowires [6], nanorods [15,16] and nanobelts [17] from

different methods like solvothermal [18], hydrothermal [19,20], sol-gel [21] and template assisted routes [22]. These compounds have many attractive applications in gas-exhaust convectors [23], optical coatings [24], catalysts [15], superconductors [25], hydrogen storage materials [26] and next generation of high dielectric constant gate dielectrics [27].

Among the various methods developed for the preparation of anisotropic nanostructures, chemical processing routes based on treatment of raw materials in 5-10M NaOH solutions, introduced by Kasuga, et al [28], has initiated many investigations in the preparation of 1D nanostructures such as nanotubes [29] and nanowires [30]. In this investigation, we have utilized the same approach to produce lanthanum hydroxide nanostructures in the presence of NaOH and KOH as solvents. We have also compared the effect of these solvents and the temperature of thermal treatment on crystallinity, morphology and thermal behavior of the obtained materials. To the best of our knowledge, there is no report on comparing the effect of NaOH and KOH on preparation of lanthanum hydroxide nanostructures.

2. EXPERIMENTAL PROCEDURE

All the materials were purchased from Aldrich and used upon arrival. In a typical experiment, 0.3 gr of La_2O_3 powder was added to 30 ml of KOH and NaOH solutions with the following concentrations: (A) 10 M KOH, (B) and (C) 10 M NaOH. The mixtures were called (A) and (B) which were put into Teflon-lined stainless steel autogenous pressure controlled autoclaves without stirring and kept at 200°C for 24 hours. The mixture (C) was kept at room temperature for 24 hours to naturally precipitate. The resultant powders were centrifuged, washed with deionized water and dried at 60°C for 24 hours. The obtained powders were characterized with scanning electron microscope (SEM, Philips XL30), transmission electron microscope equipped with a field emission gun (FEG-TEM, Philips CM200), and powder X-ray diffraction analysis (XRD, Simens D500 diffractometer) in the range of 20°-60° which were plotted after α_2 -stripping. Differential thermal

analysis (DTA/TG, STA 1640) was also carried out to assess the thermal behavior of the obtained products.

3. RESULTS AND DISCUSSIONS

The powders obtained after 24 hours of thermal treatment (samples A and B) and/or room temperature precipitation (sample C), were characterized with powder X-ray diffraction method to determine their phase, crystal structure and crystallinity. From the XRD results (Figure 1), it can be clearly understood that the powders were composed of lanthanum hydroxide ($\text{La}(\text{OH})_3$) phase with hexagonal crystal structure which belongs to $P6_3/m$ (No. 176) space group with cell constants of $a = 6.5286 \text{ \AA}$ and $c = 3.8588 \text{ \AA}$. The peaks were indexed according to the JCPDS card No. 36-1481. There were no peaks observed, which would be attributed to the existence of the impurities in XRD patterns. The intensities of the peaks were stronger when the precursor was treated with KOH (compare Figures 1a and b), which indicated that obtained $\text{La}(\text{OH})_3$ crystallinity were more than when KOH was used for treatment [18]. When the initial precursor was treated with NaOH, increasing the temperature culminated in increasing the crystallinity (compare Figures 1b and c). However, since the broadening of the peaks

