熔盐快速合成 Pb$_{1-x}$La$_x$TiO$_3$ 粉体

蔡宗英 [1,2]　邢献然 [*,1]　邓金侠 [1]　于然波 [1]　刘桂荣 [1]

(^{1} 北京科技大学理化系,北京　100083)

(^{2} 军械工程学院,石家庄　050003)

摘要: 采用全氧化物为原料,利用熔盐法合成了 Pb$_{1-x}$La$_x$TiO$_3$(0.0≤x≤0.40),当 x=0.45 时,烧绿石相 La$_2$Ti$_2$O$_7$ 出现。计算了合成反应活化能,并在 700 ℃下在 NaCl-KCl 体系中仅用 5 min 就合成了 Pb$_{0.9}$La$_{0.1}$TiO$_3$。Pb$_{1-x}$La$_x$TiO$_3$ 陶瓷在 0.00≤x<0.25 时,晶体结构为四方相,在 0.25≤x≤0.40 时为立方相。采用 700 ℃ NaCl-KCl 和 900 ℃的 Na$_2$SO$_4$-K$_2$SO$_4$ 两种熔盐体系获得了尺寸分布集中的球形颗粒,这些表明熔盐法晶体生长为扩散控制生长机理。

关键词: 熔盐合成(MSS);PLT;陶瓷粉末

中图分类号: O645.5　　**文献标识码:** A　　**文章编号:** 1001-4861(2006)08-1421-05

Rapid Synthesis of Pb$_{1-x}$La$_x$TiO$_3$ Powders in Molten Salt Flux

CAI Zong-Ying[1,2]　XING Xian-Ran[*,1]　DENG Jin-Xia[1]　YU Ran-Bo[1]　LIU Gui-Rong[1]

(^{1}*Department of Physical Chemistry, University of Science & Technology Beijing, Beijing* 100083)

(^{2}*Institute of Ordnance Engineering, Shijiazhuang* 050003)

Abstract: Perovskite-type compounds Pb$_{1-x}$La$_x$TiO$_3$ in the composition range of x from 0 to 0.45 were synthesized using simple oxides from 700 ℃ to 1 000 ℃ by molten salt synthesis (MSS) and a small amount of La$_2$Ti$_2$O$_7$ pyrochlore phase was detected in the XRD patterns for x=0.45. The activation energy for particle growth in MSS was calculated, and the Pb$_{0.9}$La$_{0.1}$TiO$_3$ was synthesized at 700 ℃ for only 5 min. The perovskite phase for the material prepared was tetragonal for 0.0≤x≤0.25 and cubic for 0.25≤x≤0.40. The average particle size was different for samples prepared in NaCl-KCl and Na$_2$SO$_4$-K$_2$SO$_4$ system, but the shape was all spherical for samples obtained from both systems. The same spherical shape could be explained by the diffusion control mechanism for the particle growth into spherical shapes.

Key words: molten salt synthesis (MSS); PLT; ceramic powder

0　Introduction

The perovskite-type compounds PbTiO$_3$ and La-doped PbTiO$_3$ are well-known as high dielectric constant ferroelectric materials. Much attention has been paid to the solid solutions of Pb$_{1-x}$La$_x$TiO$_3$ (0≤x<0.45), which are more useful than pure PbTiO$_3$ because of

the existence of cavities in the perovskite structure. Lead lanthanum titanate (PLT) is one of the most important ferroelectric materials because of its excellent dielectric, ferroelectric, pyroelectric and electro-optic properties. These compounds are generally synthesized by solid-state reaction of the corresponding oxides at temperatures >1 000 ℃. Solid-state synthesis has been

extensively used for the fabrication of the perovskite ceramics compounds. However, $Pb_{1-x}La_xTiO_3$ with desired composition is difficult to be synthesized by the high temperature method because of high vapor pressure of the led component at high temperature.

