



## Preparation and Characterization of Ag-MWO<sub>4</sub>/Zeolite (M = Fe, Ni) Composites by Cyclic Microwave-Assisted Metathetic Method

CHANG SUNG LIM

Department of Advanced Materials Science & Engineering, Hanseo University, Seosan 356-706, Republic of Korea

Corresponding author: Tel/Fax: +82 41 6601445; E-mail: cslim@hanseo.ac.kr

Received: 25 May 2013;

Accepted: 24 July 2013;

Published online: 10 March 2014;

AJC-14915

Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites were successfully synthesized by a cyclic microwave-assisted metathetic route followed by heat treatment. The characteristics of the exothermic reaction accompanying the by-product of NaCl were found to drive the microwave-assisted metathetic reaction for Wolframite-type FeWO<sub>4</sub> and NiWO<sub>4</sub> toward completion. The Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites were formed completely at 600 °C. Monoclinic-like crystals of FeWO<sub>4</sub> and NiWO<sub>4</sub> were primarily co-mixed with porous zeolite-A. Small spherical silver particles were well immobilized in the MWO<sub>4</sub>/zeolite (M = Fe, Ni) matrix.

**Keywords:** Cyclic MAM synthesis, Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites, Microstructure, Immobilization.

### INTRODUCTION

Metal tungstates with large bivalent cations (*e.g.*, Ca, Ba, Pb and Sr) tend to have a Scheelite-type tetragonal structure, whereas small cationic radii (*e.g.*, Zn, Fe, Mn, Co and Ni) favour the formation of a Wolframite-type monoclinic structure. The main difference between the above two structures is that every W atom is surrounded by four O atoms in a Scheelite-type structure, whereas six O atoms surround every W atom in metal tungstate crystallizing in the Wolframite-type structure<sup>1,2</sup>. In recent years, metal tungstates have attracted considerable attention for potential applications as a scintillator, microwave devices, luminescent material and photocatalyst<sup>3-7</sup>. The physical, chemical and photochemical properties of metal tungstates are dependent on the manufacturing method. Several processes have been developed over the past decade to enhance the applications of FeWO<sub>4</sub> and NiWO<sub>4</sub>. FeWO<sub>4</sub> and NiWO<sub>4</sub> are prepared by a range of processes, such as solid-state reactions<sup>8</sup>, co-precipitation<sup>9,10</sup>, molten salt<sup>11</sup>, combustion<sup>12</sup>, mechano-chemical<sup>13</sup>, polymeric precursor<sup>14</sup>, hydrothermal reaction<sup>1,15,16</sup>.

Microwave irradiation<sup>16-18</sup>, as a heating method, has a number of applications in chemistry and ceramic processing. Compared with the usual method, microwave synthesis has the advantages of a short reaction time, small particle size, narrow particle size distribution and high purity method for preparing polycrystalline samples. Among these methods, the solution-based chemical synthetic methods play a key role in the design and production of fine ceramics and have been suc-

cessful in overcoming many of the limitations of traditional solid-state as well as high-temperature methods. In addition, the use of solution chemistry can eliminate major problems, such as long diffusion paths, impurities and agglomeration, which result in products with improved homogeneity.

Wet chemical methods have disadvantages, such as complicated synthetic steps, use of expensive equipment, high synthetic temperature and long sintering times. On the other hand, the solid-state reaction requires complex apparatus and techniques, which are becoming gradually unpopular due to excessive energy consumption. However, cyclic microwave-assisted metathetic (MAM) route is a simple method of synthesis, cost-effective, high yield and easy scale up and is emerging as a viable alternative approach for synthesizing high-quality novel inorganic materials in a short time<sup>19,20</sup>. The solid state metathetic approach assisted by microwave irradiation has been applied successfully to the synthesis of metal tungstate of Wolframite-type MWO<sub>4</sub> (M = Zn, Mn, Ni) and Scheelite-type MWO<sub>4</sub> (M = Ca, Sr, Ba)<sup>21</sup>, ZrCr<sub>2</sub>O<sub>4</sub><sup>22</sup>, ZnSiO<sub>4</sub> and MCrO<sub>4</sub> (M = Ca, Sr, Ba, Pb)<sup>23</sup> and MMoO<sub>4</sub> (M = Ca, Sr, Ba)<sup>24,25</sup>. Ag-MWO<sub>4</sub>/zeolite composites are expected to have excellent adsorption and synergy effects in an immobilization mechanism of metallic catalysts for a wide range of applications, such as sensors, photocatalysts, luminescence, anti-bacterial matrices and optical effects in the UV and visible region.