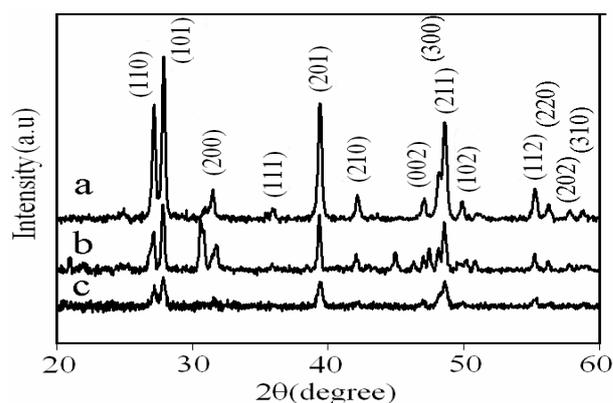
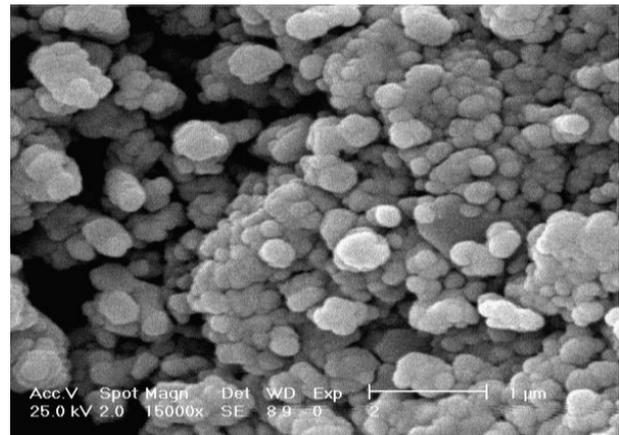


Figure 1. X-ray diffraction patterns of the particles obtained through treatment of La_2O_3 in (a) KOH and (b) NaOH solutions, under hydrothermal conditions and (c) NaOH under room temperature precipitation.

looks the same, it can be concluded that the crystallites should be in the same size. Utilizing Scherrer formula ($d = \frac{0.9\lambda}{B\cos\theta}$, where d , λ , B and θ , are the average crystallite size, Cu- k_{α} wavelength (0.1541 nm), full width at half maximum intensity (FWHM) of (101) peak in radians and Bragg's diffraction angle, respectively), the average crystallite sizes of the powders were calculated to be about 57, 65 and 50 nm for samples A, B and C, respectively. Considering the Scherrer formula errors, there is not any significant difference between the crystallite sizes which is in accordance with the width of the XRD peaks.

Scanning electron microscope images revealed the morphology of the obtained powders (Figure 2). It was obvious that the size and morphology of powders were different according to the utilized solvent and the temperature of thermal treatment. Hydrothermal treatment of the La_2O_3 powder in the presence of KOH, as solvent resulted in the formation of $\text{La}(\text{OH})_3$ nanoparticles with the average diameter of 230 nm (Figure 2a). Octahedral rods with sharp tips and average diameter of 550 nm and an average length of about 1.7 μm (Figure 2b), were obtained with NaOH at 200°C. Comparing Figures 2a and b revealed that KOH seemed not to enhance the one dimensional growth of $\text{La}(\text{OH})_3$ while NaOH clearly acted as a template for its anisotropic growth. The influence of NaOH in promoting the one-dimensional growth of nanostructures such as titania was reported previously [30]. However, according to the SEM images (Figures 2b and c), it can be concluded that there are some other factors such as the temperature of thermal treatment, which also affect the anisotropic growth. This fact can be demonstrated with the following observation that, although sample C was prepared under the influence of NaOH, irregular nanoparticles were the most common shapes observed in the SEM image (Figure 2c) and as a result, increasing the temperature has intensified the templating effect of NaOH in directional growth of $\text{La}(\text{OH})_3$.

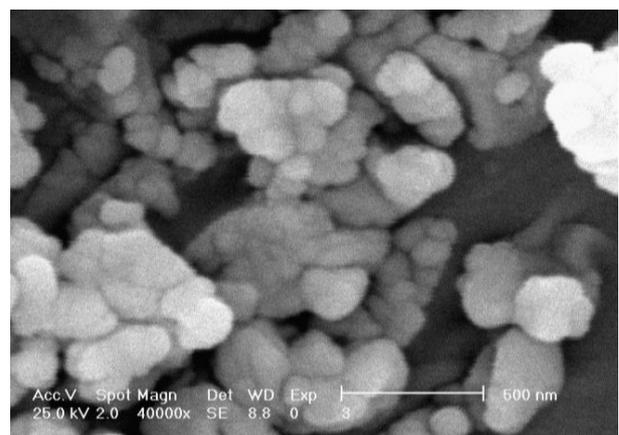
Nanostructures of the synthesized powders were characterized with transmission electron microscope (TEM) observations. Some interesting results were obtained through these investigations. First, unlike SEM images, it was observed that KOH has promoted the directional growth of



(a)



(b)



(c)

Figure 2. SEM images of the obtained $\text{La}(\text{OH})_3$ nanostructure particles, after treatment of La_2O_3 in (a) KOH and (b) NaOH solutions, under hydrothermal conditions and (c) NaOH under room temperature precipitation.

