

## Preparation of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ phosphor by molten salt assisted method

HUANG Yan(黄燕)<sup>1,2,3</sup>, YE Hong-qi(叶红齐)<sup>1</sup>, ZHUANG Wei-dong(庄卫东)<sup>2</sup>,  
HU Yun-sheng(胡运生)<sup>2</sup>, ZHAO Chun-lei(赵春雷)<sup>2</sup>, LI Cui(李萃)<sup>2</sup>, GUO Song-xia(郭松霞)<sup>2</sup>

1. School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China;

2. National Engineering Research Center for Rare Earth Materials, General Research Institute for Nonferrous Metals, Beijing 100088, China;

3. Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414000, China

Received 1 September 2006; accepted 11 December 2006

**Abstract:** A kind of fine and quasi-spherical  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  phosphor was prepared by firing a preparative precursor at 1200 °C for 2 h with the molten salts of  $\text{Na}_2\text{CO}_3$ , S and NaCl. The precursor was obtained by homogeneous precipitation of yttrium and europium with oxalic acid when using EDTA, citric acid or starch as complexant. The structure and morphology of the phosphors were characterized by XRD and SEM, respectively. The influence of complexing environment, firing temperature and molten salts on formation of the phosphor  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  was discussed. The result shows that the prepared  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  phosphor is of quasi-spherical structure with size of 2–3 μm. Its luminescent intensity is 30% higher than that of the same phosphor prepared by the same procedure but without molten salts, and is 5% higher than that of commercial  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  red phosphor.

**Key words:**  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ ; molten salt; homogeneous precipitation; morphology; luminescent property

## 1 Introduction

$\text{Y}_2\text{O}_3$  phosphor activated by  $\text{Eu}^{3+}$ , which is widely used in fluorescent lamps, color TV, projective TV etc, is the red component of the tri-color phosphors. With the development of high definition display and solid state lighting, luminescent properties and morphology of phosphors are required to investigate. It is well known that the quality of phosphor relates not only to its purity but also to morphology, particle size and its distribution. In recent years, the research on phosphor is focused on the relationship among its morphology, size and luminescent properties[1–4], and phosphor with fine particle, quasi-spherical, even spherical morphology and high luminescent intensity is desirable. However, it is not easy to reach the balance perfectly.

Generally, phosphor is prepared by solid state reaction technology at high temperature. The phosphor prepared by this method has good quality of crystal and high luminescent efficiency, but large particle size, broad particle distribution and nonuniform morphology.

Spherical phosphor with small particle size can improve brightness, resolution when coated with screen. Therefore, the soft chemical methods, such as co-precipitation, sol-gel, spray pyrolysis, are popular in preparing luminescent materials[5–10]. In this study, co-precipitation was applied to prepare the precursor of  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ , and then the precursor was used to synthesize objective phosphor by molten salt technology. At the same time, the precipitation condition, firing temperature and molten salts on particle size and growth of  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  phosphors were also studied.

## 2 Experimental

### 2.1 Reagents and instruments

Reagents were  $\text{Y}_2\text{O}_3$  (2 mol/L),  $\text{Eu}_2\text{O}_3$  (2 mol/L), oxalic acid(AR), citric acid(AR), NaCl(AR),  $\text{Na}_2\text{CO}_3$  (AR), S(AR) and hydrochloric acid(AR).

HORIBA LA-300 laser scattering particle size analyzer was used to test particle size and the distribution of phosphor. Scanning electron microscope (JSM-6400, JEOL) was used to characterize morphology. XRD

analysis was conducted on X'Pert PRO MPD, PANalytical X-ray diffractometer. FluoroMax-2 spectrophotometer and PMS-50 ultraviolet-visible-near infrared spectrophotometer were used to record emission spectrum, color coordinate, color purity and luminescent intensity of phosphor.

