SOL-GEL SYNTHESIS AND CHARACTERIZATION OF LITHIUM YTTRIUM OXIDE

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Abstract

Lithium yttrium oxide $LiYO_2$ was synthesized for the first time by a simple citric acid-assisted sol-gel method. Three different molar ratios from low to high concentration of lithium precursor were used. The higher lithium precursor content provided purer $LiYO_2$ powders, which were obtained by calcining the amorphous powders from the sol-gel process at lower temperature, compared to those synthesized by solid-state reaction. The optimum experimental conditions for sol-gel preparation process is 1:3 and 1:2 molar ratio of $[Li(CH_3COO]\cdot 2H_2O]/[Y(NO_3)_3\cdot 6H_2O]$ at 950°C and 1000°C respectively, with 6 hours of holding time. The reaction and synthesis mechanism for $LiYO_2$ was analyzes and proposed. It was found that the calcination of dried gel generated exothermic reactions and synthesize of $LiYO_2$ was performed by simple reaction of Li_2O and Y_2O_3.

Keywords: *Lithium yttrium oxide ($LiYO_2$), Sol–gel synthesis, mechanism.*

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1. INTRODUCTION

The sol–gel method attracts much interest as a process for preparing ceramic and glass materials, through a solution state and a gel state. Sol-gel technique is simple and cheap, with good mixture of the reagents, low processing temperature and wide possibility to change the properties by varying the composition of the solutions [1, 2]. The sol-gel process can be used to prepare thin films, fibers and powders, which finds wide applications in protective coating, superconductors, photocatalysis, glasses, dielectrics, ferroelectrics, electronics, sensors and insolating materials [1-7].

Recently, the challenges in environmental issues for reduction of greenhouse gases in atmosphere have been gaining worldwide attention. The significant pollution sources are due to the increasing growth of industries and the advancements in technology, particularly in the transportation, energy generation, cement and coal-based industries. Lithium yttrium oxide or lithium yttriate ($LiYO_2$) is a novel material for the CO_2 absorbent in the temperature range of 300 to 980˚C [8]. $LiYO_2$ has wider temperature range than Li_2ZrO_3 (450-500˚C) [9] and Li_4SiO_4 (up to 720˚C) [10]. Apart from these, $LiYO_2$ has been widely studied for its promising engineering applications such as insulation coating [11], CO_2 absorbent [8], lithium sensor [12] and electrical conductivity [11, 13]. Furthermore, when $LiYO_2$ is doped with lanthanides (Eu^{3+}, Tb^{3+}) ions, it shows outstanding optical and magnetic properties [14-16].

The crystal structure of $LiYO_2$ depends on the temperature condition of synthesis and nature of impurities. There exist two crystalline structures: α-$LiYO_2$ tetragonal structure with $I4_1/amd$ group space and β-$LiYO_2$ lower symmetric monoclinic structure [17]. In α- and β-type structures, the Y ions are coordinated octahedrally by six oxide ions and each YO_6 octahedron shares four edges and four corners with the surrounding YO_6 octahedral [16] and the coordinated polyhedron around Li is almost planar [18]. Nonetheless, at room temperature pure $LiYO_2$ is monoclinic with space group $P2_1/c$ [14, 19]. The monoclinic structure presents slightly distorted NaCl structure which consists of mixed cation layers of closed-packed O^{2-} [20].

Previously, $LiYO_2$ was synthesized by solid-state sintering of mixture of $LiNO_3$ or Li_2CO_3 with Y_2O_3 precursors in the temperature range of 900-1400˚C and 2-48 h as holding time [12, 14-16, 21]. Recently, various preparation methods including solid-state reaction and spark plasma sintering (SPS) have received much attention for the synthesis of $LiYO_2$ [11]. However, to our present knowledge, sol-gel synthesis of $LiYO_2$ has not yet been reported.

In this work, the sol-gel process was investigated to synthesize $LiYO_2$. This method has been performed in order to increase the chemical homogeneity and reactivity of the precursor powder.