La(OH)₃ nanoparticles to some extent (Figure 3a) and made elliptical nanoparticles with low aspect ratio (~2). Therefore, the nanoparticles observed in SEM image (Figure 2a) can be agglomerations of these low aspect ratio elliptical nanoparticles. The high resolution TEM (HRTEM) image captured from the tip of an elliptical nanoparticle (indicated by a circle in Figure 3a) synthesized with the help of KOH revealed that the spacing between the fringes is about 3.18 Å which is attributed to the d-spacing of (101) crystallographic planes perpendicular to the <101> orientation (Figure 3b). Figure 3c shows nanostructure octahedral rods with an average diameter of about 480 nm and sharp tips, treated with NaOH solution. The SAED pattern (inset of Figure 3c) from the tip of a typical rod exhibits a dotted pattern which indicates the single crystalline nature of the tip of the selected rod. The SAED also shows that the growth direction in octahedral rods is also <101> which is the most dens crystallographic direction in lanthanum hydroxide lattice structure. Figure 3d shows the TEM image of the lanthanum hydroxide nanoparticles with diameter of about 50-130 nm which were obtained under the influence of NaOH at room temperature. The SAED (inset of Figure 3d) indicates the ring patterns attributed to the polycrystalline and nanocrystalline nature of nanoparticles. It can totally be concluded by TEM observations that KOH has more effect on crystallization of the obtained nanostructures and the elliptical nanoparticles have higher crystallinity. This phenomenon is in harmony with the sharpness of XRD peaks (Figure 1). Also it was observed in TEM investigations that both KOH and NaOH have enhanced the anisotropic growth of La(OH)₃ along <101> orientation with lesser influence of KOH solvent.

Based on the results obtained in this work, the directional growth of the nanostructures under the influence of ionic solvents such as KOH and NaOH could occur due to the following mechanism. The ionic solvent dissociate in the solution making free cations (Na⁺ or K⁺) and anions (OH⁻). These experiments have been conducted in the high concentrated alkali conditions, therefore La₂O₃ precursor hydrolyses and La(OH)₄⁻ species form [22] which can attach

to the Na⁺ or K⁺ species present in the solution due to electrostatic interactions and make polar molecular complexes such as Na⁺-La(OH)₄⁻ and K⁺-La(OH)₄⁻. These polar molecular complexes may attach each other directionally (Figure 4) in order to attain equilibrium between attraction and repulsion forces and oriented attachment mechanism [5,31] that can be originated from the inherent characteristic of the hexagonal crystal structure of La(OH)₃ phase [19]. It is clear that the growth rate of different planes in a crystal lattice structure is dependent on their energy. Therefore, the mentioned primary nanocrystals can attach each other and grow, based on the surface energies of their planes. Among all the La(OH)₃ planes, the (101) plane has the lowest energy and therefore the highest growth rate, which culminates in the formation of one-dimensional morphology in the hydrothermal process [26], as clearly observed in TEM investigations.

The above proposed mechanism can easily justify the observed results in this study. The more ionic nature of the NaOH culminates in its more dissociation in aqueous media producing more ionic species specially OH⁻. A higher OH⁻ concentration is more preferable for growth and formation of 1D nanostructures with higher aspect ratios [19]. Also dissociation rate of the solvent depends strongly on the temperature of the treatment, which resulted in obtaining one dimensional structures at elevated temperature. In other words, rising the temperature culminated in increasing the dissociation rate and production of more OH⁻ ions is preferred for one dimensional growth species present in the solution.