In this study, Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites were synthesized using a cyclic MAM route the characteristics of the exothermic MAM reaction accompanying the by-product NaCl were discussed in detail. The Ag-MWO<sub>4</sub>/zeolite (M =

Fe, Ni) composites were immobilized from mixed metathetic precursors at moderate temperatures. The crystallization process, thermal decomposition and morphology of the synthesized Ag-MWO<sub>4</sub>/zeolite-A (M = Fe, Ni) composites were evaluated.

## EXPERIMENTAL

Fig. 1 shows a flow chart for the synthesis of Ag-MWO<sub>4</sub>/zeolite (M= Fe, Ni) composites by a cyclic MAM method. FeCl<sub>2</sub>·4H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were used to prepare the metal tungstate compound. The preparation of metal tungstates were carried out by reacting well-ground mixtures of FeCl<sub>2</sub>·4H<sub>2</sub>O and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O for FeWO<sub>4</sub> and NiCl<sub>2</sub>·6H<sub>2</sub>O and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O for NiWO<sub>4</sub> at a molar ratio of 1:1. The sample mixtures were dried at 100 °C for 12 h and 5 wt % AgNO<sub>3</sub> and 25 wt % synthetic zeolite-A were then added. The mixtures were transferred into 120 mL Teflon vessels. Teflon vessel was placed into a microwave oven operating at a frequency of 2.45 GHz with a maximum out-power of 1250 W for 23 min. The working cycle of the MAM reaction was controlled precisely between 30 s on and 30 s off for 8 min and followed by a further treatment of 30 s on and 60 s off for 15 min. The resulting samples were treated with ultrasonic radiation and washed many times with hot distilled water. The white precipitates were collected and dried at 100 °C in a dry oven. The final products were heat-treated at 600 °C for 3 h.

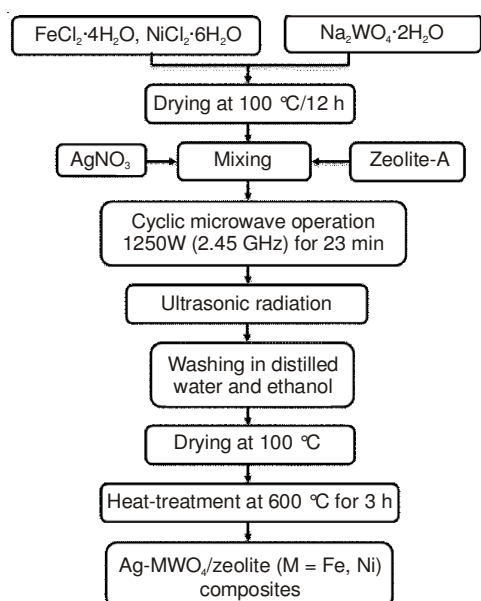


Fig. 1. Flow chart for the synthesis of Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites by a cyclic MAM method

The crystallization of the existing phase in the powders after heat-treatment was examined by powder X-ray diffraction (XRD, CuK $\alpha$ , 40 kV, 30 mA, Rigaku, Japan) at a scan rate of 3°/min. Fourier transform infrared spectroscopy (FT-IR, Model IR 550, Magna, Nicolet Company) was used to examine the thermal-decomposition behaviour of the metathetic reaction and heat-treated powders over frequency range, 4000-400 cm<sup>-1</sup>. The FT-IR spectra were measured in KBr pellets. The micro-structure and surface morphology of the Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites were observed by scanning electron

microscopy (SEM, JSM-35CF, JEOL) and energy-dispersive X-ray spectroscopy (EDS).