　　Molten salt synthesis (MSS) method has been reported to be one of the simplest techniques to prepare pure, stoichiometric ceramic powders of multicomponent oxides, by using low-melting, water-soluble salt or salt mixture as the reaction aid or medium. Because of the high diffusivities of the components in the molten salt flux, the preparation temperature and time can be significantly reduced compared to the solid-state reaction[1~3]. Various electronic ceramics, such as $BaTiO_3$[4~6], $Bi_4Ti_3O_{12}$[7], ferrite[8~10], lead-based perovskite ceramics[1,2,11~14], have been studied by adjusting the MSS method using chlorides, sulphates or nitrates. Because of the small diffusion distances of oxide mixtures in molten salt solvents, high reactivity of salts and high mobility of species, reactions can be completed in a relatively short time.

　　In the present work, the preparation of single-phase $Pb_{1-x}La_xTiO_3$ (0.0<x<0.40) powders by molten salt method is described. The oxides and salt were reacted at temperature from 700 ℃ to 1 000 ℃ (depending on the molten salt system and x values) for different time by the MSS method. The MSS procedure in this work is simple, fast and cost-effective, compared with other chemical methods[15]. At the same time, the low temperature and salt can reduce the PbO evaporation.

1　Experimental

　　The nominal composition in the present study was 0.0≤x≤0.45 for $Pb_{1-x}La_xTiO_3$. The starting materials used were reagent-grade oxides TiO_2 (99.9%), La_2O_3 (99.9%), PbO (99.9%), NaCl (99.5%), KCl (99.5%), Na_2SO_4 (99.9%) and K_2SO_4 (99%). The stoichiometric amounts of oxides were ground with a mortar and pestle in ethanol for 1 h to obtain uniformly distributed mixtures. The oxides mixtures were mixed with chlorides NaCl-KCl (1:1 molar ratio) or Na_2SO_4-K_2SO_4 (0.8:0.2 molar ratio) in a weight ratio varying

from 1:1 to 1:3 by wet ball-milling for 12 h. The mixed slurry was dried at 120 ℃ for 2 h for the complete removal of ethanol. The mixed powders then were placed in alumina crucibles and then reacted between 700 ℃ to 900 ℃ for 5 min to 3 h. After calcination, the salts were ultrasonically washed using hot distilled water several times until the filtrate being Cl^- free by $AgNO_3$ test. The obtained powders were fully dried at 120 ℃ for 4 h.

　　The powders were characterized by using XRD (model: M21XVHF22, Mac Science, Yokohama, Japan) using a diffractometer with Cu $K\alpha$ radiation, SEM (Model: Cambridge S360) with EDS, respectively. The experimental procedure is shown in Fig.1.
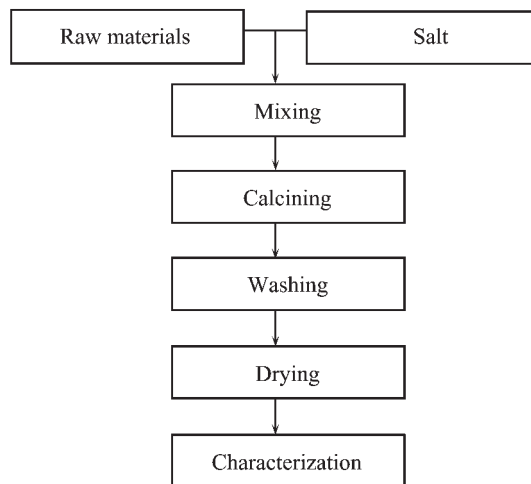