Thermal analyses (DTA/TG) were used to determine the effect of the solvents on transformation of La(OH)₃ to LaOOH and La₂O₃ phase. For all three samples, DTA studies indicated two distinct endothermic peaks and one exothermic peak (Figure 5, bold lines). The first peaks occurred at temperatures ~ 350, ~ 343 and ~ 342°C for samples A, B and C, respectively. It was reported previously that the lanthanum hydroxide phase was transformed to the lanthanum oxide hydroxide (LaOOH) phase at temperatures about 330-400°C [25,32-34]. LaOOH is an intermediate phase with monoclinic crystal structure and P2₁/m (No.11) space group, which can be obtained during the dehydration of lanthanum hydroxide to

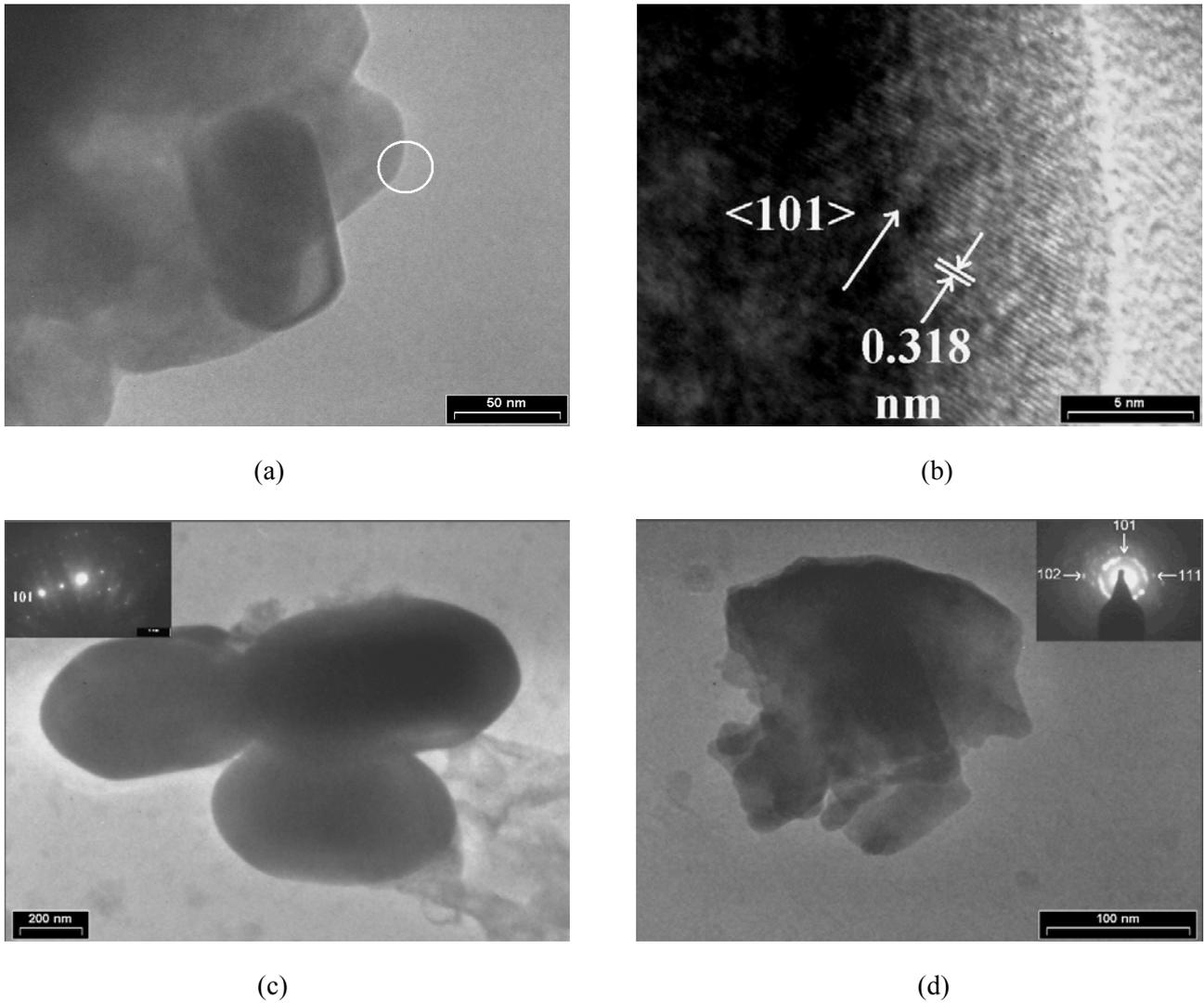


