

Synthesis of New Solid Solutions on Neodymium-stabilized $\text{La}_2\text{Mo}_2\text{O}_9$

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Abstract: A new ionic conductor $\text{La}_{2-x}\text{Nd}_x\text{Mo}_2\text{O}_9$ ($x=0.0-2.0$) has been synthesized by wet-chemistry method. The precursors and the resultant oxide powders were characterized by DTA/TG, DSC, XRD and XPS techniques. Effect of substituting Nd for La reveals that the phase transition which occurs in $\text{La}_2\text{Mo}_2\text{O}_9$ around 565°C disappears when $x>0.2$. And the maximum amount of Nd stabilized the high temperature phase of $\beta\text{-La}_2\text{Mo}_2\text{O}_9$ from cubic to tetragonal is about $x=1.6$. The measurements of impedance spectroscopy indicate that the ionic conductivity becomes considerably higher in comparison to that of $\text{La}_2\text{Mo}_2\text{O}_9$.

Keywords: $\text{La}_{2-x}\text{Nd}_x\text{Mo}_2\text{O}_9$, thermal analysis, ionic conductor, molybdate.

Oxide ion conductors form a class of materials which are widely sought for and studied since they can be used in different field among solid oxide fuel cells (SOFC), oxygen sensors, oxygen pumping devices, or oxygen-permeable membrane catalysts, for instance¹⁻³. Now research focuses on the oxide ion conductors with new structure and improving the conductivity or lowering the operating temperature. Recently P.Lacorre *et al.*⁴ have reported a novel oxide-ion conductor based on $\text{La}_2\text{Mo}_2\text{O}_9$. F. Goutenoire *et al.*⁵ further investigated the crystal structure of $\text{La}_2\text{Mo}_2\text{O}_9$. It undergoes a slight structural phase transition around 580°C and behaves as a good ionic conductor. But structural instabilities may limit their use in fuel cells. Therefore, various substitutions have been attempted on the lanthanum site $\text{La}_{2-x}\text{A}_x\text{Mo}_2\text{O}_9$ (with $\text{A}=\text{Sr}, \text{Ba}, \text{K}, \text{Ca}, \text{or Bi}$) in order to stabilize the high-temperature cubic $\beta\text{-La}_2\text{Mo}_2\text{O}_9$ phase^{6, 7}.

In this work, we report the synthesis of the Nd-stabilized $\text{La}_2\text{Mo}_2\text{O}_9$ compound by wet-chemistry method. The results showed that the high temperature cubical phase of $\text{La}_2\text{Mo}_2\text{O}_9$ is transported to tetragonal phase of $\text{La}_{2-x}\text{Nd}_x\text{Mo}_2\text{O}_9$. Substitutions of Nd for La showed a broad compositional range ($x=0.0-1.6$). Substituting Nd in some degree ($x>0.2$) for La^{3+} can suppress the phase transition. The sample of $\text{LaNdMo}_2\text{O}_9$ exhibits a better oxide ion conducting compared to the $\text{La}_2\text{Mo}_2\text{O}_9$.

$\text{La}_x\text{Nd}_{2-x}\text{Mo}_2\text{O}_9$ solid solutions ($x=0.0-2.0$) were prepared by using a modified citrate complex method⁸. All starting materials are 99.99% purity. $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ were dissolved in water and mixed with an aqueous solution of citric acid and then a water solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$ was added, the mixture was

