

Short Communication

## Synthesis of $\text{Li}_2\text{FeSiO}_4/\text{C}$ Composite as Cathode Materials for Lithium Ion Battery via a New Citric Acid-Assisted Sol-Gel Process

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A new citric acid-assisted sol-gel process is introduced in this work with the aim of getting  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite. The effect of carbon coating on the structure, morphological and electrochemical characteristics is studied in detail. The  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon delivers much higher electrochemical performance, in terms of reversible discharge capacity, cycling performance and rate capability. At 0.2 C and 2 C, it exhibits a discharge capacity of 138 mAh  $\text{g}^{-1}$  and 64 mAh  $\text{g}^{-1}$ , respectively, and after 100 cycles at 0.2 C, 97.1 % of the maximum discharge capacity is retained.

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**Keywords:** Lithium ion battery; sol-gel process;  $\text{Li}_2\text{FeSiO}_4/\text{C}$ ; citric acid

### 1. INTRODUCTION

Recently, a new group of polyanion material,  $\text{Li}_2\text{MSiO}_4$  (M=Fe, Mn, Co), has been demonstrated as a promising candidate of lithium insertion cathode materials for the next generation of Li-ion secondary batteries[1]. Among them  $\text{Li}_2\text{FeSiO}_4$  has attracted the greatest attention, with good thermal stability, nontoxicity, environmental friendliness and low cost[2-6]. Unfortunately, just like  $\text{LiFePO}_4$ , the low intrinsic electronic conductivity[7] and slow lithium ion diffusion ability[8] across the  $\text{Li}_2\text{FeSiO}_4/\text{LiFeSiO}_4$  interface have been a main obstacle to its applications. Several strategies have been proposed to solve this problem, including synthesizing the nanosized particles via various methods[1-3,9-10], creating conductive carbon coating on  $\text{Li}_2\text{FeSiO}_4$  particle surface[11-16] and

cation doping in Fe and Si sites [8,17-19]. Furthermore, many synthesis routes, such as the solid-state reaction method [6,13-14,16,20], the sol-gel process [1-3,8,18,21-23], and the hydrothermal synthesis [5, 24] have also been reported to prepare pure  $\text{Li}_2\text{FeSiO}_4$ , carbon coated  $\text{Li}_2\text{FeSiO}_4$  or polyvalent cation doped  $\text{Li}_2\text{FeSiO}_4$ .

The presence of vacancies in the Li crystallographic sites has been demonstrated to effectively improve the electrochemical behavior of cathode materials such as  $\text{LiFePO}_4$  [25-27], as Li vacancies may contribute to intrinsic ionic conductivity, thereby leading to improved electrochemical performance. In our previous studies [28-29],  $\text{Li}_{1.95}\text{FeSiO}_4/\text{C}$  composite and  $\text{Li}_{1.95}\text{FeSiO}_4/\text{C}/\text{CNTs}$  composite were prepared by a solid-state method. It could be clearly seen in those studies that impurity  $\text{Fe}_3\text{O}_4$  was detected in all the as-obtained samples. In order to further verify the presence of vacancies in the Li crystallographic sites, a new route for synthesis of pure  $\text{Li}_2\text{FeSiO}_4$  needs to be explored. Thus, a new citric acid-assisted sol-gel process is introduced to synthesize phase-pure  $\text{Li}_2\text{FeSiO}_4$ . The impacts of in situ carbon coating on the structural, morphological and electrochemical characteristics of  $\text{Li}_2\text{FeSiO}_4$  are investigated.