Figure 3. TEM images of (a) $\text{La}(\text{OH})_3$ elliptical nanoparticles, (b) the HRTEM image of the tip of a selected $\text{La}(\text{OH})_3$ elliptical nanoparticle indicated by circle, (c) octahedral $\text{La}(\text{OH})_3$ rods (inset is the SAED pattern of the tip of a selected rod) (d) $\text{La}(\text{OH})_3$ nanoparticles (inset is SAED pattern).

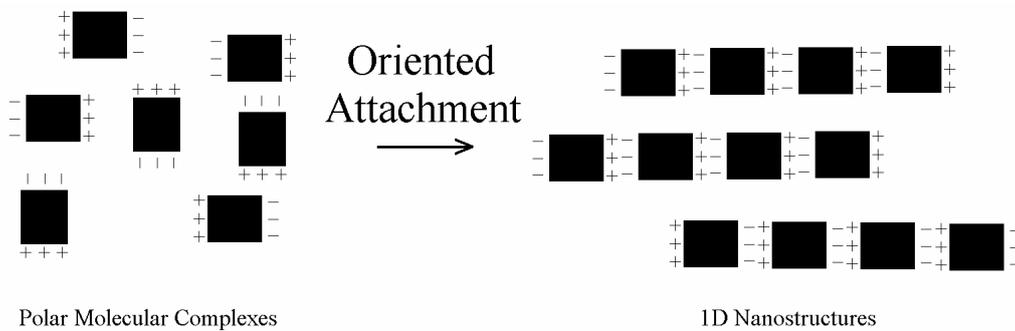


Figure 4. Schematic representation of the proposed mechanism for the formation of 1D $\text{La}(\text{OH})_3$ nanostructures.

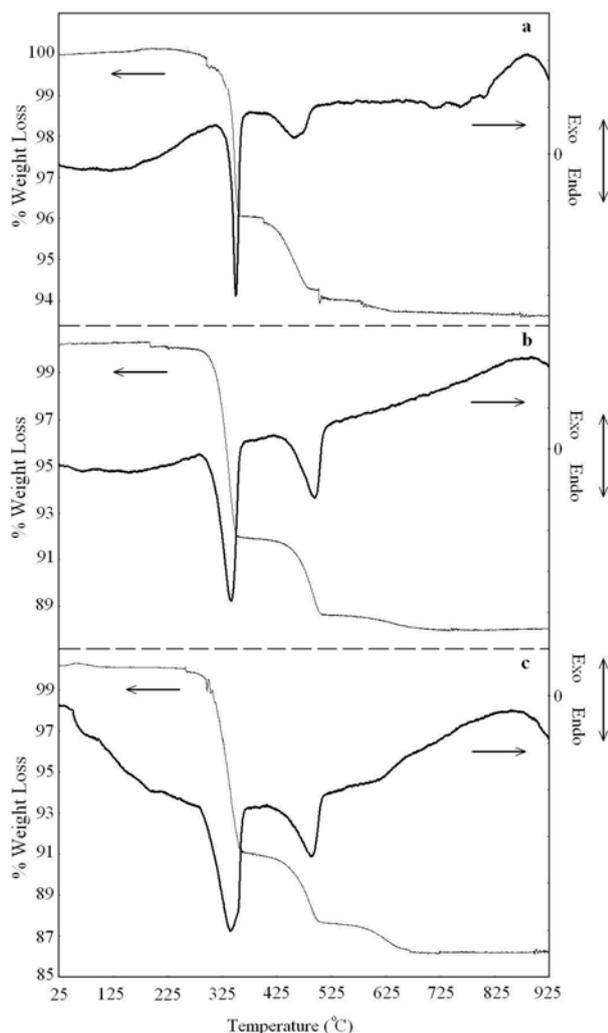


Figure 5. DTA (Bold Lines) and TG curves of the obtained powders after treatment of La_2O_3 in (a) KOH and (b) NaOH solutions, under hydrothermal conditions and (c) NaOH under room temperature precipitation.