## RESULTS AND DISCUSSION

Fig. 1 shows flow chart for the synthesis of Ag-MWO<sub>4</sub>/zeolite (M= Fe, Ni) composites by a cyclic MAM method. Post heat-treatment plays an important role in a well-defined crystallized morphology. To achieve a well-defined crystalline morphology, the Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites need to be heat treated at 600 °C for 3 h. FeWO<sub>4</sub> and NiWO<sub>4</sub> are Wolframite monoclinic crystal structures. Their lattice parameters as follows: a = 4.73 Å, b = 5.70 Å, c = 4.95 Å and  $\beta$  = 90.0° for FeWO<sub>4</sub><sup>2</sup> and a = 4.599 Å, b = 5.66 Å, c = 4.906 Å and  $\beta$  = 90.03° for NiWO<sub>4</sub><sup>21</sup>. Fig. 2 shows FT-IR spectra of the synthesized Ag-FeWO<sub>4</sub>/zeolite composites after (a) cyclic MAM reaction (Ag-FeWO<sub>4</sub>-Z-m) and (b) heat-treated at 600 °C for 3 h (Ag-FeWO<sub>4</sub>-Z-m600). The absorption bands at 473 and 532 cm<sup>-1</sup> can be assigned to symmetric and asymmetric deformation mode of Fe-O in FeO<sub>6</sub> octahedra. The absorption bands with their maxima at 633 and 710 cm<sup>-1</sup> can be due to the stretching modes of W-O in WO<sub>6</sub> octahedra. The bands at 834 and 877 cm<sup>-1</sup> were due to symmetrical vibrations of bridge oxygen atoms of the Fe-O-W groups. These vibrations could be identified to the synthesized FeWO<sub>4</sub>. The band at 1450 and 1630 cm<sup>-1</sup> can in Fig. 2(a) Ag-FeWO<sub>4</sub>-Z-m are assigned to the HOH bending vibrations. It is assumed that the samples prepared contain a significant amount of surface-adsorbed water and alcohol. Obviously, the bands at 1450 cm<sup>-1</sup> disappeared after heat-treated at 600 °C for 3 h in Fig. 2(b) Ag-FeWO<sub>4</sub>-Z-m600.

