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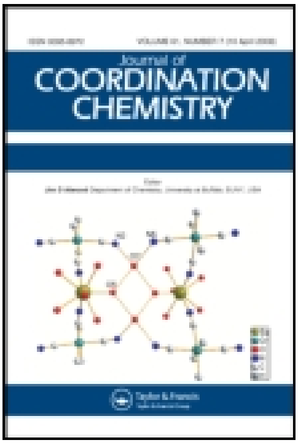

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Greener solid state synthesis of a ternary lanthanum complex at room temperature

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Wet chemical synthesis of rare-earth complexes often requires large amounts of solvents to dissolve reactants, and the use of base to neutralize acidic solution. We have explored a green alternative route that involves solid-state synthesis of ternary lanthanum complex at room temperature by using lanthanum chloride hydrate ($LaCl_3 \cdot 6H_2O$), sodium p-hydroxybenzoate (PBA), and 8-hydroxyquinoline (8-hq). The structure and composition of the ternary lanthanum complex were confirmed by microanalysis, Fourier transform infrared (FT-IR), UV-Vis, X-ray diffraction (XRD), electron diffraction, and thermogravimetric analysis. UV-Vis and FT-IR spectra confirms coordination of lanthanum ion with two ligands and XRD results show that signals of the product are not from the three reactants, and are believed to originate from the ternary lanthanum complex prepared by solid-state reaction. Effects of reaction conditions such as molar ratios and synthetic method on the formation of ternary lanthanum complex were also investigated. The structure and composition of the ternary lanthanum complex are independent of molar ratios of reactants. Compared to the ternary lanthanum complex prepared *via* solution-phase synthesis, although the ternary lanthanum complex prepared by solid-state reactions has the same composition and structure, the synthesis is scalable and greener.

Keywords: Solid state synthesis; Ternary lanthanum complex; X-ray techniques; Coordination

1. Introduction

Rare-earth complexes have been widely used in luminescent, magnetic, and biomedical materials [1–6]. The coordination chemistry of rare-earth ions plays an important role in the synthesis and application of functional materials. Over the past few years much work has been done to design and synthesize ternary rare-earth complexes using solution-based processes [7–12]. However, solution-phase synthesis of ternary rare-earth complexes has normally been in alcohol/water co-solvent systems, and base has usually been involved.

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The low heating solid state coordination method is a simple and effective method to prepare a series of compounds and functional materials. Over the past few decades, a large number of compounds and nanomaterials including transition metal complexes, cathode materials, metal oxide composites, clusters, nanoparticles, and nanorods have been synthesized using this method [13–22]. In comparison with solution-based processes, many compounds can be obtained *via* this facile and greener method without using solvent. To the best of our knowledge, solid-state synthesis of ternary rare-earth complexes has been rarely reported, preliminary work in our group aimed at the synthesis, characterization of binary rare-earth complexes as well as ternary rare-earth complexes derived from sodium salicylate (Sal) and 8-hydroxyquinoline (8-hq) [23, 24]. Herein, we extend our previous approach and synthesize the ternary lanthanum complex by room temperature solid-state reaction of lanthanum chloride hydrate ($LaCl_3 \cdot 6H_2O$), sodium p-hydroxybenzoate (PBA) and 8-hq. Full characterization and detailed studies on the composition and structure of the ternary lanthanum complex were investigated. The feasible and greener synthetic method makes possible large-scale synthesis of rare-earth complexes as well as lanthanide coordination materials at room temperature.

2. Experimental

2.1. *Materials*

$LaCl_3 \cdot 6H_2O$ was obtained by dissolving corresponding oxide (99.99%, Shanghai Yuelong, China) in $6\,\mathrm{mol\,L^{-1}}$ HCl, the resulting solution was evaporated and dried in vacuum to give the product as a light yellow solid. Sodium p-hydroxybenzoate (PBA, AR), 8-hydroxyquinoline (8-hq, AR), and absolute ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received.

2.2. *Synthesis of ternary rare-earth complexes*

In a typical synthesis, accurately weighed PBA and 8-hq were ground, respectively, in an agate mortar to give a fine powder, two ligands were then mixed and ground for a further 10 min, followed by addition of the appropriate amount of $LaCl_3 \cdot 6H_2O$ with continuous grinding. The mixture gradually turned yellow, indicating the occurrence of solid-state reactions of lanthanum ions with both ligands. The resulting mixture was continued grinding at room temperature for 1 h before washing with deionized water and absolute ethanol three times. The obtained precipitates were then dried *in vacuum* at 80°C for 12 h to give the product as yellow solids.