## 2.2 Experimental procedure

Put solution of  $\text{YCl}_3$  and  $\text{EuCl}_3$  into  $80^\circ\text{C}$  water and mix them by magnetic blender. Then  $\text{H}_2\text{C}_2\text{O}_4$  and complexant solutions were dropped into solution of  $\text{YCl}_3$  and  $\text{EuCl}_3$  synchronously at a certain speed. At the same time, pH value was controlled at about 5–6 by dilute ammonia. The obtained deposition was aged in  $80^\circ\text{C}$  water for 1 h. After filtered and dried, three different precursors: A (Solutions of  $\text{YCl}_3$  and  $\text{EuCl}_3+\text{H}_2\text{C}_2\text{O}_4+\text{EDTA}$ ), B (solutions of  $\text{YCl}_3$  and  $\text{EuCl}_3+\text{H}_2\text{C}_2\text{O}_4$ , citric acid and ammonia) and C (solutions of  $\text{YCl}_3$  and  $\text{EuCl}_3+\text{H}_2\text{C}_2\text{O}_4$ , amylaceous solution) were gained.

Then, the precursors A, B and C were directly fired individually at  $1\,200^\circ\text{C}$  for 2 h into phosphors A', B' and C'. On the other hand, the precursors A, B and C mixed with molten salts ( $\text{Na}_2\text{CO}_3+\text{S}+\text{NaCl}$ ) were fired at  $1\,200^\circ\text{C}$  for 2 h into phosphors A'', B'' and C''. These sintered cakes were washed by deionized water and then dried to obtain objective phosphors.

## 3 Results

### 3.1 XRD analysis

Figs.1 and 2 show the X-ray diffraction patterns of phosphors B' and B'', respectively. Their diffraction positions and relative strength are all in agreement with those of standard card (JCPDS 25–1011) of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ . This means that the molten salts have not brought about impurities at  $1\,200^\circ\text{C}$ . Phosphor B'' prepared with molten salts also belongs to cubic crystal system. By comparing Fig.1 with Fig.2, phosphor B'' with molten salts has a narrower diffraction peak and higher diffractive intensity

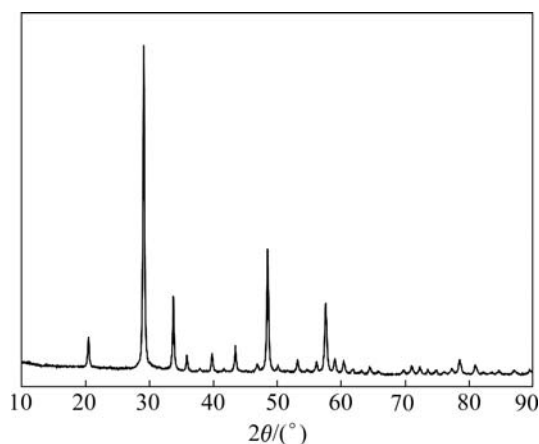


Fig.1 XRD pattern of phosphor B'

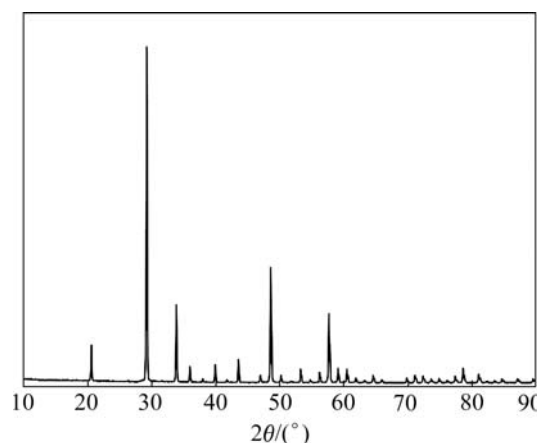


Fig.2 XRD pattern of phosphor B''

than phosphor B' without molten salt. This proves that molten salts can improve the crystallinity of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ , because molten salts can provide a more stable and even temperature field.