2. EXPERIMENTAL PROCEDURE

$LiYO_2$ powders were prepared by sol-gel route. In a typical synthesis method, lithium acetate $Li(CH_3COO)\cdot 2H_2O$ (Shanghai Chemical Reagent Co., LTD, 99%) and yttrium nitrate hexahydrate $Y(NO_3)_3\cdot 6H_2O$ (Sinopharm Chemical Reagent Co., Ltd, ≥99.0%) were used as precursor materials. The starting charges were dissolved, stoichiometrically with excess ratio of Li precursor, in aqueous solution of citric acid monohydrate $C_6H_8O_7\cdot H_2O$ (Chengdu Kelong Chemical Reagent Factory, 99.5%). The starting sols were prepared by dissolving three different molar ratios (1:1, 1:2 and 1:3) of $Li(CH_3COO)\cdot 2H_2O$ and $Y(NO_3)_3\cdot 6H_2O$ in distilled water and equal volume of aqueous solution of citric acid (1.2 $mol\cdot L^{-1}$). In the experiment, 0.05 mole of Li precursor was fixed and Y precursor mole ratio was varied from 1:1, 1:2 and 1:3 respectively. The corresponding masses were weighed and dissolved in water. The ratio of water and total mass of precursors was fixed to 2.9. These mixtures were stirred at room temperature for 30 min to increase the homogeneity of the mixture. The aqueous solution of citric acid was added slowly to the homogenous solution and then further stirred for 30 min at room temperature to stabilize the sol. Subsequently, the solution was heated in water bath at 80°C with continuous stirring until the transparent viscous gel was obtained. The experimental procedure adopted for the preparation of $LiYO_2$ is schematically shown in Fig. 1.