Solid-state reactions of ternary lanthanum complexes using different molar ratios of reactants were also investigated; moreover, solution-phase synthesis of ternary lanthanum complexes using precipitation method reported by Wang *et al.* [25] was further studied for reference.

2.3. *Characterization*

Elemental analyses (C, H, N) were carried out using a Flash 111A elemental analyzer. UV-Vis spectra were recorded from 200 to 600 nm using a Shimadzu UV2450 spectrometer. Fourier transform infrared (FT-IR) spectra were recorded from 4000 to

400 cm^{-1} using a Nicolet Nexus 470 IR spectrometer with KBr pellets and operating in the transmittance mode. X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8 Superseed X-ray diffractometer using Ni-filtered Cu-Kα radiation (40 kV, 250 mA). Electron diffraction of the obtained products was analyzed by transmission electron microscopy (TEM, JEOL JEM-2100). Thermogravimetric analysis (TGA) of as-prepared samples was recorded on a Netzsch STA 449C simultaneous thermal analyzer from 25°C to 800°C.

3. Results and discussion

3.1. *Elemental analysis results*

The reaction conditions used for the synthesis of ternary lanthanum complexes as well as elemental analysis results are shown in table 1. Either in solid-state reactions or in solution-phase reactions, the ratios of reactants have no effects on the composition of ternary lanthanum complexes. All ternary lanthanum complexes have a general formula of La(PBA)(hq)$_2$.

3.2. *UV-Vis spectra*

In figure 1(a), the spectrum of 8-hq shows peaks at 243 and 318 nm, corresponding to π–π* transition from quinoline ring while the spectrum of PBA exhibits a peak at 251 nm assigned to a π–π* transition from benzene. Obvious changes were observed in ternary lanthanum complex samples where only two peaks are found at 269 and 380 nm, respectively, suggesting coordination of lanthanum with PBA and 8-hq. The red shift is caused by decrease in energy between two energy levels because of the redistribution of energy after coordination. The similarity in the spectra of SPR001 and SSR001 reveals that the synthetic method does not affect the composition and structure of the ternary lanthanum complex. No evidence was found for shifts in figure 1(b) when different ratios of reactants were employed in solid-state reactions for control experiments.

3.3. *IR spectra*

As shown in figure 2(a), three characteristic peaks appear in the IR spectra of 8-hq, the peak at 1223 cm^{-1} attributed to O–H bending and two peaks at 1093 cm^{-1} and

Table 1. Reaction conditions for synthesis of ternary lanthanum complex.

	mmol			Elemental analysis			
Sample	RE	PBA	8-hq	C (%)	H (%)	N (%)	Structure
SSR001	10, La^{3+}	10	20	53.11 (53.21)	3.17 (3.04)	5.11 (4.96)	La(PBA)(hq)$_2$
SPR001	10, La^{3+}	10	20	53.07 (53.21)	3.11 (3.04)	5.08 (4.96)	La(PBA)(hq)$_2$
SSR002	10, La^{3+}	10	10	53.09 (53.21)	3.14 (3.04)	5.01 (4.96)	La(PBA)(hq)$_2$
SPR002	10, La^{3+}	10	10	53.10 (53.21)	3.09 (3.04)	5.09 (4.96)	La(PBA)(hq)$_2$
SSR003	10, La^{3+}	20	10	53.02 (53.21)	3.15 (3.04)	5.04 (4.96)	La(PBA)(hq)$_2$
SPR003	10, La^{3+}	20	10	53.01 (53.21)	3.19 (3.04)	5.07 (4.96)	La(PBA)(hq)$_2$

SSR: solid-state reactions, SPR: solution-phase reactions; Numbers in brackets are data after calculation.