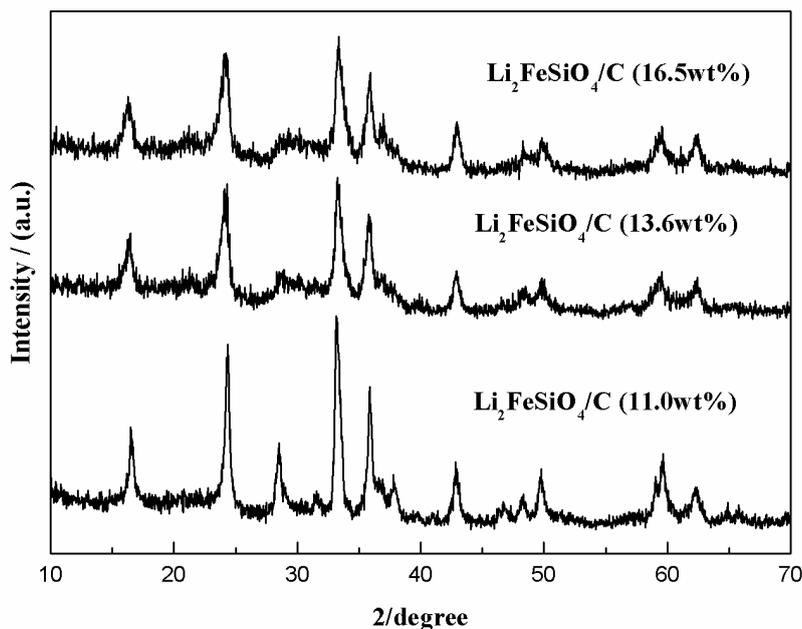
## 2. EXPERIMENTAL

All the  $\text{Li}_2\text{FeSiO}_4$  samples were prepared by a citric acid-assisted sol-gel method. Firstly, 0.04 mol Fe powder and citric acid were mixed in 150 ml deionized water under vigorous magnetic stirring at 80 °C, resulting in a light green solution with release of  $\text{H}_2$ . Secondly, lithium acetate (0.08 mol) and PVP (0.06 mol) were dissolved gradually into the solution, then  $\text{NH}_3$  solution was added in order to keep the pH at 7.0-8.0. Thirdly, 0.04 mol nan- $\text{SiO}_2$  was added into the solution and stirred for 1 h, and then kept at 80 °C under magnetic stirring to evaporate water. Finally, the resulting wet gel was dried in a vacuum circumstance at 100 °C to form dried powder. The dried powder was heated in a horizontal quartz tube oven under flowing argon gas, first at 350 °C for 5 h and then at 650 °C for 10 h to obtain the final  $\text{Li}_2\text{FeSiO}_4$ .

The crystallographic structural characterization of the as-received samples was performed by X-ray powder diffraction analysis (XRD) measurement with Cu K $\alpha$  radiation (DX 2700). The particle morphologies of the as-synthesized materials were observed by scanning electron microscope (SEM, HITACHI SU1510). The carbon content of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites was confirmed by means of a carbon-sulfur analyzer.

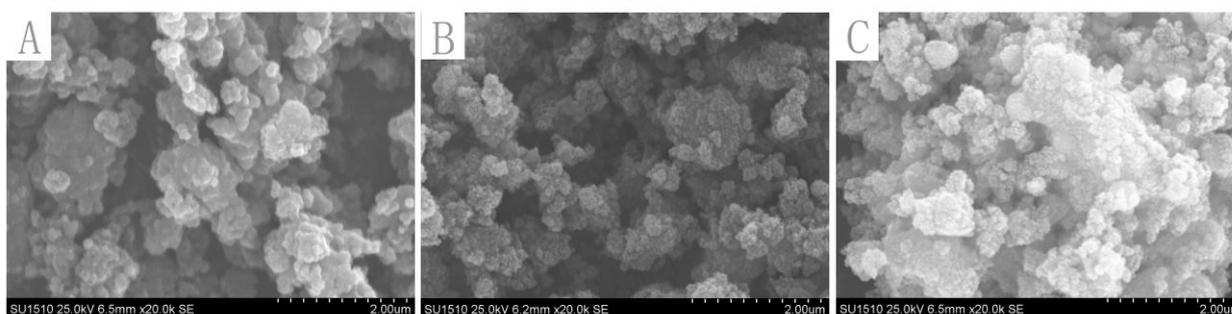
The electrodes were prepared by mixed with 80 wt% of active material, 10 wt% of Super-P carbon as a conductive material and 10 wt% of LA-132 as a binder in water solvent to form homogeneous slurry. The slurry was then coated on an aluminum foil and dried at 100 °C for 10 h in a vacuum oven. Finally, CR2032 coin-type cells were assembled in an argon-filled glove box, using lithium foil as the counter electrode, Celgard 2400 as the separator, and 1 mol/L  $\text{LiPF}_6$  dissolved in a mixture of EC, DEC, DMC with a volume ratio of 1:1:1 as the electrolyte. The coin cells were assembled in an argon-filled glove box. Galvanostatic charge and discharge measurements were performed in a potential range of 1.5-4.8 V at room temperature (25 °C).