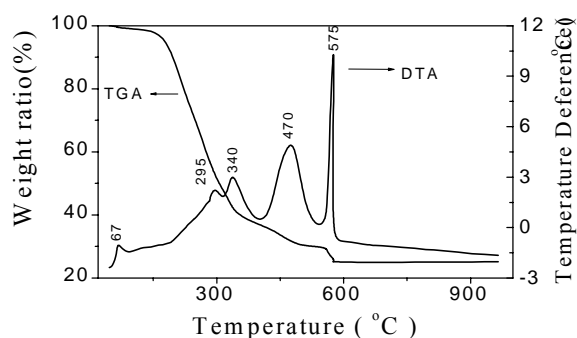
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stirred and then a quantity of polyethylene glycol 20000 was added (as dispersing agent). Finally, the solutions were vaporized, the resulting sol was dried at 100°C for 24 h. The so-precursor was heated at various temperatures in air for 8 h and cooled slowly to room temperature. Finally, the oxide powders were prepared and then pressed into ϕ 20 mm pellets followed by sintering in air at 1000°C for 8 h. The X-ray diffraction (XRD) patterns for all the samples were recorded on a Rigaku D/max-IIB X-ray Diffractometer. The particle size of the sample was measured on ZETASIZER 1000HSA (Malvern Instruments). TG-DTA/DSC thermal analysis were carried out on SDT 2960 simultaneous DSC-TGA(TA instruments) with the heating temperature from 20 to 1000°C at 10°C/min in air. Oxide ionic conductivity was measured by a conventional ac two-probe technique with a frequency response analyzer (Solatron1260) in a frequency range from 1MHz to 0.1Hz. The valence state of the La and Mo ions for the solid solutions were determined by EXCA-LAS MK II X-ray photoelectron spectrometer with Al K α radiation and 10^{-7} torr. The C_{1s} signal was used to correct the charge effects on the sample surface.

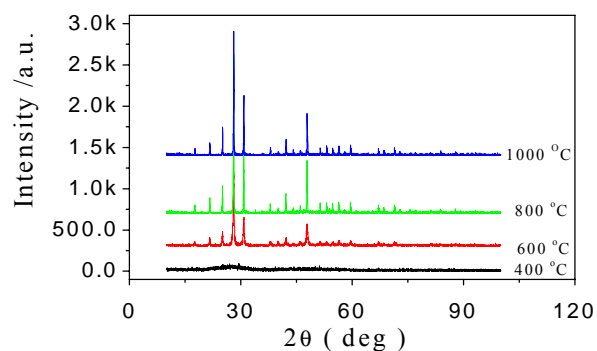
Results and Discussion

Figure 1 shows DTA/TG curves of the LaNdMo₂O₉ precursor dried at 100°C. There are two exothermic peaks at 295°C and 340°C in DTA curves and TG curves showed about 60% weight loss corresponding to the complete decomposition of citrate or citric acid monohydrate. DTA curves showed that the thermal decomposition of the precursor with two exothermic peaks at 470°C, 575°C and TG curve reveals the weight loss of 10%. This suggests that the combustion of the polymer between the metal ion and citric acid monohydrate or polyethylene glycol 20000. From 600 ~ 1000°C, no change in weight was found.

Figure 1 The DTA/TG curves for LaNdMo₂O₉ dried at 100°C



The phase evolution of LaNdMo₂O₉ precursor during calcinations was studied by the XRD analysis. (**Figure 2**)

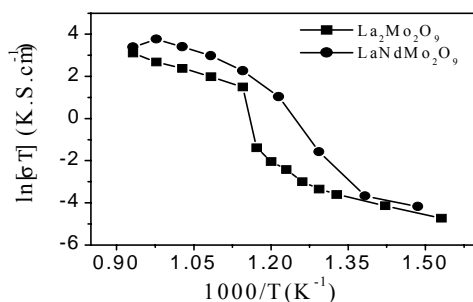
Figure 2 Comparison of the XRD patterns of $\text{LaNdMo}_2\text{O}_9$ precursors

Below 400°C the precursor was amorphous, when the temperature reached 600°C the sample displayed almost all the characteristic reflections with the tetragonal structure of $\text{LaNdMo}_2\text{O}_9$. Diffraction lines of the samples calcined at 600°C were broadened in comparison to those calcined above 600°C. The facts indicated that the formation temperature of the compound was as low as 600°C. The result is in coincidence with that of thermal analysis. The higher sintering temperature was, the better the crystallinity became. We have indexed the pattern of XRD to tetragonal symmetry with P4 space group, $a = 0.71124\text{nm}$, $c = 0.70971\text{nm}$ and $V = 0.3590\text{nm}^3$ ($R = 92\%$) using the CELL program⁹. The average particle sizes of sample produced in this wet-chemistry method were high-equally 490 nm. XPS spectra measured at room temperature showed that the $\text{La}3d_{5/2}$ signal for the sample consists of a photoelectron peak (835.4eV), which is consistent with the La_2O_3 ¹⁰. A similar spectrum had been obtained for the $\text{Mo}3d_{5/2}$ (232.8eV), which is consistent with the MoO_3 ¹¹.