### 3.2 Emission spectra

Fig.3 shows the emission spectra of phosphors A', B' and C'. As shown in Fig.3, phosphor B' with citric acid as complexant has the strongest emission intensity. The comparison of the emission spectra of phosphors B', B'' with that of commercial  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  is shown in Fig.4. It can be seen that: 1) Phosphors B' and B'' exhibit the same emission as the commercial one. It is the characteristic emission of trivalent  $\text{Eu}^{3+}$  ion, and the main peak is located at 611 nm, which is attributed to the transition of  $4f-5d$  of  $\text{Eu}^{3+}$ . This proves once again that the molten salts do not make the change of the crystal structure of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphor. 2) The emission intensity

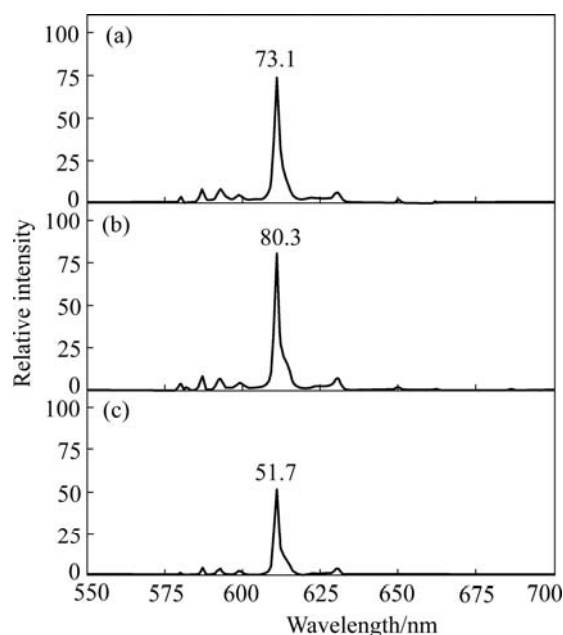


Fig.3 Emission spectra of phosphors A' (a), B' (b) and C' (c)

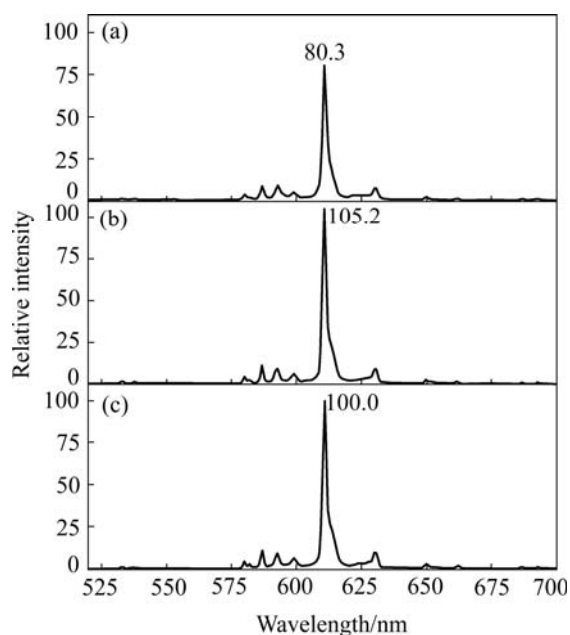


Fig.4 Comparison of emission spectra of phosphors B' (a), B'' (b) and commercial  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  (c)

of phosphor B'' produced with molten salts is 30% higher than that of phosphor B' without molten salt. This implies that the molten salts can promote the crystalline degree and will not produce impurities that are harmful to the luminescence of phosphor. 3) The emission intensity of phosphor B'' with molten salts is 5% higher than that of commercial phosphor.

Generally,  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphor is synthesized by high temperature solid state reaction technology at around 1 400 °C. With the assist action of molten salts, the temperature is reduced to 1 200 °C in the procedure.