### 3. RESULTS AND DISCUSSION



**Figure 1.** XRD profiles of as-prepared  $\text{Li}_2\text{FeSiO}_4/\text{C}$  samples

The X-ray diffraction patterns of the as-received samples are shown in Fig. 1. It can be seen that no impurities were detected in the as-synthesised  $\text{Li}_2\text{FeSiO}_4$  samples. The main diffraction peaks are in good agreement with the previous report by Nishimura et al. [30]. Then we identified it as  $\text{Li}_2\text{FeSiO}_4$  phase with good crystallization fitted using  $P2_1$  space group (PDF#97-024-0207). There is no evidence of diffraction peaks for carbon, indicating that the carbon is amorphous[4]. Carbon-sulfur analysis confirms that the carbon contents of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites are 11.0%, 13.6% and 16.5%, respectively.



**Figure 2.** SEM images of the  $\text{Li}_2\text{FeSiO}_4$  samples: (A)  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 11.0% carbon; (B)  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon; (C)  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 16.5% carbon

Fig.2 shows the influence of carbon coating on the SEM images of three samples. Cleraly, As the content of carbon increases from 11.0% to 16.5%, the size of the  $\text{Li}_2\text{FeSiO}_4$  primary particles tends to reduce, which might be due to the presence of carbon hindering the growth of  $\text{Li}_2\text{FeSiO}_4$  particles during the calcination process[31]. However, larger agglomeration is observed in the SEM when the content of carbon reaches 16.5%. It is due to the agglomeration of carbon particles as the carbon content is high. As a result, the  $\text{Li}_2\text{FeSiO}_4$  primary particles poorly disperse and agglomerate dramatically[12].

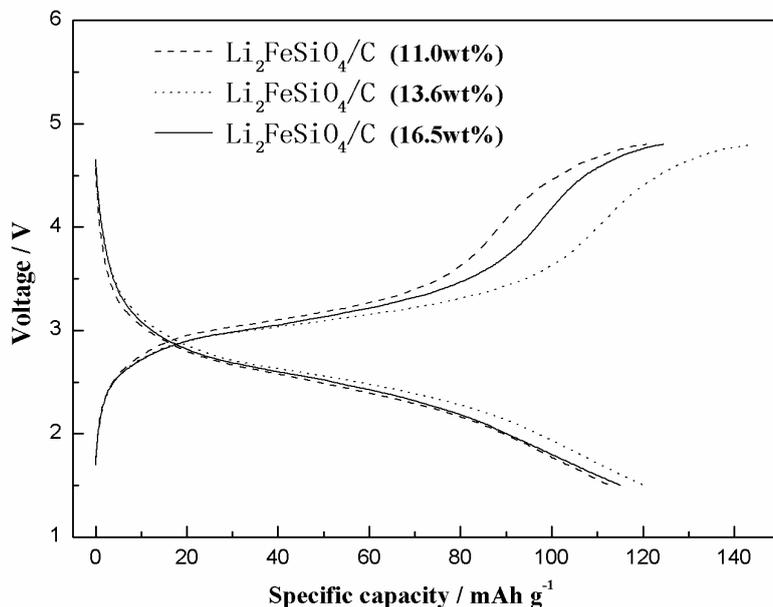


Figure 3. The charge and discharge curves for  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites.