Fig.1　Experimental procedure

2　Results and discussion

　　The melting points of eutectic NaCl-KCl and 0.8Na_2SO_4-0.2K_2SO_4 are 658 ℃ and 823℃, respectively. Fig.2 shows the powders diffraction patterns collected on these materials synthesized by NaCl-KCl salts from 700 ℃ to 900 ℃ and Na_2SO_4-K_2SO_4 from 900 ℃ to 1 000 ℃ for 2 h. As shown in Fig.2(a), the as-prepared PLT powders are single-phase at above 700 ℃ and also a small amount unreacted oxides impurity when synthesized at 700 ℃ for x≥0.35. However, the unreacted oxides can be avoided through rising the temperature to 800 ℃. This indicates that the preparation of $Pb_{1-x}La_xTiO_3$ (x<0.35) single phase particles was possible by NaCl-KCl flux at the tempera-

ture as low as 700 ℃ and $Pb_{1-x}La_xTiO_3$ $(x \geqslant 0.35)$ at 800 ℃. As the solution of La increasing the temperature of synthesized by molten salt increased. Sulphates could also be used in the synthesis of PLT powders and no impurity phase and difference identified in the samples prepared from 900 ℃ to 1 000 ℃ as shown in Fig.2(b).
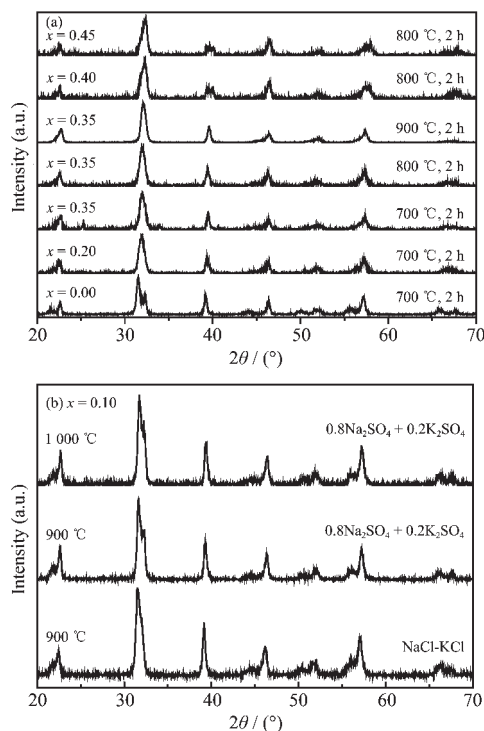

Fig.2　XRD patterns of $Pb_{1-x}La_xTiO_3$ $(x=0.0\sim0.45)$ synthesized at different temperatures in NaCl-KCl and Na_2SO_4-K_2SO_4 molten salts

The single phase perovskite ceramic PLT with different La content can be synthesized by molten salt method above 800 ℃ according to the method described previously. Fig.3(a) shows that single phase $Pb_{1-x}La_xTiO_3$ can be formed for $0.0 \leqslant x \leqslant 0.40$, and a small amount of $La_2Ti_2O_7$ pyrochlore phase was detected in the XRD patterns for $x=0.45$. The solid solution compound PLT was indexed in a tetragonal structure for $0.0 \leqslant x \leqslant 0.20$, and in a cubic one for $0.25 \leqslant x \leqslant 0.40$. The structure parameters of $Pb_{1-x}La_xTiO_3$ $(0.0<x<0.40)$ are shown in Fig.3(b) that fits with the peak separation between the 001 and 100 reflections and the tetragonality (c/a) decreases with the La content.

Fig.4 shows the SEM micrographs of typical $Pb_{1-x}La_xTiO_3$ $(x=0.10)$ powders prepared by different