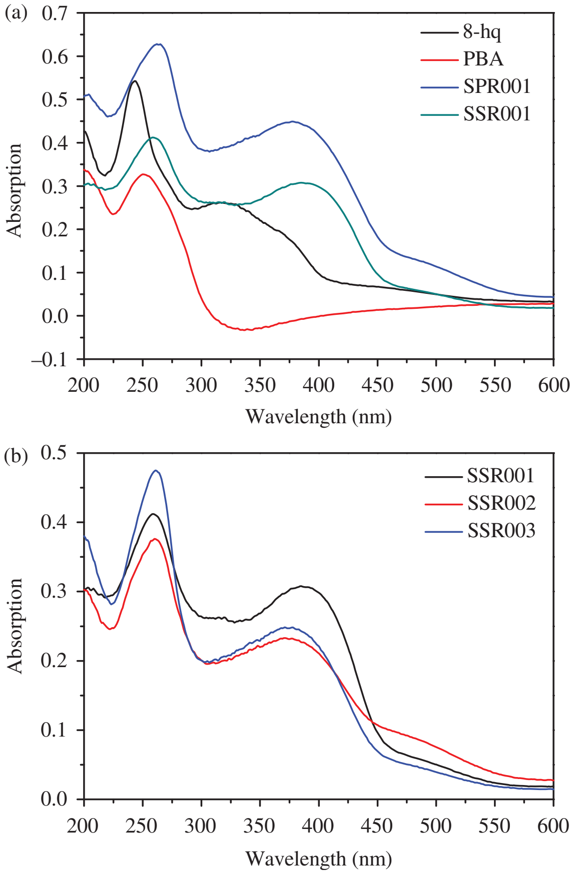

Figure 1. (a) UV-Vis spectra of ligands and (b) ternary lanthanum complex.

1578 cm^{-1} correspond to C–O and C=N stretching vibrations, respectively. Three main peaks in the IR spectra of PBA are 1412 cm^{-1} and 1547 cm^{-1} assigned to symmetric and asymmetric stretching vibrations of COO group, and 1259 cm^{-1} for the bending vibration of O–H. However, in the IR spectrum of SSR 001, sharp peaks corresponding to symmetric (ν_s), asymmetric stretching (ν_{as}) vibrations of COO group and $\nu_{C=N}$ of O–H exhibit obvious shifts, from 1412 cm^{-1}, 1547 cm^{-1}, and 1578 cm^{-1} to lower frequency 1383 cm^{-1}, 1497 cm^{-1}, and 1569 cm^{-1}, indicating chelation of lanthanum with both PBA and 8-hq. The difference between symmetric (ν_s, 1412 cm^{-1}) and asymmetric stretching (ν_{as}, 1547 cm^{-1}) vibrations of COO group ($\Delta\nu = 135$ cm^{-1}, PBA), $\Delta\nu = 114$ cm^{-1} for SSR 001 is indicative of bidentate chelation of lanthanum with PBA [26]. In the IR spectrum of SSR001, bending vibration ($\delta_{O\text{–}H}$, 8-hq) at 1223 cm^{-1} disappears and the stretching vibration ($\nu_{C=N}$, 8-hq) at 1093 cm^{-1} moves to higher frequency, also suggesting coordination of lanthanum with 8-hq. No evidence was found for shifts or changes in IR spectra of SSR001 and SPR001. Different molar ratios of reactants have no effects on the formation of ternary lanthanum complex (figure 2b).

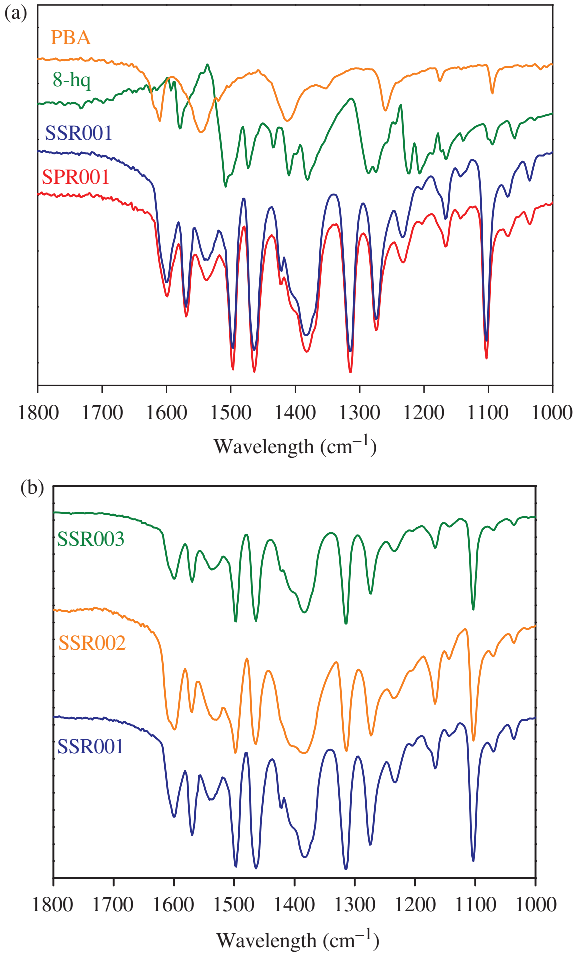

Figure 2. (a) FT-IR spectra of ligands and (b) ternary lanthanum complex.