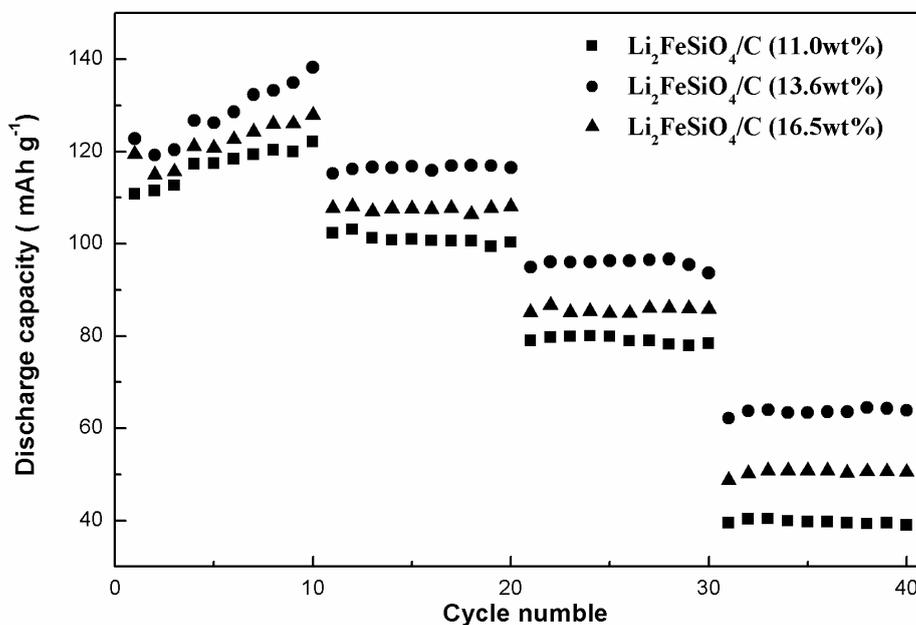
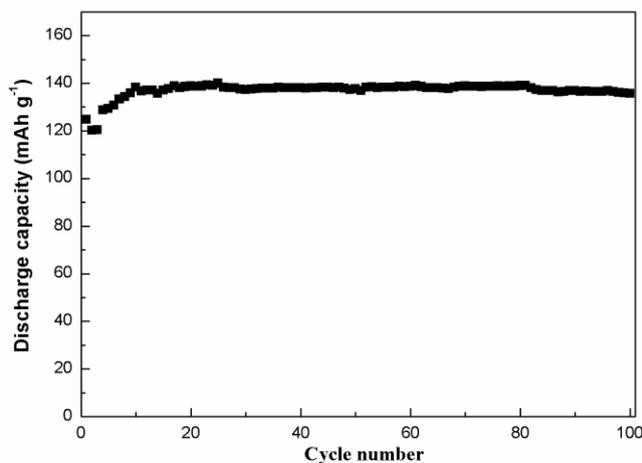


Figure 4. Cyclic performance of  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites at difference rates

Fig.3 shows the third charge-discharge capacity plateaus vs. the working voltage at 0.2C. As evidenced, three samples show similar charge-discharge curves with potential plateaus, which corresponds to the lithium deintercalation and intercalation process. Furthermore, the difference between the charge and discharge plateau potentials of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon is smaller than that of other  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites. According to recent reports[32-35], the small voltage difference between charge and discharge plateaus of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon is representative of its better kinetics, especially on consideration of the low electrochemical diffusion rate of lithium ions in a solid phase and the poor electronic conductivity. This suggests smaller electrode resistance and excellent transport properties of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon.