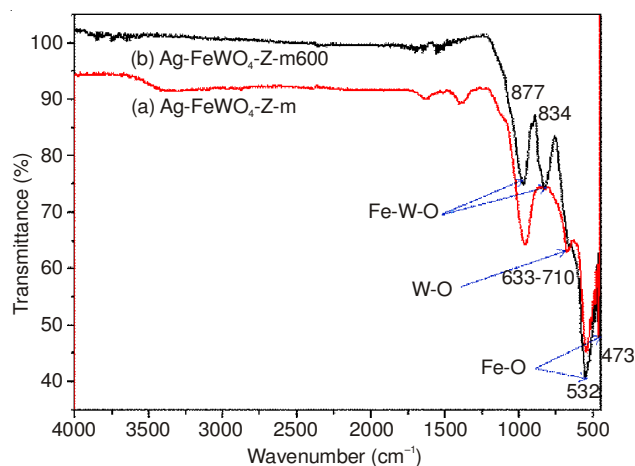


Fig. 2. FT-IR spectra of the synthesized Ag-FeWO<sub>4</sub>/zeolite composites

Fig. 3 shows FT-IR spectra of the Ag-NiWO<sub>4</sub>/zeolite composites after (a) cyclic MAM reaction (Ag-NiWO<sub>4</sub>-Z-m) and (b) heat-treated at 600 °C for 3 h (Ag-NiWO<sub>4</sub>-Z-m600). The absorption bands at 532 cm<sup>-1</sup> can be assigned to symmetric and asymmetric deformation mode of Ni-O in NiO<sub>6</sub> octahedra. The absorption bands with their maxima at 633 and 710 cm<sup>-1</sup> can be due to the stretching modes of W-O in WO<sub>6</sub> octahedra. The bands at 834 and 877 cm<sup>-1</sup> were due to symmetrical vibrations of bridge oxygen atoms of the Ni-O-W groups. These vibrations could be identified to the synthesized NiWO<sub>4</sub>. The band at 1630 cm<sup>-1</sup> can in Fig. 3(a) Ag-NiWO<sub>4</sub>-Z-m are assigned

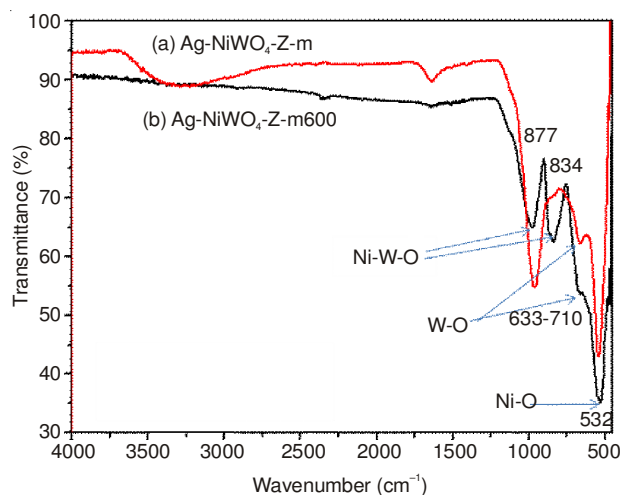


Fig. 3. FT-IR spectra of the synthesized Ag-NiWO<sub>4</sub>/zeolite composites

to the HOH bending vibrations. It is assumed that the samples prepared contain a significant amount of surface-adsorbed water and alcohol. Obviously, the bands at 1630 cm<sup>-1</sup> disappeared after heat-treated at 600 °C for 3 h in Fig. 3(b) Ag-NiWO<sub>4</sub>-Z-m600.

Fig. 4 shows SEM images of the synthesized Ag-FeWO<sub>4</sub>/zeolite composites after (a) cyclic MAM reaction and (b) heat-treated at 600 °C for 3 h and Ag-NiWO<sub>4</sub>/zeolite composites after (c) cyclic MAM reaction and (d) heat-treated at 600 °C for 3 h. Fig. 4(a) and (c) show SEM images of the Ag-FeWO<sub>4</sub>/zeolite and Ag-NiWO<sub>4</sub>/zeolite composites synthesized by cyclic MAM reaction after removing the NaCl. Parhi *et al.*<sup>21</sup> reported the MAM synthesis of various metal tungstates and showed that microwave radiation provided the energy required to overcome the energy barrier that precludes a spontaneous reaction and helped heat the bulk of the material uniformly, resulting in fine particles with a controlled morphology and the formation of the product in a green manner without the generation of solvent waste. In Fig. 4(b) and (d), the SEM images of Ag-FeWO<sub>4</sub>/zeolite and Ag-NiWO<sub>4</sub>/zeolite composites heat-treated at 600 °C for 3 h show the well crystallized FeWO<sub>4</sub> and NiWO<sub>4</sub> on the zeolite synthesized by the cyclic MAM reaction. The monoclinic-like crystals of FeWO<sub>4</sub> and NiWO<sub>4</sub> were primarily co-mixed with Ag on the porous zeolite surfaces. The spherical small particles of silver were well immobilized in the porous FeWO<sub>4</sub>/zeolite and NiWO<sub>4</sub>/zeolite composites matrix. It indicates that the cyclic MAM synthesis is adequate for the growth of FeWO<sub>4</sub> and NiWO<sub>4</sub> crystallites and development of Ag-FeWO<sub>4</sub>/zeolite and Ag-NiWO<sub>4</sub>/zeolite composites. Microwave-assisted methathetic reactions, such as  $\text{ACl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{AWO}_4 + 2\text{NaCl}$ , involves the exchange of atomic/ionic species, where the driving force is the exothermic reactions accompanying the formation of a high lattice energy of NaCl. The thermodynamic basis for such MAM reactions has been reported<sup>21,26-28</sup>. Parhi *et al.*<sup>21</sup> calculated the enthalpy ( $\Delta H$ ) and free energy change ( $\Delta G$ ) associated with the formation of tungstates and reported  $\Delta H = -36.17$  KJ/mol for ZnWO<sub>4</sub> showing that both the enthalpy change favours the MAM reaction. MAM reactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products, usually raising the alkali halide near or above its normal boiling point