3.4. *XRD results*

Figure 3(a) and (b) exhibits the XRD patterns of lanthanum chloride, 8-hq, PBA, and the ternary lanthanum complex SSR001 prepared from solid-state reaction. It is clearly shown that no signal from the three reactants was detected in the XRD pattern of SSR001 and new peaks were found, although the intensities are weak, suggesting completion of the solid-state reactions at room temperature. Figure 3(c) shows the XRD patterns of SSR001, SSR002, and SSR003 prepared using different molar ratios of reactants. The similarity in the XRD patterns of three complexes indicates that solid-state reactions of $LaCl_3 \cdot 6H_2O$ with 8-hq and PBA result in the same product La(PBA)(hq)$_2$, consistent with the results obtained from UV-Vis and IR spectra. Figure 3(d) demonstrates the XRD patterns of two ternary lanthanum complexes SSR001 and SPR001; the complexes formed using two different methods have the same structures as described above. Further investigation of phases of SSR001 and SPR001

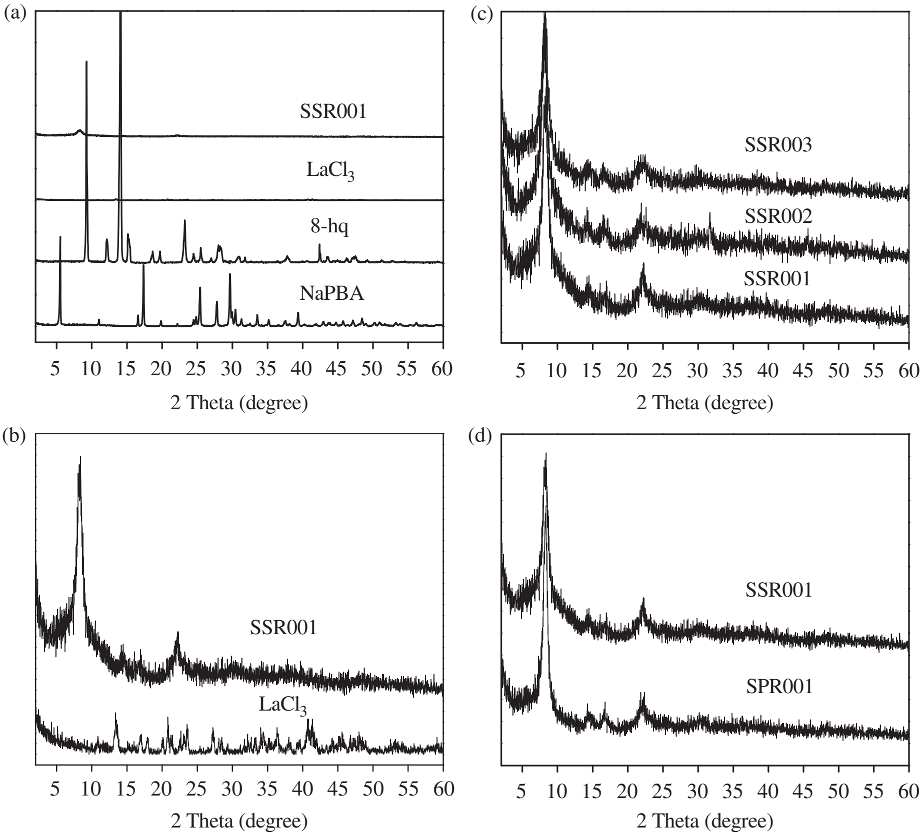

Figure 3. XRD patterns of reactants and ternary lanthanum complex.

was carried out by using electron diffraction and it is clearly shown in figure 4(a) and (b) that both SSR001 and SPR001 are non-crystalline, confirming that low-heating solid-state reaction is insufficient for formation of crystalline ternary lanthanum complex in our work, which is consistent with weak intensities and board peaks of ternary lanthanum complexes either prepared from solid-state reactions or solution-phase reactions.