Fig.4. shows cyclic performance of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites at various charge-discharge rates from 0.2 C, 0.5 C, 1.0 C to 2C. As seen clearly, the discharge capacities decrease with increasing the rate for three samples. However, the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon delivers a relatively higher capacities and better rate capacities in comparison with other  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites. The maximum discharge capacity measured for the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon at a rate of 0.2 C, 0.5 C, 1C and 2 C is  $138 \text{ mAh g}^{-1}$ ,  $117 \text{ mAh g}^{-1}$ ,  $96 \text{ mAh g}^{-1}$  and  $64 \text{ mAh g}^{-1}$ , respectively. Without a doubt, the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon exhibits much better rate capacity than the other  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites. As well known[31], the small particle size is key to improve the electrochemical performance for it shorts the distance of  $\text{Li}^+$  diffusion in the solid phase. Therefore, the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon shows better electrochemical performance compared with the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 11.0% carbon. Unfortunately, serious agglomeration of the  $\text{Li}_2\text{FeSiO}_4$  results in the difficult activation of the cathode [12], property of  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 16.5% carbon fades slightly in comparison with the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon.



**Figure 5.** Cyclic performance of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with at 0.2 C

The cycle performance of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% carbon was studied up to 100 cycles at a rate of 0.2 C, and the results are described in Fig.5. As shown, the maximum discharge

capacity of  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite is  $138 \text{ mAh g}^{-1}$ , and 97.1 % of the maximum discharge capacity after 100 cycles is remained. This result indicates that the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite has good cycle performance.

#### 4. CONCLUSIONS

The phase-pure  $\text{Li}_2\text{FeSiO}_4$  samples were successfully prepared by a citric acid-assisted sol-gel method. The effect of the carbon content on the structure, morphological, and electrochemical performance of the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites were investigated and the optimal carbon content was determined to be 13.6%. The  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composite with 13.6% shows a uniform particle distribution, and thus exhibits excellent electrochemical characteristics with a maximum discharge capacity of  $138 \text{ mAh g}^{-1}$  at 0.2 C, and remains 97.1 % of the maximum discharge capacity after 100 cycles.

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#### References

1. S. Zhang, C. Deng, S. Y. Yang, *Electrochem. Solid-State Lett.* 12 (2009) A136- A139.
2. Z. L. Gong, Y. X. Li, G. N. He, J. Li, Y. Yang, *Electrochem. Solid-State Lett.* 11 (2008) A60- A63.
3. Z. P. Yang, S. Cai, X. Zhou, Y. M. Zhao, L. J. Miao, *J. Electrochem. Soc.* 159 (2012) A894- A898.
4. Z. M. Zheng, Y. Wang, A. Zhang, T. R. Zhang, F. Y. Cheng, Z. L. Tao, J. Chen, *J. Power Sources* 198(2012)229-235.
5. M. Zheng, Q. P. Chen, Z. X. Xi, Y. G. Hou, Q. L. Chen, *J. Mater. Sci.* 47 (2012) 2328-2332.
6. D. Ensling, M. Stjernedahl, A. Nyten, T. Gustafsson, J. O. Thomas, *J. Mater. Chem.* 19 (2009) 82-88.
7. R. Dominko, *J. Power Sources* 184(2006)462-468.
8. S. Zhang, C. Deng, B. L. Fu, S. Y. Yang, L. Ma, *J. Electroanal. Chem.* 644 (2010) 150-154.
9. K. C. Kam, T. Gustafsson, J. O. Thomas, *Solid State Ionics* 192 (2011) 356-359.
10. B. Shao, I. Taniguchi, *J. Power Sources* 199 (2012) 278-286
11. Z. P. Yan, S. Cai, L. J. Miao, X. Zhou, Y. M. Zhao, *J. Alloys Compd.* 511 (2012) 101-106.
12. H. J. Guo, K. X. Xiang, X. Cao, X. H. Li, Z. X. Wang, L. M. Li, *Trans. Nonferrous Met. Soc. China* 19 (2009) 166-169.
13. L. M. Li, H. J. Guo, X. H. Li, Z. X. Wang, W. J. Peng, K. X. Xiang, X. Cao, *J. Power Sources* 189 (2009) 45-50.
14. X. B. Huang, X. Li, H. Y. Wang, Z. L. Pan, M. Z. Qu, Z. L. Yu, *Solid State Ionics* 181 (2010) 1451-1455
15. B. Huang, X. D. Zheng, M. Lu, *J. Alloys Compd.* 525 (2012) 110-113.
16. X. B. Huang, X. Li, H. Y. Wang, Z. L. Pan, M. Z. Qu, Z. L. Yu, *Electrochim. Acta* 55 (2010) 7362-7366.
17. S. Zhang, C. Deng, B. L. Fu, S. Y. Yang, L. Ma, *Electrochim. Acta* 55 (2010) 8482-8489.