### 3.3 SEM analysis

Figs.5 and 6 show the SEM images of phosphors B'' and A', respectively. It is obvious that phosphor B'' shows quasi-spherical morphology with particle size of 2–3  $\mu\text{m}$ , while B' shows quasi-cubic morphology with heavy agglomerate phenomenon. This phenomenon proves that the transformation of morphology originates

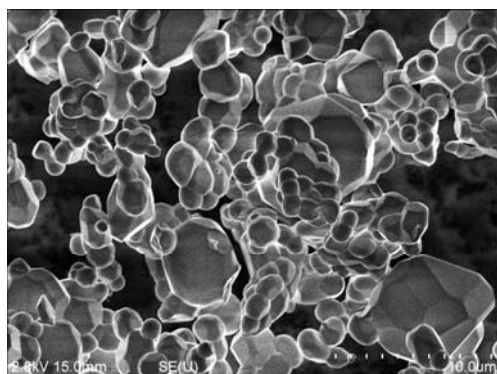


Fig.5 SEM image of phosphor B''

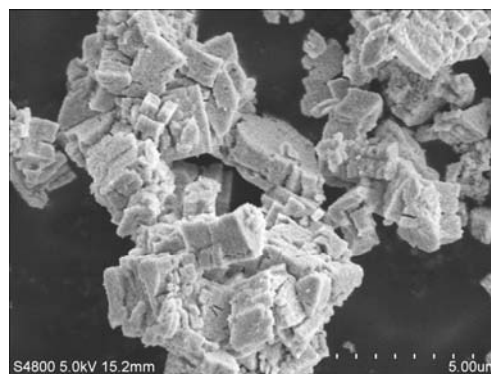


Fig.6 SEM image of phosphor A'

from the action of molten salts. That is to say, the ( $\text{Na}_2\text{CO}_3+\text{S}+\text{NaCl}$ ) molten salts system has influence on the growth surroundings of crystal. At the same time, it is easy to find that the particle size of B'' is bigger than that of A' because the molten salts can promote the growth of crystal.

## 4 Discussion

### 4.1 Effect of precipitation condition

#### 4.1.1 Influence of precipitator concentration on particle size of precursor

Fig.7 shows the influence of the concentration of precipitator  $\text{C}_2\text{O}_4^{2-}$  on particle size of precursor B. It is obvious that particle size of precursor B decreases with the increase of precipitator concentration when the concentration is less than 0.5 mol/L, while the particle size becomes larger when the concentration is beyond 0.5 mol/L. The reason is that when the precipitator concentration is too low, it will take much time to become nucleus, and then the particles grow easily into bigger particles. On the other hand, if the precipitator concentration is too high, it is very easy to become nucleus, agglomerate and accumulate into big floccula-

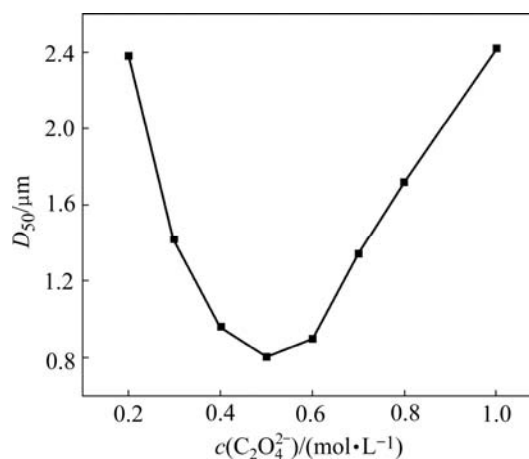


Fig.7 Influence of  $\text{C}_2\text{O}_4^{2-}$  concentration on particle size of precursor B

tion. Therefore, there is an optimum precipitator concentration, resulting from the trade-off of the above two trends; wherein the favorable concentration of precipitator  $\text{C}_2\text{O}_4^{2-}$  is 0.5 mol/L, under which sub-micron precursor can be obtained.

#### 4.1.2 Influence of precipitation temperature

Temperature is an important factor to decide the precipitation speed. Temperature will influence supersaturation and stickiness of the solution, and then affect particle size and uniformity of precipitation particles. According to the speed theory of chemical reaction, the speed of forming nucleus and growth will be accelerated with increase of precipitation temperature, therefore resulting in bigger particle. But at the same time, the increase of temperature accelerates the precipitation process and lowers supersaturation of the solution, so the solubility of precipitation becomes higher, and it is not so easy to form grains. On the other hand, the decrease of temperature will result in viscid solution, which will slow down the movement of precipitation grains in the solution and finally form agglomeration. Therefore, proper temperature control is favorable to the growth of precipitation in good quality. In this experiment, 70–80 °C can make the precipitation fine and uniform.