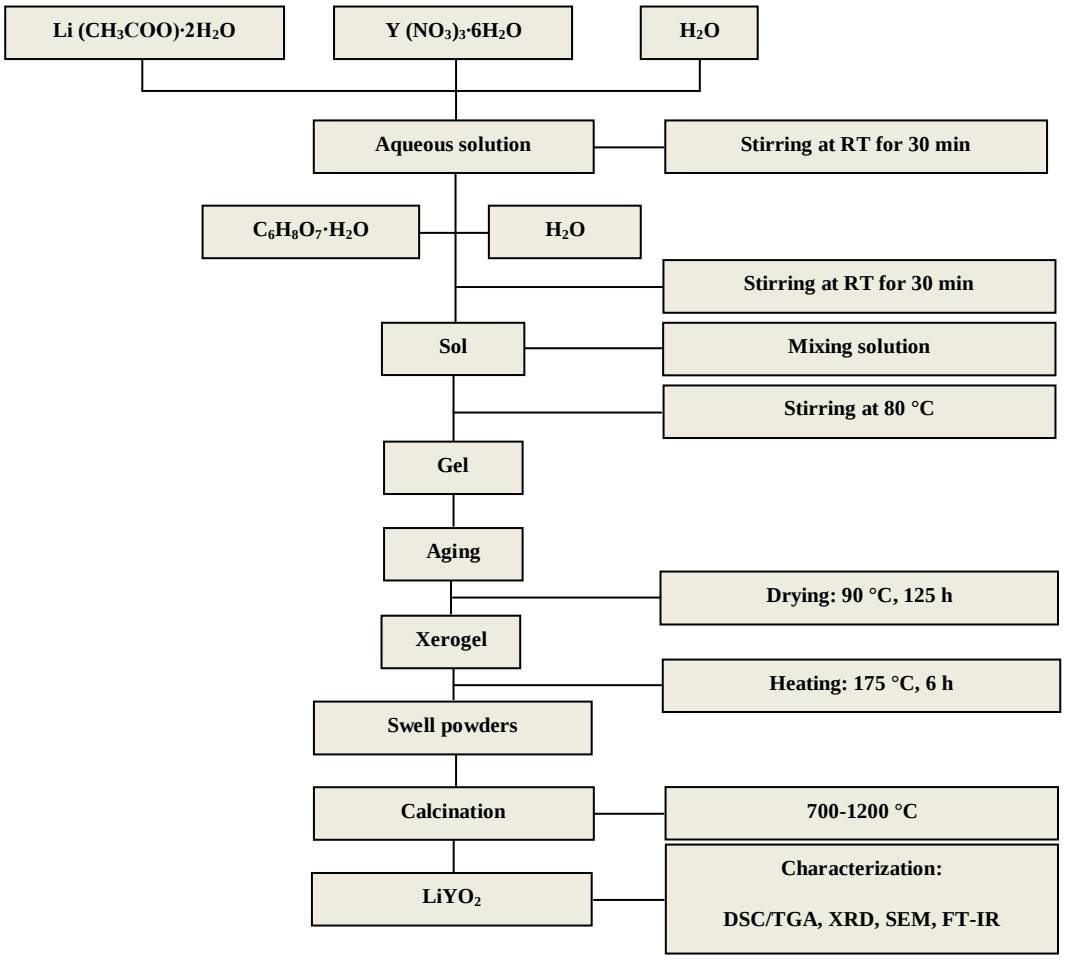


Fig.-1: Schematic diagram of sol-gel preparation process of $LiYO_2$

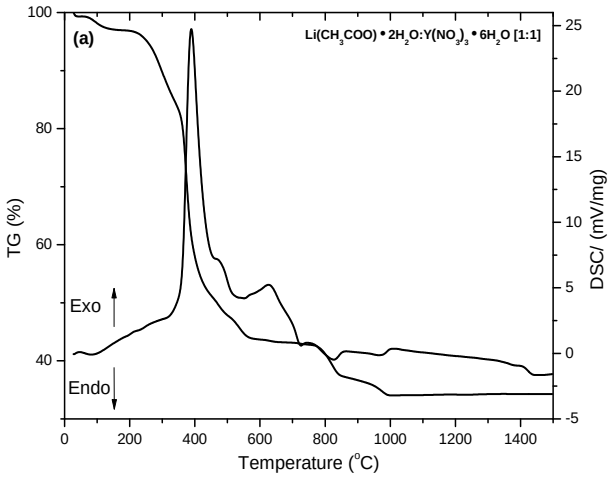
The gel was dried for 125 hours at 90˚C to obtain xerogel. Furthermore, these xerogels were heated at 175˚C for 6 hours to obtain swelled powders. The as-prepared xerogels were calcined from 700 to l200˚C with heating rate of 5 ˚C/min by varying different holding time. The phase structure and purity of as-prepared $LiYO_2$ were identified by X-ray diffractometer.

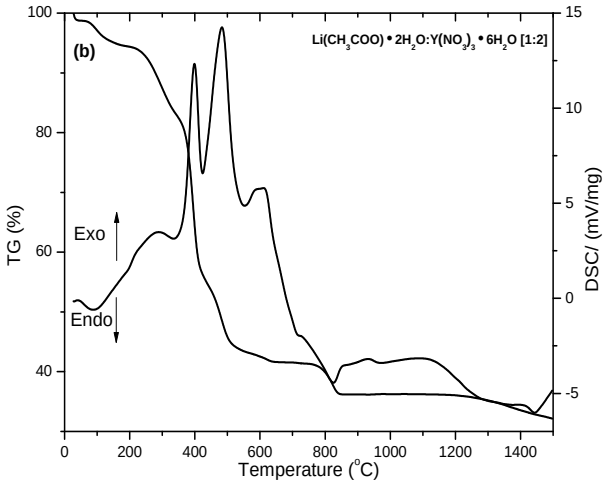
Differential scanning calorimetric and thermogravimetric analysis (DSC/TGA) of the precursor was conducted under 10 mL/min air flow at a heating rate of 15-30 K/min from room temperature to 1500˚C, using a Netzsch STA 449C (Netzsch Instruments Inc., Burlington, MA) with alumina crucible. Component mixtures prepared by sol-gel method were taken as raw powders. Fourier transform infrared spectroscopy (FT-IR) adsorption spectra were obtained using a FT-IR spectrophotometer (Thermo Fisher Scientific, Madison, WI) with wavenumber in 4000-400 cm^{-1}. X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-2500/PC X-ray diffractometer with CuKα radiation (λ= 1.54056 Å). The microstructure analysis was carried out with the scanning electron spectroscopy (Hitachi S-3400N SEM).

3. RESULTS AND DISCUSSION

3.1 Thermal Characterization

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of as-prepared samples with 1:1, 1:2 and 1:3 molar ratio obtained after heating xerogel at 175°C for 6 hours are shown in Fig. 2. The main exothermic reactions occurs at temperature range of 220 to 750°C which could be related to the decomposition of nitrates, acetates and citrates used as chelating agents [22, 23]. DSC curves shows increase in peaks with the decrease of molar ratio of Y precursor. This is due to the citrate-nitrate ions ratio (c/n), which plays significant role on the exothermic reactions [24].