lanthanum oxide as follows [18,25]:



It was observed in DTA curves that when the treatment was performed in the presence of NaOH, the onset and the peak temperatures related to the transformation of $\text{La}(\text{OH})_3$ to LaOOH were lower, but the transformation to La_2O_3 occurred at higher temperatures in comparison with $\text{La}(\text{OH})_3$ obtained

in the presence of KOH. This phenomenon suggests that NaOH increased the temperature range for the stability of LaOOH phase in comparison with KOH solvent. The second endothermic peaks which were observed at ~ 460 , ~ 498 and $\sim 492^\circ\text{C}$ (for A, B and C, respectively) are attributed to the LaOOH to La_2O_3 transformation [25]. The third peaks observed between 800 - 900°C can be attributed to the polymorphism of hexagonal (A-type) to cubic (C-type) La_2O_3 phase [35,36]. When the treatments were performed under the influence of NaOH (samples B and C), the general shapes of DTA curves were similar for the phase transformation regions above 300°C . This observation indicates that although the initial chemical treatment temperature affected the crystallinity and morphology of the obtained powders, it did not significantly alter the transformation sequences and phase stability temperature during the decomposition of obtained $\text{La}(\text{OH})_3$ nanostructures to La_2O_3 . Thermogravimetric (TG) analyses (Figure 5, normal lines) exhibit two clear steps of weight loss. The weight loss percentages in the first step which were attributed to the $\text{La}(\text{OH})_3$ to LaOOH transformation, were about 3.74 %, 8.05 % and 8.87 % for A, B and C, respectively and for the second steps (LaOOH to La_2O_3), were ~ 1.66 %, 3.37 % and 3.44 %. As the theoretical values for the weight loss percentages of the mentioned transformations were reported to be about 9.5 % and 4.5 % respectively [25], it can be concluded that KOH has significantly affected the weight loss during above transformations.

4. CONCLUSION

Nanostructure lanthanum hydroxide powders were chemically obtained under the influence of KOH and NaOH as the solvents. It was shown that KOH and NaOH have different influences on crystallinity, morphology and thermal behavior of the obtained $\text{La}(\text{OH})_3$ powders. The powders obtained under the influence of KOH were more crystalline than NaOH-treated materials and had lower particle sizes, weight loss percentages and reduced temperature range for the stability of LaOOH as an intermediate phase during

decomposition of La(OH)₃. Also it was shown that although the temperature of initial thermal treatment altered the crystallinity, particle size and morphology of the obtained powders, seemed not to significantly affect their thermal behavior. The mechanism for the effect of the solvent was proposed based on the formation of polar complexes in the solution and the orientation of their attachment to prepare 1D nanostructures.

