

First Synthesis of Zirconia-pillared Layered Lanthanum Niobate

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Abstract: A zirconia-pillared layered lanthanum niobate was prepared by first preswelling layered HLaNb_2O_7 with *n*-hexadecylamine ($n\text{-C}_{16}\text{H}_{33}\text{NH}_2$), then further reacting with zirconyl chloride aqueous solution, and finally calcining the resultant solid product in air. The obtained new material has an interlayer spacing of 1.36nm, and a high thermal stability above 700°C.

Keywords: Layered lanthanum niobate, Zirconia, Pillaring, Preparation.

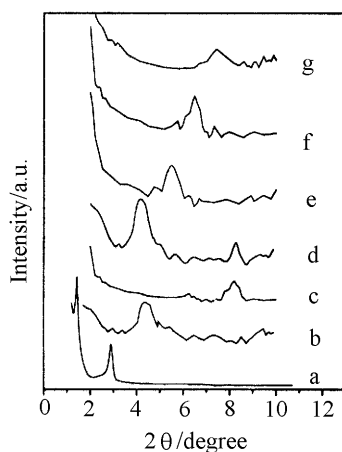
It was reported that tetrameric zirconium cations can be intercalated into layered solids such as smectite clays and phosphates to form zirconia-pillared materials^{1,2}. Layered transition-metal oxides are a new kind of layered raw materials developed recently which could be propped open by alumina, silica and chromia^{3,4,5}. Layered lanthanum niobic acid was found to show strong Brönsted acidity, but it loses its acidity and surface area after heat treatment at 773K. To overcome this, one promising technique is pillaring layered lanthanum niobic acid with inorganic oxides. We successfully prepared the silica-pillared layered lanthanum niobic acids⁶, but so far there is no report of zirconia-pillared layered lanthanum niobic acid.

HLaNb_2O_7 , *n*-hexylamine-intercalated HLaNb_2O_7 (denoted as HA-LN) and *n*-hexadecylamine-intercalated HLaNb_2O_7 (denoted as HDA-LN) were prepared according to literature⁶. HDA-LN was added to the zirconyl chloride solution, and the mixture was refluxed for 4 days with stirring. After the reaction, the solid product (denoted as Zr-LN) was separated by centrifugation and air-dried.

HDA-LN has an interlayer space of 5.89 nm ($2\theta=1.5^\circ$) (**Figure 1a**). As shown in **Figure 1b** and **1c**, calcination of HDA-LN in air at 473K for 4 h led to a shift of the (001) reflection peak (2θ) from 1.5° to 4.3° , suggesting a partial decomposition of the interlayered organics and therefore a decrease of the interlayer distance. A further calcination at 773K for 2 h resulted in a material with an interlayer distance of only 1.10 nm, near that of HLaNb_2O_7 . It was suggested that the interlayered organics were fully decomposed at this temperature.

After reaction with zirconyl chloride solution, the interlayer distance of HDA-LN decreased from 5.89 nm ($2\theta=1.5^\circ$) to 2.16 nm ($2\theta=4.1^\circ$) (**Figure 1d**). Such an extent of decrease could be explained by the fact that the originally intercalated *n*-hexadecylammonium ions were exchanged by the oligomeric zirconium cations formed in the aged

Figure 1 XRD patterns of HDA-LN and Zr-LN calcinated in air at different temperatures. (a) HDA-LN at 298K; (b) HDA-LN at 473K for 4h; (c) HDA-LN at 773K for 2h; (d) Zr-LN at 298K; (e) Zr-LN at 573K for 2h; (f) Zr-LN at 773K for 2h; (g) Zr-LN at 973K for 2h



zirconyl chloride solution. C, H, N elemental analysis results also supported this. After calcination at 773K, the interlayered organics had been fully decomposed, meanwhile, the interlayered oligomers of zirconium was dehydrated to form zirconia. Therefore, the product obtained at this time was zirconia-pillared lanthanum niobate and its interlayer distance was 1.36 nm ($2\theta=6.5^\circ$) (**Figure 1f**). It can be also seen from **Figure 1** that the zirconia-pillared lanthanum niobate has a high thermostability above 973K.

The original HLaNb_2O_7 is actually a non-porous solid with a very small BET surface area of $5\text{m}^2/\text{g}$. By comparison, the obtained zirconia-pillared material is porous and has a relatively high BET surface area of $23\text{m}^2/\text{g}$.

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