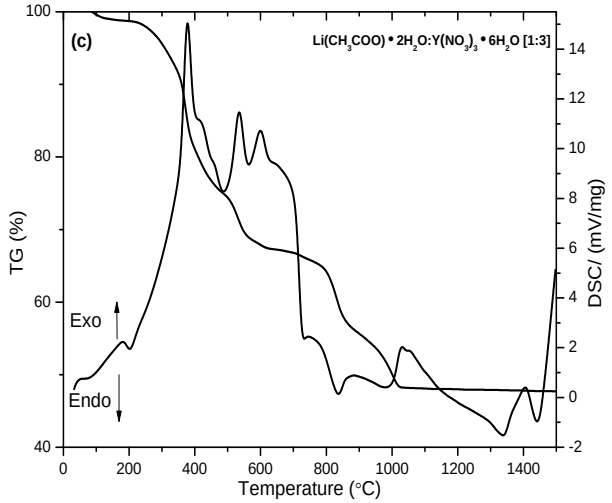


Fig.-2: DSC/TGA curves of samples prepared at different mole ratio (a) 1:1, (b) 1:2 and (c) 1:3

The first major peak corresponded to the release of citric acid at 400˚C for the first two (1:1 and 1:2) samples and at 385˚C for the last sample shows citric acid decomposition at above 380˚C [22]. In fact, according to the concepts employed in propellant chemistry [25], the redox reaction combustion between nitrate (oxidant) and citrate ions (reductant) should be:

$$18Y(NO_3)_3+15C_6H_8O_7 \rightarrow 9Y_2O_3+90CO_2+27N_2+60H_2O \quad (1)$$

However, the heating of xerogel at 175˚C for 6 hours leads to the conversion of citric acid to aconitic acid ($C_6H_6O_6$) and then to itaconic acid ($C_5H_6O_4$) inducing the swell of precursor as reported by Sigh et al. [24], the exothermic redox reaction generated can be written as:

$$18Y(NO_3)_3+15C_5H_6O_4 \rightarrow 9Y_2O_3+75CO_2+27N_2+45H_2O \quad (2)$$

The second major peak, present in samples with molar ratio 1:2 and 1:3 corresponding to 483 and 535˚C respectively, can be attributed to the formation of Li_2O at above 477˚C [26]. Hence, lithium hydroxide obtained after hydrolysis of $Li(CH_3COO)$ is exothermically decomposed into Li_2O:

$$2LiOH \rightarrow Li_2O+H_2O \quad (3)$$

The event observed at 600˚C (or 627˚C for sample 1:1) is due to the decarburization of the decomposed products [22]. These processes are relatively slow and continue at about 1000°C for 1:1 and 1:3 but observed earlier for 1:2 molar ratio sample (850°C). Endothermic peaks are displayed at 824, 827 and 837°C for 1:1, 1:2 and 1:3 respectively, which are due to the crystallization of $LiYO_2$ by the following reaction:

$$Li_2O+ Y_2O_3 \rightarrow 2LiYO_2 \quad (4)$$

The peaks present at 1031 and 1339°C for sample 1:3 are absent in others samples, which can be explained by reactions occurring with excess of gases due to the increase of c/n ratio and/or increase of atmospheric gases. At the same temperature, no weight loss is observed in TGA curve. Beyond, 1400°C, peaks (weak for 1:1 and 1:2) might have formed from the release of Li at high temperature. Moreover, as shown in TGA curves, the decompositions were accompanied by the decrease of weight in samples corresponding to 63.45 % for 1:1, 66.65 % for 1:2 and 52.54 % for 1:3 respectively. On the other hand, the weight loss observed for all samples up to 350°C can be associated with the decomposition of residual water, nitrate and acetate ions [23].

3.2 FT-IR Characterization of $LiYO_2$

The FT-IR was utilized to investigate the room temperature spectra of the as-dried gel at 90°C after 125 hours, the powder after heating at 175°C and calcination at 1000°C for the sample ratio 1:2. Fig. 3 showes the infrared feature of $LiYO_2$ which displays a broad band at around 3450 cm^{-1} related to the O–H stretching vibration mode of water [27]. The presence of O–H vibration for sample heated at 1000˚C is due to the moisture sensitive of Li^+ ion [28]. A closer examination of frequency bands at 3075, 2642 and 2540 cm^{-1} and the typical vibration at 1715 cm^{-1} indicates that the shoulder exists around 3000-2800 cm^{-1} could be attributed to the stretching vibrations of C–H and COO–H vibration of citric acid, which proves that no complexes were formed even after 125 hours. Moreover, carboxylic group and nitro compounds peaks were also observed in the region of 1600 to 825 cm^{-1} [29]. The outstanding CO_2 vibration peaks are observed at 1630-1420 cm^{-1} after heated at 175°C for 6 hours. These peaks are reduced to their lowest level beyond 800˚C corresponding to the crystallization of $LiYO_2$ as shown in DSC curves. Residual peaks in a range of 1089 to 400 cm^{-1} after heat treatment at 1000°C could be attributed to the presence of $LiYO_2$.