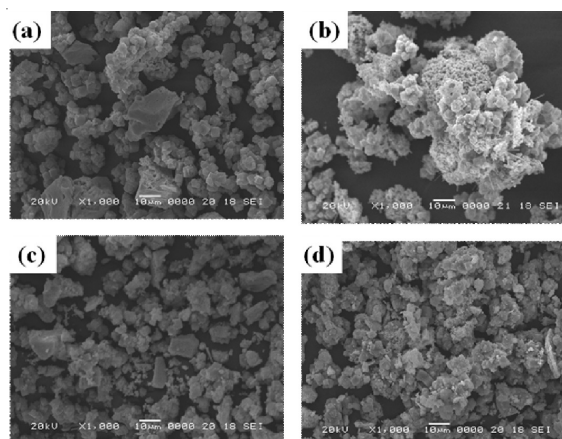


Fig. 4. SEM images of the synthesized Ag-FeWO<sub>4</sub>/zeolite composites after (a) cyclic MAM reaction and (b) heat-treated at 600 °C for 3 h and Ag-NiWO<sub>4</sub>/zeolite composites after (c) cyclic MAM reaction and (d) heat-treated at 600 °C for 3 h

and have been recognized to be approximately adiabatic in nature<sup>29</sup>.

Fig. 5 shows (a) EDS patterns, (b) quantitative compositions, (c) a SEM image and (d) quantitative results of the synthesized Ag-FeWO<sub>4</sub>/zeolite composites at 600 °C for 3 h. The EDS patterns and quantitative compositions of the synthesized Ag-FeWO<sub>4</sub>/zeolite composites were composed of Ag, FeWO<sub>4</sub> and zeolite-A. Fig. 6 shows (a) EDS patterns, (b) quantitative compositions, (c) a SEM image and (d) quantitative results of the synthesized Ag-NiWO<sub>4</sub>/zeolite composites at 600 °C for 3 h. The EDS patterns and quantitative compositions of the synthesized Ag-NiWO<sub>4</sub>/zeolite composites were composed of Ag, NiWO<sub>4</sub> and zeolite-A. For tungstate materials to be used for practical applications, versatile characteristics are required for the particle size distribution and morphology of the particles. The well-defined particle features of the Ag-FeWO<sub>4</sub>/zeolite and Ag-NiWO<sub>4</sub>/zeolite composites synthesized by the cyclic MAM reactions have control over the morphology of the final particles and can be used for such technological applications. Owing to the exothermic reaction by the driving force for the formation of NaCl, the MAM reactions affect not only the morphology of the FeWO<sub>4</sub> and NiWO<sub>4</sub> particles, but also the formation of functional zeolite and Ag immobilized in the porous composite matrix. Therefore, the cyclic MAM reactions are required to control the well-defined particle features of the Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites.