#### 4.1.3 Effect of complexant

Three kinds of complexants were compared: EDTA, citric acid plus ammonia and amylum. The results show that phosphor B'' prepared with citric acid plus ammonia has the smallest particle size and highest brightness. This is because citric acid plus ammonia takes action as both complexant and buffer reagent. Though the complexometric ability of citric acid with the metal is not as good as EDTA, it can assure  $\text{Y}^{3+}$  and  $\text{Eu}^{3+}$  ion to release successfully. And at the same time, being a good buffer solution, citric acid plus ammonia has good adjustment ability to the pH value during titration. So, during the whole reaction the pH value could be maintained steadily around 5–6 in order to co-precipitate  $\text{Y}^{3+}$  and  $\text{Eu}^{3+}$  in required proportion. Therefore, being a complexant, citric acid plus ammonia is better than EDTA and amylum.

## 4.2 Influence of molten salts on growth of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor

Generally, the morphology of phosphor has close relationship with its growth surroundings[11]. The surroundings can be controlled through salt, temperature and time, etc. In this work, the precursor of phosphor was firstly prepared through co-precipitation method, and then dealt with molten salts assistant technology, and finally red phosphor  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  was obtained. Molten salt

has the following advantages[12–13]: wide work temperature, facile selectivity and being easy to meet the synthesized requirements of different crystal materials, being soluble and easy to be filtered and removed, stable and not to react with host materials, producing and maintaining stable liquid surroundings for reaction and crystal growth, low stickiness, and good liquidity of medium in favor of ion movement and diffusion to accelerate reaction. The above factors assure the reactants ions to move in liquid surroundings and form special morphology. This mechanism is that the surface energy between precursor and molten salts reaches approximately the minimum, thus resulting in special morphology[14–17].

In general, existence of trace solutes will greatly influence surface tension of molten materials. Even if small amount of additive with small surface tension in original state was added, the surface tension of whole molten materials will be decreased apparently[13]. Based on this theory, little sulfur was added into complex molten salts in this study, and the surface tension of molten salts is greatly decreased, which leads to the cubic  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  physically growing to spherical or quasi-spherical morphology. When the temperature increases up to a certain extent, salts melt and liquid surrounding is formed, thus hastening transfer of reactants and speeding up the reaction. At the same time, owing to obstructing effect of molten salts, the resultants will not aggregate, so the fine and non-aggregate particle can be obtained. With the increase of firing time or temperature, molten salts play the role of catalyst, promoting the diffusion of  $\text{Y}^{3+}$ ,  $\text{Eu}^{3+}$  and the ligands, making the activator  $\text{Eu}^{3+}$  easy and well-proportioned to enter host, promoting crystallization degree, decreasing surface defects and improving emission brightness.

## 5 Conclusions

1) By choosing synchronization titration during co-precipitation, sub-micron precursor can be obtained when citric acid plus ammonia is used as complexant.

2) Quasi-spherical  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  red phosphor with particle size of 2–3  $\mu\text{m}$  can be prepared by firing the mixture of precursor and complex molten salts ( $\text{Na}_2\text{CO}_3+\text{S}+\text{NaCl}$ ) at 1 200 °C for 2 h. Its luminescent intensity is 30% higher than that of the same phosphor prepared by the same procedure but without molten salts, and is 5% higher than that of commercial  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  red phosphor.

3) The complex molten salts have good solubility in water and are easy to be washed and removed. They will not bring about impurities and are suitable for producing high-quality phosphor.