Comparatively to the similar structure of aluminum oxide hydroxide or diaspore (α-AlOOH) having three distinct region separated by large gaps [30], FT-IR curve of as-calcined $LiYO_2$ obtained in this study also shows the same tendency. The first region at 864-519 cm^{-1} is consistent with Y–O octahedron vibration modes, second located at 1474-1089 cm^{-1} is assigned to Y–OLi bending mode and the third at above 3400 cm^{-1} corresponding to O–H stretching vibration. The characteristic spectrum of FT-IR of $LiYO_2$ can be expected after heat treatment from 800°C up to 1000˚C. Further, DSC-TG curves also shows crystallization of $LiYO_2$ at above 800˚C.

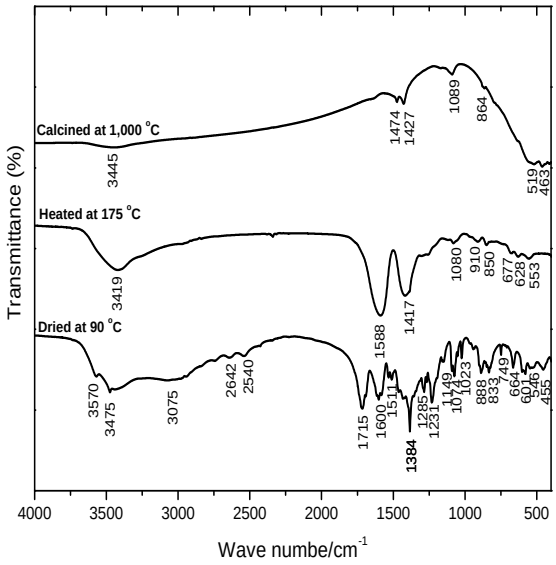


Fig.-3: FT-IR spectra of gels prepared at 1:2 mole ratio which is dried at 90°C, heated at 175°C and calcined at 1000°C

3.3 XRD Characterization

All samples were calcined at different temperature and holding time. The Fig. 4 shows XRD of patterns of samples prepared at 1:1 mole ratio at 700-1200°C with holding time of 2 and 4 hours. Fig. 5 shows XRD patterns of $LiYO_2$ powders prepared with excessive Li precursor ratios up to 1000˚C. From the XRD results we can conclude that the crystallization of Y_2O_3 occurs at 700°C and $LiYO_2$ peaks also started to generate which are identified from XRD patterns, which agrees well with phase changes observed in DSC/TGA studies and reaction mechanisms as shown above.

When the temperature is increased to 700˚C, the XRD patterns show Y_2O_3 as a major crystalline in all mole ratios. At 800˚C, weak intensity peaks of $LiYO_2$ started to generate especially for samples containing excessive Li precursor. According to the thermal treatment studies, this corresponds to the onset crystallization of $LiYO_2$. Beyond this reference temperature, the release of lithium oxide for 1:1 ratio is evident at 1200˚C with no expected peak of $LiYO_2$ (See Fig. 4). For samples containing excessive Li precursor, the XRD results are almost the same and complete crystallization of $LiYO_2$ occurs at 950 to 1000˚C for samples with molar ratio 1:3 and 1:2, respectively.

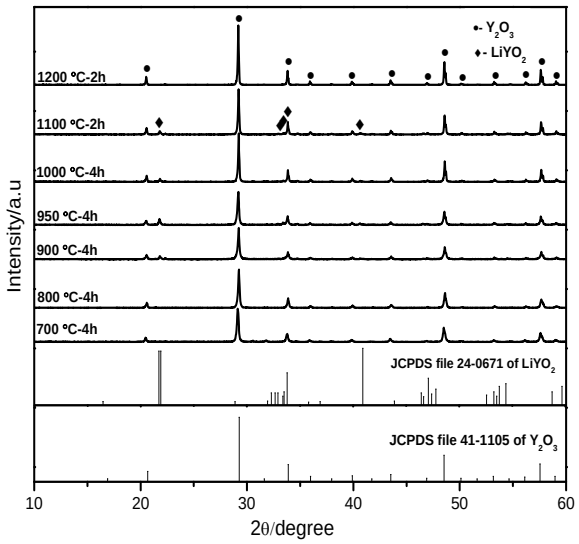


Fig.-4: XRD patterns of samples prepared at 1:1 mole ratio

Only the patterns 1:3 molar ratio is reported in this paper (Fig. 5). Furthermore, it is evident that low temperature synthesis of $LiYO_2$ requires excess of Li precursor and long holding time, which is inevitable for the growth of particles sizes. Hence, the pure $LiYO_2$ phase was obtained at 950°C (1:3) and 1000°C (1:2) molar ratio after 6 hours of holding. These temperatures are lower than high sintered solid-state reaction process at 1400°C for 4 hours [21], 1200°C for 15 hours [12]. Otherwise, much longer annealing time (12-48 hours) was needed to synthesize $LiYO_2$ at 900°C [16].