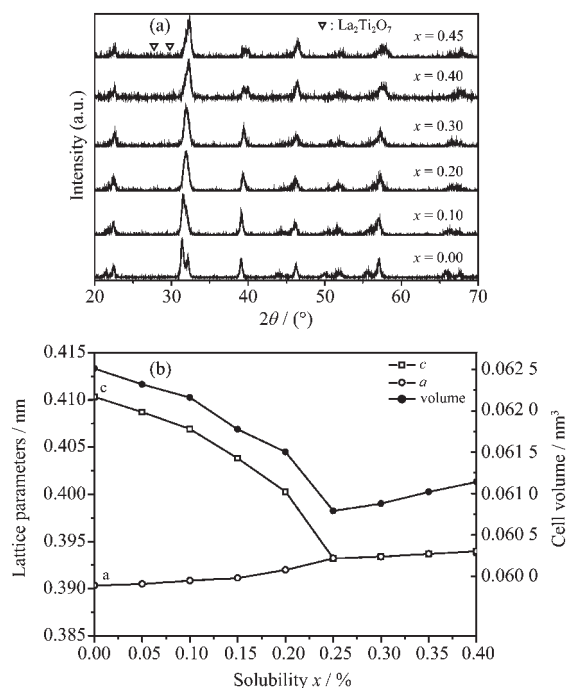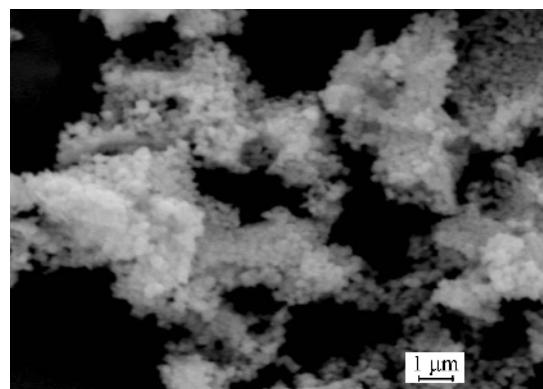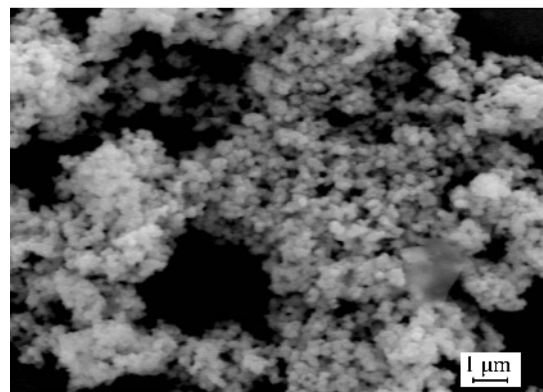Fig.3　XRD and Lattice parameters of $Pb_{1-x}La_xTiO_3$ $(0.0 \leqslant x \leqslant 0.45)$ solid solution synthesized at 800 ℃

(a) Na-KCl　　900 ℃

(b) $0.8Na_2SO_4 + 0.2K_2SO_4$　　900 ℃

Fig.4　Typical scanning electron micrographs of $Pb_{1-x}La_xTiO_3$ $(x=0.10)$ powders prepared by different molten salt synthesis at 900 ℃

molten salt at 900 ℃ for 2 h. The size distribution of PLT was quite narrow. The particles are spherical in shape, which indicates that the particle growth is under the diffusion control mechanism, the shap and size for sample prepared by sulphate appear to be a little larger than by chloride. The particles growth behavior with temperature for different kinds of salt can be represented by the following equation[15].

$$D^2 - D_0^2 = k(t - t_0)\exp(-E/RT)$$

Where D is the average particle size at time t, D_0 is the initial particle size at initial t_0, k is the rate constant, E is the activation energy for particle growth, R is the gas constant, and T is the firing temperature. When the initial particle size, D_0, is small compared with the average particle size, D, at the time t, the factor D_0^2 can be neglected relative to D^2. So the e-quation can be expressed as follows:

$$D^2 = k(t - t_0)\exp(-E/RT)$$

From the plot of $\ln D^2$ vs $1/T$, the activation ener-gy can be calculated. Fig.5 shows the plots drawn for the PLT particles synthesized by changing the species of the salts. The apparent activation energies for parti-cle growth, the values calculated from the data pre-sented in Fig.5 are 94 and 108 kJ·mol⁻¹ for formation temperature 700 to 1 000 ℃ in chlorides and sul-phates, respectively, suggesting that the activation en-ergy is not influenced by the salts species. The acti-vation energies obtained from the molten salt synthesis method belong to low activation reaction, the rate of reaction in molten salt was quickly confirmed by $Pb_{1-x}La_xTiO_3$ (x=0.10). The $Pb_{1-x}La_xTiO_3$ (x=0.10) syn-thesized at 700 ℃ in 5 min is shown in Fig.6. On fur-
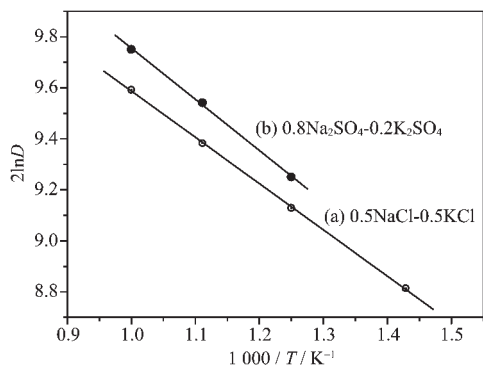

Fig.5　Plots of $2\ln D$ (average particle size) vs $1/T$ for (a) $0.5NaCl + 0.5KCl$ and (b) $0.8Na_2SO_4 + 0.2K_2SO_4$

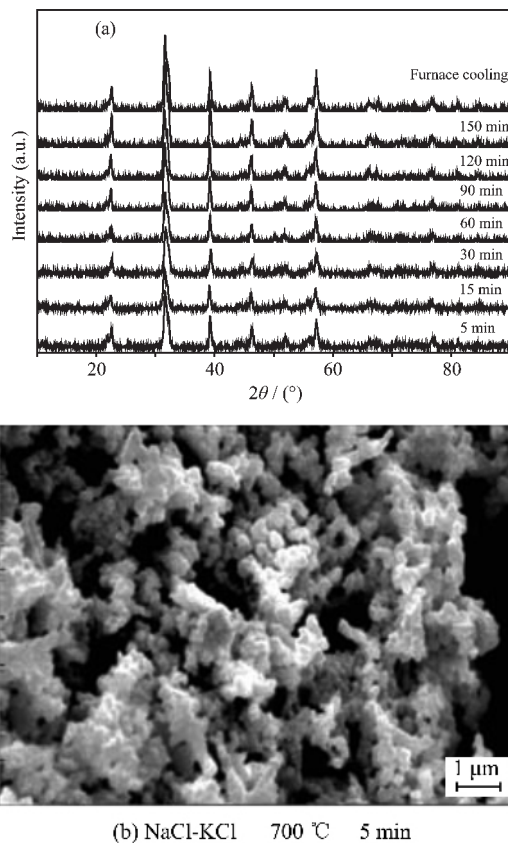ther prolonging holding time to 2 h, as presented in Fig.6, no significant changes in XRD pattern could be found.

Fig.6　XRD patterns of the $Pb_{0.9}La_{0.1}TiO_3$ solid solution with different time at 700 ℃ and SEM for reaction at 700 ℃ for 5 min

　　The formation of a high purity $Pb_{1-x}La_xTiO_3$ (x= 0.10) phase occurred at a low temperature of 700 ℃, and was completed within a relatively narrow tempera-ture range, leading to a small average particle size of ~100 nm with a controlled component by molten salt synthesis method. The single phase $Pb_{0.9}La_{0.1}TiO_3$ solid solution was observed beyond 5 min at 700 ℃. The completion of this reaction in a very short time is due to the short diffusion distance and the high mobility of species in the liquid state. Arendt et al.[1] reported that the creatively high mobility of species in the molten salt (1×10^{-5}~1×10^{-8} cm²·s⁻¹) compared with as little as 1×10^{-18} cm²·s⁻¹ in the solid state. The morphologi-cal size difference can be explained that the sulphates have higher solubility for PbO under the same condi-tions than the chlorides. The perovskite phase is be-

lieved to be formed on the surface of the slow-dissolving component by transporting the fast-dissolving component. In the case of PLT, PbO is considered to be the fast-dissolving component[11]. Therefore, the solubility for PbO in different salts can be used to explain the different particle size distribution observed in the powders. The relatively large solubility of PbO in the sulphate flux increases the solubility of PbO and then accelerates the formation reactions. Consequently, the PLT crystallites grown in the sulphate slats show a larger particle size.