5. REFERENCES

- Iijima, S., "Helical Microtubules of Graphitic Carbon", *Nature*, Vol. 354, (1991), 56-58.
- Remskar, M., Mrze, A., Skraba, Z., Jesih, A., Ceh, M., Demšar, J., Stadelmann, P., Lévy, F. and Mihailovic, D., "Self-Assembly of Subnanometer-Diameter Single-Wall MoS₂ Nanotubes", *Science*, Vol. 292, (2001), 479-481.
- Chopra, N. G., Luyken, R. J., Cherrey, K., Crespi, V. H., Cohen, M. L., Louie, S. G. and Zettl, A., "Boron Nitride Nanotubes", *Science*, Vol. 269, (1995), 966-967.
- Reches, M. and Gazit, E., "Casting Metal Nanowires within Discrete Self-Assembled Peptide Nanotubes", *Science*, Vol. 300, (2003), 625-627.
- Alivisatos, A. P., "Biomaterialization: Enhanced: Naturally Aligned Nanocrystals", *Science*, Vol. 289, (2000), 736-737.
- Bocchetta, P., Santamaria, M. and Quarto, F. D., "Template Electrosynthesis of La(OH)₃ and Nd(OH)₃ Nanowires Using Porous Anodic Alumina Membranes", *Electrochem. Commun.*, Vol. 9, (2007), 683-688.
- Xiao, X., Xu, S. and Yan, B., "Photoluminescent Properties of Eu³⁺, Tb³⁺ Activated M₃Ln(PO₄)₃ (M = Sr, Ca; Ln = Y, La, Gd) Phosphors Derived from Hybrid Precursors", *J. Alloys Comp.*, Vol. 429, (2007), 255-259.
- Murugan, A. V., Navale, S. C. and Ravi, V., "Synthesis of Nanocrystalline La₂O₃ Powder at 100 °C", *Mater. Lett.*, Vol. 60, (2006), 848-849.
- Wu, Q. Z., Shen, Y., Liao, J. F. and Li, Y. G., "Synthesis and Characterization of Three-Dimensionally Ordered Macroporous Rare Earth Oxides", *Mater. Lett.*, Vol. 58, (2004), 2688-2691.
- Capobianco, J. A., Vetrone, F., Boyer, J. C., Speghini, A. and Bettinelli, M., "Visible up-Conversion of Er³⁺ Doped Nanocrystalline and Bulk Lu₂O₃", *Opt. Mater.*, Vol. 19, (2002), 259-268.
- Palmer, M. S., Neurock, M. and Olken, M. M., "Periodic Density Functional Theory Study of Methane Activation Over La₂O₃: Activity of O²⁻, O⁻, O₂²⁻, Oxygen Point Defect, and Sr²⁺-Doped Surface Sites", *J. Am. Chem. Soc.*, Vol. 124, (2002), 8452-8461.
- Peruski, A. H., Johnson, L. H. and Peruski, L. F., "Rapid and Sensitive Detection of Biological Warfare Agents Using Time-Resolved Fluorescence Assays", *J. Immunol. Methods*, Vol. 263, (2002), 35-41.
- Wang, X., Sun, X., Yu, D., Zou, B. and Li, Y., "Rare Earth Compound Nanotubes", *Adv. Mater.*, Vol. 15, (2003), 1442-1445.
- Wang, X., Wang, M., Song, H. and Ding, B., "A simple Sol-Gel Technique for Preparing Lanthanum Oxide Nanopowders", *Mater. Lett.*, Vol. 60, (2006), 2261-2265.
- Ma, X., Zhang, H., Ji, Y., Xu, J., and Yang, D., "Synthesis of Ultrafine Lanthanum Hydroxide Nanorods by a Simple Hydrothermal Process", *Mater. Lett.*, Vol. 58, (2004), 1180-1182.
- Jiawen, D., Yanli, W., Weili, S. and Yongiu, L., "Preparation of La(OH)₃ and La₂O₃ with Rod Morphology by Simple Hydration of La₂O₃", *J. Rare Earths*, Vol. 24, (2006), 440-442.
- Hu, C. G., Liu, H., Dong, W. T., Zhang, Y. Y., Bao, G., Lao, C. S., and Wang, Z. L., "La(OH)₃ and La₂O₃ Nanobelts-Synthesis and Physical Properties", *Adv. Mater.*, Vol. 19, (2007), 470-474.
- Tang, B., Ge, J., Wu, C., Zhuo, L., Niu, J., Chen, Z., Shi, Z. and Dong, Y., "Sol-Solvothetical Synthesis and Microwave Evolution of La(OH)₃ Nanorods to La₂O₃ nanorods", *Nanotechnology*, Vol. 15, (2004), 1273-1276.
- Wang, X. and Li, Y., "Synthesis and Characterization of Lanthanide Hydroxide Single Crystal Nanowires", *Angew. Chem. Int. Ed.*, Vol. 41, (2002), 4790-4793.
- Wang, X. and Li, Y., "Rare-Earth-Compound Nanowires, Nanotubes, and Fullerene-Like Nanoparticles: Synthesis, Characterization, and Properties", *Chem. Eur. J.*, Vol. 9, (2003), 5627-5635.
- Djerdj, I., Garnweitner, G., Su, D. S. and Niederberger, M., "Morphology-Controlled Nonaqueous Synthesis of Anisotropic Lanthanum Hydroxide Nanoparticles", *J. Solid State Chem.*, Vol. 180, (2007), 2154-2165.
- Bouyer, F., Sanson, N., Destarac, M. and Gérardin, C., "Hydrophilic Block Copolymer Directed Growth of Lanthanum Hydroxide Nanoparticles", *New J. Chem.*, Vol. 30, (2006), 399-408.
- Mekhemer, G. A. H. and Balboul, B. A. A., "Thermal Genesis Course and Characterization of Lanthanum Oxide", *Colloids Surf. A Physicochem. Eng. Asp.*, Vol. 181, (2001), 19-29.
- Jo, S. J., Ha, J. S., Park, N. K., Kang, D. K., and Kim, B. H., "5 nm Thick Lanthanum Oxide Thin Films Grown on Si(100) by Atomic Layer Deposition: The Effect of Post-Annealing on the Electrical Properties", *Thin Solid Films*, Vol. 513, (2006), 253-257.
- Neumann, A. and Walter, D., "The Thermal Transformation from Lanthanum Hydroxide to Lanthanum Hydroxide Oxide", *Thermochim. Acta*, Vol. 445, (2006), 200-204.
- Hou, B., Xu, Y., Wu, D. and Sun, Y., "Synthesis and Characterization of Ultralong Lanthanum Hydroxide Nanorods Via Solvothetical Method", *J. Mater. Sci.*, Vol. 42, (2007), 1397-1400.
- Jun, J. H. and Choi, D. J., "Effects of the wet air on the Properties of the Lanthanum Oxide and Lanthanum Aluminate Thin Films", *Thin Solid Films*, Vol. 504,