The substitution of Nd^{3+} for La^{3+} was tried synthetically to observe the change of the crystalline structure. The tetragonal symmetry structure was retained in the solid solution range for $0.4 < x < 1.8$. Some additional diffraction peaks appeared in the XRD pattern above $x = 1.8$ and a monoclinic phase were obtained for $x < 0.4$, which agree with earlier results described in literature⁵.

It has been found that the endothermic peaks in DSC around 565°C for $\text{La}_2\text{Mo}_2\text{O}_9$ shifted to about 578°C for $\text{La}_{1.8}\text{Nd}_{0.2}\text{Mo}_2\text{O}_9$ and these peaks disappeared when $x > 0.2$. It indicated that the phase transition were suppressed and the cubic phase of $\beta\text{-La}_2\text{Mo}_2\text{O}_9$ in high-temperature were stabilized to room temperature with the increasing doping Nd. Meanwhile, the endothermic peak around 578°C in $\text{La}_{1.8}\text{Nd}_{0.2}\text{Mo}_2\text{O}_9$ can be attributed to the structural transition from tetragonal to cubic phase.

The conductivity as a function of reciprocal temperature in air is shown in **Figure 3**. It is obvious that the conductivity of $\text{LaNdMo}_2\text{O}_9$ decreases continuously with decreasing temperature, while the conductivity curve of $\text{La}_2\text{Mo}_2\text{O}_9$ has a drop at the temperature range from 500 to 600°C associated phase transition. At the same temperature the total conductivity of $\text{LaNdMo}_2\text{O}_9$ is higher than that of $\text{La}_2\text{Mo}_2\text{O}_9$. Therefore, $\text{LaNdMo}_2\text{O}_9$ is expected to be a better oxide-ion conductor than $\text{La}_2\text{Mo}_2\text{O}_9$. Perhaps this phenomenon is attributed to the association of defects.

Figure 3 Temperature dependence of conductivity for $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{LaNdMo}_2\text{O}_9$.

T. Ishihara *et al.*¹² reported that doping of Co ions is effective for enhancing oxide ion conductivity in $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$, which originated from the oxidation state change of Co at high temperature from +3 to +2. This explanation may be adapt to the replacement of La by Nd based on $\text{La}_2\text{Mo}_2\text{O}_9$. Therefore, it is thought that the change of oxidation state of Nd took place as a result of the distribution of Mo ion at high temperature. However, the exact cause of oxidation state change needs the support of other experiments, for instance, magnetic susceptibility, EXAFS, chemical analysis *etc.*

Acknowledgments

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References

1. J. A. Lane, S. J. Benson, D. Waller, J. A. Kilner, *Solid State Ionics*, **1999**, *121*, 201.
2. K. R. Kendall, C. Navas, J. K. Thomas, H. C. Z. Loye, *Solid State Ionics*, **1995**, *82*, 215.
4. P. Lacorre, F. Goutenire, O. bohnke, R. Retoux, Y. Laligant, *Nature*, **2000**, *404*, 856.
5. F. Goutenoire, O. Isnard, R. Retoux, P. Lacorre, *Chem. Mater.*, **2000**, *12*, 2575.
6. F. Goutenoire, O. Isnard, E. Suard, O. bohnke, Y. Laligant, R. Retoux, Ph. Lacorre, *J. Mater. Chem.*, **2001**, *11*, 119.
7. X. P. Wang and Q. F. Fang, *Solid State Ionics*, **2002**, *146*, 185.
8. C. Marcilly, P. Courty, B. Delmon, *J. Am. Ceram. Soc.*, **1970**, *53*, 56.
9. Y. Takaki, T. Taniguchi, K. Hori, *J. Ceram. Soc. Jpn.*, **1993**, *101*, 373.
10. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, *Hand book of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, Minn., **1979**, 55344.
11. S. L. T. Andersson, R. F. Howe, *J. Phys. Chem.*, **1989**, *93*, 4913.
12. T. Ishihara, H. Furutani, M. Honda, T. Yamada, T. Shibayama, T. Akbay, N. Sakai, H. Yokokawa, Y. Takita, *Chem. Mater.*, **1999**, *11*, 2081.

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