18. C. Deng, S. Zhang, S. Y. Yang, B. L. Fu, L. Ma, *J. Power Sources* 196 (2011) 386–392.
19. H. Hao, J. B. Wang, J. L. Liu, T. Huang, A. S. Yu, *J. Power Source* 210 (2012) 397-401.
20. K. Gao, J. Zhang, S. D. L, *Materials Chemistry and Physics*, 139 (2013) 550-556.
21. D. P. Lv, J. Y. Bai, P. Zhang, S. Q. Wu, Y. X. Li, W. Wen, Z. Jiang, J. X. Mi, Z. Z. Zhu, Y. Yang, *Chem. Mater.* 25 (2013) 2014–2020.
22. G. Peng, L. L. Zhang, X. L. Yang, S. Duan, G. Liang, Y. H. Huang, *J. Alloys Compd.* 570 (2013) 1-6.
23. H. T. Zhou, M. A. Einarsrud, V. B. Friddle, *J. Power Source* 235 (2013) 234-242.
24. J. L. Yang, X. C. Kang, D. P. He, T. Peng, L. Hu, S. C. Mu, *J. Power Source* 242 (2013) 171-178.
25. R. Malik, D. Burch, M. Bazant, G. Ceder, *Nano Lett.* 10 (2010) 4123–4127.
26. M. S. Islam, D. J. Driscoll, C. A. J. Fisher, P. R. Slater, *Chem. Mater.* 17 (2005) 5085-5092.
27. R. N. Sckock, Point Defects in Minerals, American Geophysical Union, Washington.D.C.1985.
28. X. B. Huang, H. H. Chen, S. B. Zhou, Y. D. Chen, J. F. Yang, Y. R. Ren, H. Y. Wang, M. Z. Qu, Z. L. Pan, Z. L. Yu, *Electrochim. Acta*, 60 (2012) 239-243.
29. X. B. Huang, H. H. Chen, H. Y. Wang, S. B. Zhou, Y. D. Chen, J. F. Yang, B. P. Liu, G. D. Zhou, Q. L. Jiang, M. Z. Qu, Z. L. Pan, Z. L. Yu, *Solid State Ionics* 220 (2012) 18-22.
30. S.-I. Nishimura, S. Hayase, R. Kanno, M. Yashima, N. Nakayama, A. Yamada, *J. Am. Chem. Soc.* 130 (2008) 13212-3213.
31. P. J. Zuo, T. Wang, G. Y. Cheng, X. Q. Cheng, C. Y. Du, G. P. Yin, *RSC Adv.* 2 (2012) 6994-6998.
32. Y. H. Nien, J. R. Carey, J. S. Chen, *J. Power Sources* 193 (2009) 822-827.
33. H. Ning, C. Y. Wang, X. Y. Kang, T. Wumair, Y. Han, *J. Alloys Compd.* 503 (2010) 204-208
34. J. L. Li, T. Suzuki, K. Naga, Y. Ohzawa, T. Nakajima, *Mater. Sci. Eng. B* 142 (2007) 86–92.
35. B. F. Wang, Y. L. Qiu, S. Y. Ni, *Solid State Ionics* 178(2007) 843-847.

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