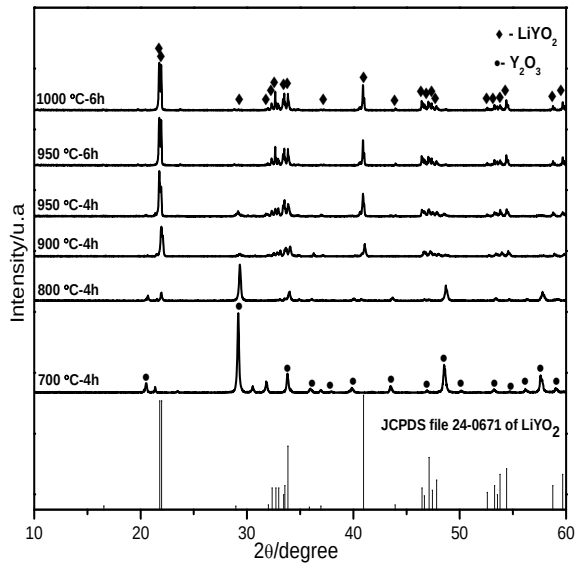


Fig.-5: XRD patterns of samples prepared at 1:3 mole ratio and calcining at different temperatures with varying holding time

3.4 SEM Characterization

The Fig. 6 is the SEM micrographs of $LiYO_2$ powders as-prepared at 950°C (1:3) and 1000°C (1:2), which shows that particle size of synthesized powders is less than 25 µm with uniform size distribution especially for sample (1:3). The low calcination rate (5°C/min) and relative long holding time might be responsible of this spectacular grains growth. Besides the various shapes in Fig. 6, strong agglomeration of particles at 1000°C in sample ratio 1:2 is observed [22, 23]. There is a need for further investigation of these agglomerated particles. As compared with previous study, no contamination from Y_2O_3 on the surface of $LiYO_2$ grains is observed [12].

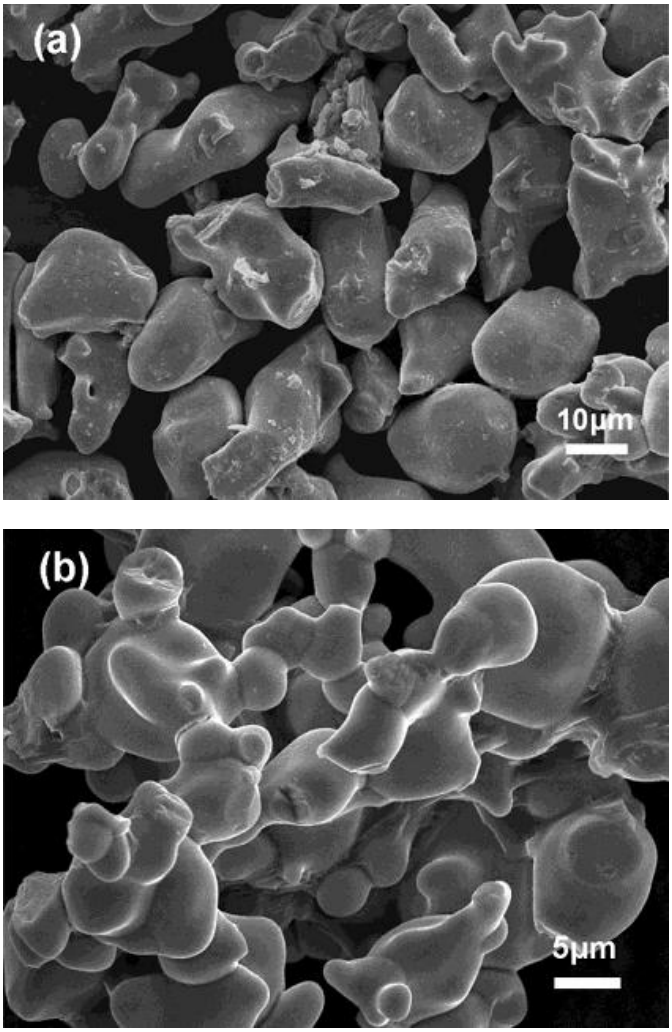


Fig.-6: SEM micrograph of $LiYO_2$ calcined at: a) 950 ˚C for 6h (1:3) and b) 1000˚C for 6h (1:2)