3 Conclusions

Pb$_{1-x}$La$_x$TiO$_3$ ($0 \leqslant x \leqslant 0.40$) compounds with good stoichiometry and Pb$_{1-x}$La$_x$TiO$_3$ ($x=0.45$) with a small amount of La$_2$Ti$_2$O$_7$ pyrochlore phase could be produced from molten salt synthesized method. The formation of a high purity Pb$_{1-x}$La$_x$TiO$_3$ ($x<0.35$) phase occurred at a low temperature of 700 ℃ and Pb$_{1-x}$La$_x$TiO$_3$ ($x \geqslant 0.35$) at 800 ℃ in NaCl-KCl flux. The formation of a high purity Pb$_{0.9}$La$_{0.1}$TiO$_3$ phase was for only 5 min in chlorides at 700 ℃. These compounds were indexed in the tetragonal phase for $0.0 \leqslant x < 0.25$, and in the cubic phase for $0.25 \leqslant x \leqslant 0.40$. The maximal La content at PLT prepared by MSS was $x=0.40$, and La$_2$Ti$_2$O$_7$ was detected at $x=0.45$. The average primary particle size of the PLT powders was uniform and the size distribution was quite narrow. The particles were spherical in shape, which indicates that the particle growth is under the diffusion control mechanism, the shape and size for samples prepared in sulphates are somewhat larger than that in chlorides. The PLT particles activation energy for particle growth in MSS method was calculated, which shows the reaction was very fast.

References:

[1] Arendt R H, Rosolowski J H, Szymaszek J W. *Mat. Res. Bull.*, **1979**,**14**(5):703~709

[2] Chiu C C, Li C C, Desu S B. *J. Am. Ceram. Soc.*, **1991**,**74**(1): 38~41

[3] Jin X, Gao L. *J. Am. Ceram. Soc.*, **2004**,**87**(4):533~540

[4] Hayashi Y, Kimura T, Yamaguchi T. *J. Mat. Sci.*, **1986**,**21**: 757~762

[5] Xu C Y, Zhang Q, Zhang H, et al. *J. Am. Chem. Soc.*, **2005**, **127**:11584~11585

[6] Mao Y, Banerjee S, Wong S S. *J. Am. Chem. Soc.*, **2003**,**125**: 15718~15719

[7] Kimura T, Kanazawa T, Yamaguchi T. *J. Am. Ceram. Soc.*, **1983**,**66**(8):597~600

[8] Park J H, Lee D H, Shin H S, et al. *J. Am. Ceram. Soc.*, **1996**,**79**(4):1130~1132

[9] Hayashi Y, Kimura T, Yamaguchi T. *J. Am. Ceram. Soc.*, **1986**,**69**(4):322~325

[10]Kimura T, Takahashi T, Yamaguchi T. *J. Mat. Sci.*, **1980**,**15**: 1491~1497

[11]Li C C, Chiu C C, Desu S B. *J. Am. Ceram. Soc.*, **1991**,**74** (1):42~47

[12]Yoon K H, Cho Y S, Lee D H, et al. *J. Am. Ceram. Soc.*, **1993**,**76**(5):1373~1376

[13]Katayama K, Abe M, Akiba T. *J. Euro. Ceram. Soc.*, **1989**, **5**:183~191

[14]Ito Y, Shimada S, Inagaki M. *J. Am. Ceram. Soc.*, **1995**,**78** (10):2695~2699

[15]Yoon K H, Cho Y S, Kang D H. *J. Mat. Sci.*, **1998**,**33**:2977~ 2984