## Conclusion

Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites were synthesized by a cyclic MAM method. The Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites were completed entirely at 600 °C for 3 h. The well crystallized FeWO<sub>4</sub> and NiWO<sub>4</sub> on the zeolite synthesized by a cyclic MAM reaction. The monoclinic-like crystals of FeWO<sub>4</sub> and NiWO<sub>4</sub> were primarily co-mixed with Ag on the porous zeolite-A surfaces. The spherical small particles of silver were well immobilized in the FeWO<sub>4</sub>/zeolite and NiWO<sub>4</sub>/zeolite composites matrix. The exothermic reactions occur so rapidly that the formation of NaCl favours the cyclic MAM reactions. The cyclic MAM reactions are essentially used to heat up the solid products of Ag-MWO<sub>4</sub>/zeolite (M = Fe, Ni) composites.

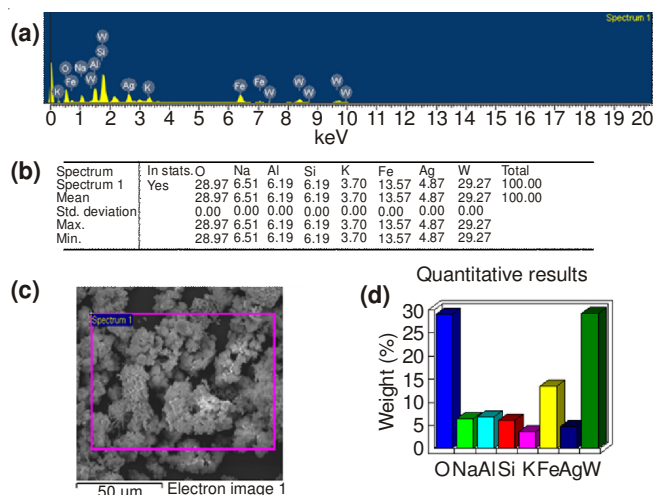


Fig. 5. EDS patterns(a), quantitative compositions(b), a SEM image(c) and quantitative results(d) of the synthesized Ag-FeWO<sub>4</sub>/zeolite composites

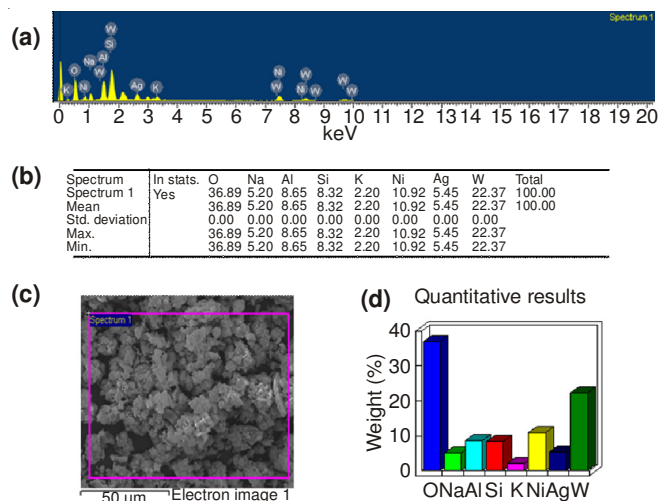


Fig. 6. EDS patterns (a), quantitative compositions (b), a SEM image (c) and quantitative results (d) of the synthesized Ag-NiWO<sub>4</sub>/zeolite composites

## ACKNOWLEDGEMENTS

This study was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2013-054508).