4. CONCLUSION

Crystalline particles of monoclinic $LiYO_2$ were synthesized by simple sol-gel process using citric acid without complexation of metal precursors. The optimum synthesis temperature is 950 to 1000°C with 6 hours holding time for samples containing excessive Li precursor, 1:3 and 1:2 molar ratios respectively. The redox combustion reaction between citrate and nitrate was generated from itaconic acid derived from citric acid. $LiYO_2$ was formed by simple reaction of lithium oxide and yttria. The synthesis

temperature is much lower and the holding time is relatively shorter than the traditional solid-state reaction method. The heat treatment results in the increase in particles size without any contamination from yttria. Moreover, FT-IR analysis proves that during sol-gel process, no complexes were formed between acid and metal oxides. It is also shown that different vibration modes inside the structure are deepened, which has to be studied in future works.

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REFERENCES

[1] M. Crişan, A. Brăileanu, M. Răileanu, M. Zaharescu, D. Crişan, N. Drăgan, M. Anastasescu, A. Ianculescu, I. Niţoi, V.E. Marinescu, S.M. Hodorogea "Sol–gel S-doped TiO_2 materials for environmental protection". Journal of Non-Crystalline Solids 354 (2008) 705–711.

[2] Z. Xiu, M. Lü, S. Liu, G. Zhou, B. Su, H. Zhang "Barium Hydroxyapatite nanoparticles synthesized by citric acid sol-gel combustion method". Materials Research Bulletin 40 (2005) 1617-1622.

[3] B.D. Mac Craith, C. Mc Donagh, A.K. Mcevoy, T. Butler, G. O'Keeffe, V. Murphy "Optical Chemical Sensors Based on Sol-Gel Materials: Recent Advances and Critical Issues". Journal of Sol-Gel Science and Technology 8 (1997) 1053–1061.

[4] S.H. Xie, J.Y. Li, R. Proksch, Y. M. Liu, Y.C. Zhou, Y.Y. Liu, Y. Ou, L.N. Lan, Y. Qiao "Nanocrystalline multiferroic $BiFeO_3$ ultrafine fibers by sol-gel based electrospinning". Applied Physics Letters 93, 222904 (2008). DOI : 10.1063/1.3040010.

[5] O. Cakiroglu, L. Arda, Y.S. Hascicek "High voltage breakdown studies of sol–gel MgO–ZrO_2 insulation coatings under various pressures at 298 K and 77 K". Physica C 422 (2005)117–126.

[6] C.D.E. Lakeman, D.A. Payne "Sol-gel processing of electrical and magnetic ceramics". Materials Chemistry and Physics 38 (1994) 305–324.

[7] J. Zhang, L. Gao "Synthesis of antimony-doped tin oxide (ATO) nanoparticles by the nitrate–citrate combustion method". Materials Research Bulletin 39 (2004) 2249–2255.

[8] M. Yamauchi, Y. Itagaki, H. Aono, Y. Sadaoka "Lithium carbonate-metal oxide mixtures and its application for a CO_2 absorbent". Journal of Ceramic Society of Japan 114 (2006) 648–650.

[9] K. Nakagawa, T. Ohashi "A Novel Method of CO_2 Capture from High Temperature Gases". Journal of The Electrochemical Society 145 (1998) 1344–1346.

[10] M. Kato, K. Nakagawa "New series of lithium containing complex oxides, lithium silicates, for application as a high temperature CO_2 absorbent". Journal of Ceramic Society of Japan 109 (2001) 911–914.

[11] M. Nagura, A. Suzuki, K. Sasaki, T. Terai "Chemical stability of $LiYO_2$ as an insulating material". Fusion Engineering and Design 85 (2010) 1098–1101.

[12] J. Wu, L. Yamarte, A. Petric "Fabrication of a Lithium Sensor based on $LiYO_2$ by Liquid Phase Processing". Journal of Electroceramics 9 (2002) 57-66.

[13] Y. Zou, A. Petric"Structure and conductivity of zirconium-doped polycrystalline lithium yttrium oxide". Materials Research Bulletin 28 (1993) 1169-1175.