## References

- [1] JONG S B, SUNG B K, JUNG H J, JUNG C P, DONG K K, SONG H B, SOUNG Y. Photoluminescence characteristics of Li-doped  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  thin film phosphors [J]. *Thin Solid Films*, 2005, 471: 224–229.
- [2] CHO S H, YOO J S, LEE J D. A new synthetic method to prepare spherical phosphors for emissive screen applications [J]. *Electrochem Soc*, 1998, 145: 1017–1019.
- [3] PHAM-THI M, MORELL A. Process optimization and characterization of the red no-mill phosphor  $\text{Y}_2\text{O}_3\text{:Eu}$  [J]. *Electrochem Soc*, 1991, 138: 1100–1103.
- [4] ZHANG Jia-hua, JIA Ming-li, LU Shao-zhe, LUO Yong-shi, REN Xin-guang, WANG Xiao-jun. Study on UV excitation properties of  $\text{Eu}^{3+}$  at the  $S_6$  site in bulk and nanocrystalline cubic  $\text{Y}_2\text{O}_3$  [J]. *Journal of Rare Earths*, 2004, 22(1): 45–48.
- [5] ZHAI Yong-qing, YAO Zi-hua, DING Shi-wen. Synthesis and characterization of  $\text{Y}_2\text{O}_3\text{:Eu}$  nanopowder via EDTA complexing sol-gel process [J]. *Materials Letters*, 2003, 57: 2901–2906.
- [6] DOSEV D, GUO B, KENNEDY I M. Photoluminescence of  $\text{Eu}^{3+}\text{:Y}_2\text{O}_3$  as an indication of crystal structure and particle size in nanoparticles synthesized by flame spray pyrolysis [J]. *Aerosol Science*, 2006, 37: 402–412.
- [7] SHI Xiao-liang, YANG Hua, SHAO Gang-qin, DUAN Xing-long. Research on ultrafine WC-10Co cemented with high properties [J]. *Journal of Wuhan University of Technology*, 2006, 21(4): 154–157. (in Chinese)
- [8] YANG Zheng-Hui, GONG Zhu-qing, MA Yu-tian, YANG Yu-fang, Li Hong-xu. Preparation and characterization of high-purity  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles [J]. *Journal of Central South University of Technology*, 2006, 13(6): 618–623.
- [9] CHEN Yong-gui, ZHANG Ke-neng, ZOU Yin-sheng, DENG Fei-yue. Removal of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  by adsorption on clay-solidified grouting curtain for waste landfills [J]. *Journal of Central South University of Technology*, 2006, 13(2): 166–170.
- [10] SUN Y, QI L, LEE M, LEE B I, SAMUELS W D, EXARHOS G J. Photoluminescent properties of  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  phosphors prepared via urea precipitation in non-aqueous solution [J]. *Journal of Luminescence*, 2004, 109: 85–91.
- [11] HIRAI T, HIRANO T, KOMASAWA I J. Progress on the study of nanometric luminescent material  $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$  [J]. *Mater Chem*, 2000, 10: 2306–2310.
- [12] LUMSDEN J. *Thermodynamics of Molten Salt Mixtures* [M]. New York: Academic Press, 1966.
- [13] XIE Gan. *Theory and Application of Molten Salts* [M]. Beijing: Metallurgical Industry Press, 1998. (in Chinese)
- [14] KIM J H, MYUNG S T, SUN Y K. Molten salt synthesis of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  spinel for 5V class cathode material of Li-ion secondary battery [J]. *Electrochimica Acta*, 2004, 49(2): 219–227.
- [15] DUPONT J, de SOUZA R F, SUAREZ P A. Ionic liquid (molten salt) phase organometallic catalysis [J]. *Chem Rev*, 2002, 102(10): 3667–3691..
- [16] GOPALAN S, VIRKAR A V. Thermodynamic stabilities of  $\text{SrCeO}_3$  and  $\text{BaCeO}_3$  using molten salt method and galvanic cells [J]. *Electrochem Soc*, 1993, 140(4): 1060–1065.
- [17] SUN Pei-mei, LIU Mao-sheng, HUANG Yong-zhong, LI Yun-jiao. Study on melting salt oxidation technology of molybdenite concentrate [J]. *Journal of Central South University of Technology*: National Science, 2000, 31(5): 407–410.

(Edited by CHEN Wei-ping)