## REFERENCES

- S. Rajagopal, D. Nataraj, O.Y. Khyzhun, Y. Djaoued, J. Robichaud and D. Mangalaraj, *J. Alloys Comp.*, **493**, 340 (2010).
- S. Rajagopal, V.L. Bekenev, D. Nataraj, D. Mangalaraj and O.Y. Khyzhun, *J. Alloys Comp.*, **496**, 61 (2010).
- X. Cao, W. Wu, N. Chen, Y. Peng and Y. Liu, *Sens. Actuators B*, **137**, 83 (2009).
- C. Yu and J.C. Yu, *Mater. Sci. Eng. B*, **164**, 16 (2009).
- S. Lin, J. Chen, X. Weng, L. Yang and X. Chen, *Mater. Res. Bull.*, **44**, 1102 (2009).
- P.K. Pandey, N.S. Bhave and R.B. Kharat, *J. Mater. Sci.*, **42**, 7927 (2007).
- R.P. Jia, G.X. Zhang, Q.S. Wu and Y.P. Ding, *Mater. Lett.*, **61**, 1793 (2007).
- S.M. Montemayor and A.F. Fuentes, *Ceram. Int.*, **30**, 393 (2004).
- A. Sen and P. Pramanik, *J. Eur. Ceram. Soc.*, **21**, 745 (2001).
- T. Montini, V. Gombac, A. Hameed, L. Felisari, G. Adami and P. Fornasiero, *Chem. Phys. Lett.*, **498**, 113 (2010).
- Z. Song, J. Ma, H. Sun, W. Wang, Y. Sun, L. Sun, Z. Liu and C. Gao, *Ceram. Int.*, **35**, 2675 (2009).
- S.L. Gonzalez-Cortes, T.C. Xiao, P.M.F.J. Costa, S.M.A. Rodolfo-Baechler and M.L.H. Green, *J. Mol. Catal. A*, **238**, 127 (2005).
- K.J.D. MacKenzie, J. Temuujin, C. McCammon and M. Senna, *J. Eur. Cer. Soc.*, **26**, 2581 (2006).
- A.L.M. Oliveira, J.M. Ferreira, M.R.S. Silva, S.C. Souza, F.T.G. Vieira, E. Longo, A.G. Souza and I.M.G. Santos, *J. Therm. Anal. Calorim.*, **97**, 167 (2009).
- D. Chen, G. Shen, K. Tang, H. Zheng and Y. Qian, *Mater. Res. Bull.*, **38**, 1783 (2003).
- J.T. Klopprogge, M.L. Weier, L.V. Duong and R.L. Frost, *Mater. Chem. Phys.*, **88**, 438 (2004).
- J.H. Ryu, C.S. Lim, W.C. Oh and K.B. Shim, *J. Ceram. Process. Res.*, **5**, 316 (2004).
- J. Bi, L. Wu, Z. Li, Z. Ding, X. Wang and X. Fu, *J. Alloys Comp.*, **480**, 684 (2009).
- S. Das, A.K. Mukhopadhyay, S. Datta and D. Basu, *Bull. Mater. Sci.*, **32**, 1 (2009).
- K.P.F. Siqueira, R.L. Moreira, M. Valadares and A. Dias, *J. Mater. Sci.*, **45**, 6083 (2010).
- P. Parhi, T.N. Karthik and V. Manivannan, *J. Alloys Comp.*, **465**, 380 (2008).
- P. Parhi and V. Manivannan, *J. Eur. Ceram. Soc.*, **28**, 1665 (2008).
- P. Parhi and V. Manivannan, *J. Alloys Comp.*, **469**, 558 (2009).
- P. Parhi, S.S. Singh, A.R. Ray and A. Ramanan, *Bull. Mater. Sci.*, **29**, 115 (2006).
- V. Thangadurai, C. Knittlmayer and W. Weppner, *Mater. Sci. Eng. B*, **106**, 228 (2004).
- E.G. Gillan and R.B. Kanar, *Chem. Mater.*, **8**, 333 (1996).
- J.J. Mack, S. Tari and R.B. Kanar, *Inorg. Chem.*, **45**, 4243 (2006).
- A.M. Nartowski, I.P. Parkin, M. Mackenzie, A.J. Craven and I. MacLeod, *J. Mater. Chem.*, **9**, 1275 (1999).
- T.K. Mandal and J. Gopalakrishnan, *J. Mater. Chem.*, **14**, 1273 (2004).