3.5. *Thermal analysis*

The TGA of SSR001 and SPR001 is shown in figure 5 between 25°C and 800°C where major weight losses occurred from 150°C to 700°C. Similar trends were observed in TGA curves of both complexes where weight losses of SSR001 occurred in three stages, first stage from removal of any remaining water and solvents before 150°C with mass loss of 1.11%; the next two stages suggest decomposition of SSR001 with a maximum endothermic peak of 495°C with a major weight loss of 25%. While a mass loss of 2.08% was observed in the first stage, the major weight loss of 22.1% was found in two following steps of SPR001 in TGA with a maximum endothermic peak of 505°C.

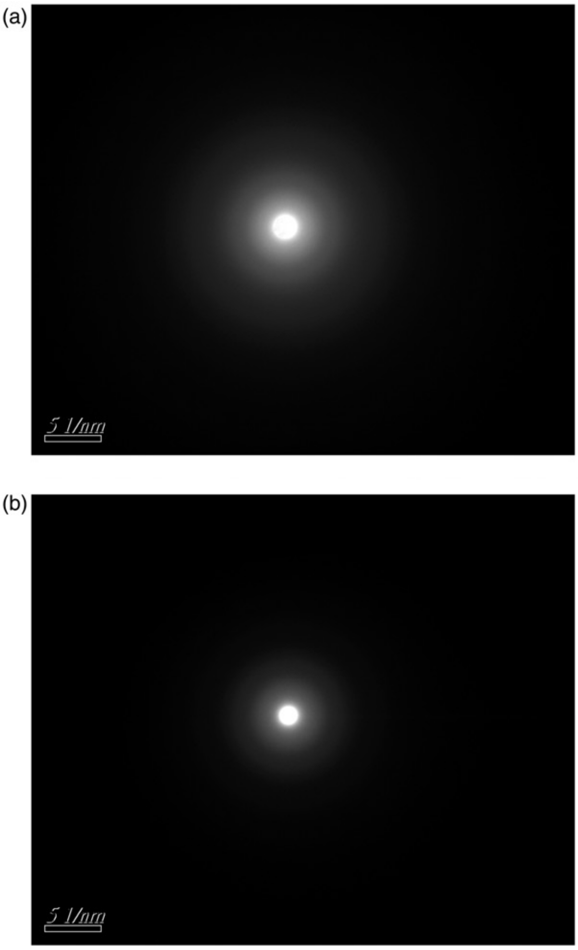

Figure 4. Electron diffraction of as-prepared samples.

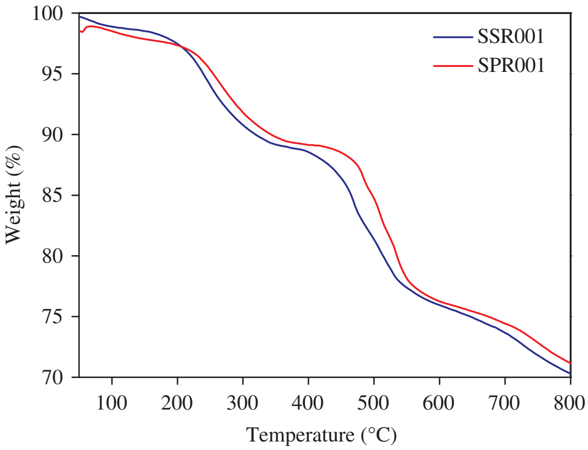

Figure 5. TG curves of as-prepared samples.

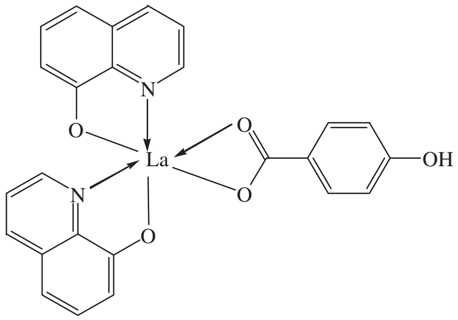

Figure 6. General structure of ternary lanthanum complex.

In comparison with lower decomposition temperature of 8-hq and PBA from 200°C to 250°C, ternary lanthanum complex showed better thermal stability.

On the basis of above results, general structure of as-synthesized ternary lanthanum complexes is proposed and shown in figure 6.

4. Conclusions

Ternary lanthanum complex, La(PBA)(hq)$_2$, was synthesized *via* a facile and greener solid-state reaction of $LaCl_3 \cdot 6H_2O$ with 8-hq and PBA; solution-phase synthesis of La(PBA)(hq)$_2$ was investigated for comparison. All the complexes were characterized by microanalysis, UV-Vis, FT-IR, XRD, electron diffraction, and TGA, ranging from composition and structure to thermal stability. The results illustrate that, compared to the lanthanum complex made from a solution-phase reaction, the same non-crystalline ternary lanthanum complex with relatively high thermal stability can be prepared *via* a one-step solid-state reaction at room temperature without using solvents and adjusting pH. This work is of general interest to the development of environmentally friendly processes for large-scale synthesis of rare-earth complexes and functional materials.