- (2006), 205-208.
28. Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T. and Niihara, K., "Titania Nanotubes Prepared by Chemical Processing", *Adv. Mater.*, Vol. 11, (1999), 1307-1311.
 29. Hong, J., Cao, J., Sun, J., Li, H., Chen, H. and Wang, M., "Electronic Structure of Titanium Oxide Nanotubules", *Chem. Phys. Lett.*, Vol. 380, (2003), 366-371.
 30. Zhang, Y. X., Li, G. H., Jin, Y. X., Zhang, Y., Zhang, J. and Zhang, L. D., "Hydrothermal Synthesis and Photoluminescence of TiO₂ Nanowires", *Chem. Phys. Lett.*, Vol. 365, (2002), 300-304.
 31. Penn, R. L. and Banfield, J. F., "Imperfect Oriented Attachment: Dislocation Generation in Defect-Free Nanocrystals", *Science*, Vol. 281, (1998), 969-971.
 32. Füglein, E. and Walter, D., "Pressure Dependency of the Thermal Transformation from MOOH to M₂O₃ (M = Fe, La)", *Z. Kristallogr. Suppl.*, Vol. 24, (2006), 82-86.
 33. Füglein, E. and Walter, D., "Thermal Behavior of Lanthanum Hydroxide in the Dependency of Pressure", *Z. Anorg. Allg. Chem.*, Vol. 632, (2006), 2154-2157.
 34. Markov, S. Z., Soboleva, L. V. L. and Chernyshova, A. M., "Physicochemical Investigation of the Reaction Between Lanthanum Hydroxide and Hydrogen Peroxide", *Russ. Chem. Bull.*, Vol. 10, (1961), 1805-1810.
 35. Wells, A. F., "Structural Inorganic Chemistry", 5th ed., Clarendon Press Oxford, Oxford University Press, Oxford, U.K., (1984).
 36. Imanaka, N., Masui, T. and Kato, Y., "Preparation of the Cubic-Type La₂O₃ Phase by Thermal Decomposition of LaI₃", *J. Solid State Chem.*, Vol. 178, (2005), 395-398.