[14] M.D. Faucher, Ph. Sciau, J-M. Kiat, M-G Alves, F. Bouree "Refinement of the Monoclinic and Tetragonal Structures of Eu^{3+}-Doped $LiYO_2$by Neutron Diffraction at 77 and 383 K Differential Scanning Calorimetry, and Crystal Field Analysis". Journal Solide State Chemistry 137 (1998) 242–248.

[15] M.D. Faucher, O.K. Moune, M-G Alves, B. Piriou, Ph. Sciau, M. Pham-Thi "Optical and Crystallographic Study of $Eu^{3+}$and Tb^{3+}Doped $LiYO_2$: Phase Transition, Luminescence Efficiency and Crystal Field Calculation". Journal Solide State Chemistry 121 (1996) 457–466.

[16] Y. Hashimoto, M. Wakeshima, K. Matsuhira, Y. Hinatsu, and Y. Ishii, "Structures and magnetic properties of ternary lithium oxides $LiRO_2$ (R=Rare Earths)". Chemistry of Materials 14 (2002) 3245–3251.

[17] H. Glaum, S. Voigt, R.Z. Hoppe "Two Representatives of the α-$LiFeO_2$ Type: $LiInO_2$ and α-$LiYbO_2$". Anorg. Allg. Chem. 598 (1991) 129. DOI: 10.1002/zaac.19915980113.

[18] Y.B. Kuo, W. Scheld, R. Hoppe "To the knowledge of thealpha-$LiFeO_2$ type: An examination of $LiScO_2$and $NaNdO_2$". Zeitschrift für Kristallographie 164 (1983) 121-127. DOI: 10.1524/zkri.1983.164.1-2.121.

[19] M.J. Weber "Handbook of Optical Materials". CRC Press, Boca Raton 1-512, 2003.

[20] X. Zhang, D.A. Jefferson, R.M. Lambert "Structure and Performance of $LiYO_2$ Methane Coupling Catalysts: Active Phases and Decay Mechanisms". Journal of Catalysis 141 (1993) 583–594.

[21] S. Chockalingam, D.A. Earl "Microwave sintering of Si_3N_4 with $LiYO_2$ and ZrO_2 as sintering additives". Materials and Design 31 (2010) 1559–1562.

[22] K. Devi, R. Choudhary, A.K. Satsangi, R.K. Gupta "Sol-gel Synthesis and Characterisation of Nanocrystalline Yttrium Aluminum Garnet Nanopowder". Defense Science Journal 58 (2008) 545–549.

[23] K. Suryakala, G.P. Kalaignan, T. Vasudevan "Synthesis and Electrochemical Improvement of Nanocrystalline $LiMn_{2-X}Mg_XO_4$ Powder Using Sol-Gel Method". International Journal of Electrochemical Science 1 (2006) 372–378.

[24] K.A. Singh, L.C. Pathak, S.K. Roy "Effect of citric acid on the synthesis of nano-crystalline yttria stabilized zirconia powders by nitrate-citrate

process". Ceramics International 33(2007) 1463-1468.

[25] S.R. Jain, K.C. Adiga, V.R. Pai Verneker "A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures". Combust Flame 40 (1981) 71–79.

[26] Y.H. Hu, E. Ruckenstein "Nanostructured Li_2O from LiOH by electron-irradiation". Chemistry Physics Letter 430 (2006) 80-83.

[27] A.L. Costa, L. Esposito, V. Medri, A. Bellosi "Synthesis of Nd-YAG material by citrate-nitrate sol-gel combustion route". Advanced Engineering Materials 9 (2007) 307-312.

[28] R.K. Kotnala, J. Shah, B. Singh, S. Singh, S.K. Dhawan, A. Sengupta "Humidity response of Li-substituted magnesium ferrite". Sensors and Actuators B: Chem 129 (2008) 909–914.

[29] M. Blosi, S. Albonetti, M. Dondi, A.L. Costa, M. Ardit, G. Cruciani, "Sol-gel combustion synthesis of chromium doped yttrium aluminum perovskites". Journal of Sol-Gel Science and Technology, 50 (2009) 449-455.

[30] R. Demichelis, Y. Noel, B. Civalleri, C. Roetti, M. Ferrero, R. Dovesi "The vibrational spectrum of α-AlOOH diaspore: an ab initio study with the crystal code". The Journal of Physical Chemistry B 111 (2007) 9337–9346.