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References

[1] E.G. Moore, A.P.S. Samuel, K.N. Raymond. *Acc. Chem. Res.*, **42**, 542 (2009).
[2] J.C.G. Bunzli. *Acc. Chem. Res.*, **39**, 53 (2006).
[3] W. Feng, L.D. Sun, Y.W. Zhang, C.H. Yan. *Coord. Chem. Rev.*, **254**, 1038 (2010).

[4] A.G. Gurek, T. Basova, D. Luneau, E. Koltsov, A.K. Hassan, V. Ahsen. *Inorg. Chem.*, **45**, 1667 (2006).
[5] W.L. Sun, S.A. Liu, B.J. He, J.B. Tang, Z.Q. Shen. *Phys. Lett. A*, **328**, 463 (2004).
[6] P. Gawryszewska, J. Sokolnicki, J. Legendziewicz. *Coord. Chem. Rev.*, **249**, 2489 (2005).
[7] W.X. Li, W.J. Chai, X.J. Sun, T. Ren, X.Y. Shi. *J. Fluoresc.*, **20**, 873 (2010).
[8] W.X. Li, Y.S. Zheng, X.J. Sun, W.J. Chai, T. Ren, X.Y. Shi. *J. Lumin.*, **130**, 1455 (2010).
[9] B.S. Murray, D. Parker, C.M.G. dos Santos, R.D. Peacock. *Eur. J. Inorg. Chem.*, 2663 (2010).
[10] L.L. Ruston, G.M. Robertson, Z. Pikramenou. *Chem. Asian J.*, **5**, 571 (2010).
[11] J. Wu, H.Y. Li, Q.L. Xu, Y.C. Zhu, Y.M. Tao, H.R. Li, Y.X. Zheng, J.L. Zuo, X.Z. You. *Inorg. Chim. Acta*, **363**, 2394 (2010).
[12] D.F. Xu, Y.M. Xu, N.N. Cheng, X.A. Zhou, Y. Shi, Q.Z. He. *J. Coord. Chem.*, **63**, 2360 (2010).
[13] Y.L. Cao, W.Y. Pan, Y. Zong, D.Z. Jia. *Sensors Actuators B*, **138**, 480 (2009).
[14] J. Zhou, D.G. Su, J.M. Luo, M.F. Zhong. *Mater. Res. Bull.*, **44**, 224 (2009).
[15] L. Liu, L. Wang, D.Z. Jia. *J. Coord. Chem.*, **61**, 1019 (2008).
[16] T. Li, W.H. Qiu, G.H. Zhang, H.L. Zhao, J.J. Liu. *J. Power Sources*, **174**, 515 (2007).
[17] Y.D. Huang, J. Li, D.Z. Jia. *J. Nanoparticle Res.*, **6**, 533 (2004).
[18] X.C. Tang, L.P. He, Z.Z. Chen, D.Z. Jia. *J. Inorg. Mater.*, **18**, 313 (2003).
[19] H. Yu, Q.F. Xu, Z.R. Sun, S.J. Ji, J.X. Chen, Q. Liu, J.P. Lang, K. Tatsumi. *Chem. Commun.*, **24**, 2614 (2001).
[20] X.Q. Xin, L.M. Zheng. *J. Solid State Chem.*, **106**, 453 (1993).
[21] Y.L. Cao, D.Z. Jia, J. Zhou, Y. Sun. *Eur. J. Inorg. Chem.*, 4105 (2009).
[22] Z.P. Sun, L. Liu, L. Zhang, D.Z. Jia. *Nanotechnology*, **17**, 2266 (2006).
[23] Q.Z. He, X.F. Yang, H.B. Guo, Y.Y. Yuan. *Mater. Lett.*, **57**, 3609 (2003).
[24] X.F. Yang, Q.Z. He, X.B. Yu, Y.Y. Yuan, H. Min. *Synth. React. Inorg. Met-Org. Chem.*, **34**, 67 (2005).
[25] Z.M. Wang, J.R. Cao, H.F. Yang. *J. Shanghai Normal Univ. (Nat. Sci.)*, **25**, 42 (1996).
[26] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1986).