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Correlation between Structure and Ionic Conductivity in Layered Perovskite Oxides, $LiLnTa_2O_7$ (Ln=La, Nd, Sm)

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A series of layered perovskite oxides, $LiLnTa_2O_7$ (Ln=La, Nd and Sm) was prepared by ion-exchange reaction of $RbLnTa_2O_7$ powders with molten salt of $LiNO_3$. According to Rietveld analysis, it is found that the tantalum ions are remarkably displaced from the center of TaO_6 octahedra, resulting in a short Ta-O_{apex} bond due to high covalent bonding character. On replacing the large constituting ion in Ln site with smaller one, TaO_6 octahedron becomes more distorted, which gives rise to a remarkably shorter Ta-O_{apex} bond. An increasing trend of Ta-O_{apex} bond strength observed by Raman spectra is well consistent with the reverse trend of Ta-O_{apex} bond distance from the Rietveld analysis. As the large La ion is replaced by the smaller one (from La to Nd, Sm), the ionic conductivity increases with a decrease of activation energy. It is therefore concluded that the strong Ta-O_{apex} bond leads to a weakening of Li-O_{apex} bond in view point of bond competition, giving rise to an enhancement of Li ion conduction.

Keyword: Dion-phase, lithium ionic conductivity, Raman spectroscopy

INTRODUCTION

A series of layered oxides with the Dion formula[1] of $A'[A_{n-1}B_nO_{3n+1}]$ (A' = alkali metal ion, n=2,3,4,···), has attracted considerable attention because of their interesting interlayer chemistry.

In the lattice of Dion phase, alkali metal ions are loosely bound inbetween

2-dimensional perovskite slabs because of the low layer charge, which gives rise to a significant ionic conducting property as well as ion-exchange capacity. Recently, efforts have been carried out in order to understand the mechanism of ion conductivity in the layered oxides such as niobate and titanate.[3,4] However, there are few researches on lithium ionic conduction, which is probably due to a difficulty in preparing well crystallized compounds and/or determining precise structures.

In this study, we attempted to synthesize a well crystallized series of lithium containing layered perovskite oxides, $LiLnTa_2O_7$ (Ln = La, Nd and Sm), and to correlate their lithium ionic conductivities with crystal structures.

EXPERIMENTAL

$RbLnTa_2O_7$ (Ln = La, Nd, Sm) was prepared by calcining appropriate mixtures of Rb_2CO_3, Ln_2O_3, Ta_2O_5 at 1100 °C for 2 days with two intermittent grindings. An excess amount of Rb_2CO_3 (25%) was added to compensate for the loss due to volatilization. The interlayer rubidium ions were exchanged with lithium ions by treating the samples with molten $LiNO_3$ at 300°C for 2 days. After ion exchange reaction, the products were washed with distilled water and dried at 130 °C for 12 hours. The crystal structures were analyzed by the Rietveld refinement using RIETAN-94[5] program based on the powder X-ray diffraction patterns and by Raman spectroscopy. Lithium ionic conductivities of $LiLnTa_2O_7$ were measured on Au sputtered pellets by a complex impedance technique in the range of 5 Hz ~ 13 MHz using a HP4192A impedance analyzer.

RESULTS AND DISCUSSION

The monophasic $LiLnTa_2O_7$ (Ln = La, Nd, and Sm) was successfully synthesized and their stuctures were found to be the layered ones analogous

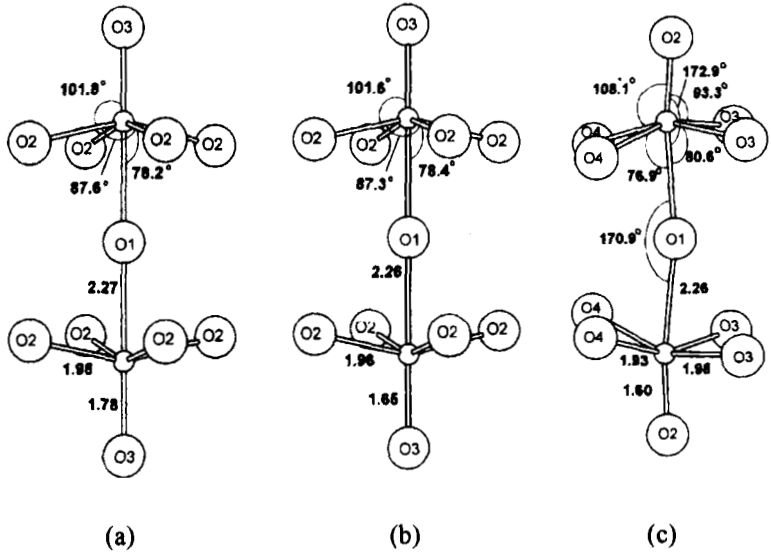

FIGURE 1 Environment around tantalum ions in the perovskite layer of (a) $LiLaTa_2O_7$ (b) $LiNdTa_2O_7$ and (c) $LiSmTa_2O_7$

to Dion-phase.[2,3]

$LiLaTa_2O_7$ crystallized in tetragonal structure with a = 3.8797(9) Å, c = 20.4473(5) Å, belongs to the space group I4/mmm, which is similar to the corresponding niobates as already revealed in the literature.[3] When La ion is substituted by smaller lanthanide ions such as Nd and Sm, however, the XRD patterns of these new compounds could be indexed in orthorhombic system with $\sqrt{2} \times \sqrt{2} \times 1$ supercell. The larger unit cell gave us difficulties on the space group determination from the systematic absences. The most reliable solutions with physically meaningful parameters are archived by adopting the space group Fmmm for $LiNdTa_2O_7$ (a = 5.4448(2) Å, b = 5.4143(2) Å, c = 20.4916(6) Å) and Cmcm for $LiSmTa_2O_7$ (a = 20.4863(6) Å,

b = 5.4284(2) Å, c = 5.3626(2) Å), respectively. The refinement converged in these space groups to R_{wp} = 7.0, R_E = 4.1 for $LiLaTa_2O_7$, R_{wp} = 7.3, R_E = 4.9 for $LiNdTa_2O_7$ and R_{wp} = 7.0, R_E = 3.5 for $LiSmTa_2O_7$.

Fig. 1 shows the local structures around tantalum ions in the compounds, where tantalum ions are stabilized in the strongly distorted octahedral site. The Ta ion is, therefore, remarkably displaced from the center of TaO_6 octahedron, resulting in a short Ta-O_{apex} bond due to high covalent bonding character. On replacing the large constituting ion in Ln site by smaller one, TaO_6 octahedron becomes more distorted, which gives rise to a remarkably shorter Ta-O_{apex}bond.

The nature of Ta-O_{apex} could be also characterized by Raman spectroscopy as shown in Fig. 2. The present spectra are comparable with those for highly distorted niobium oxides with Nb=O double bond character such as $Nb(HC_2O_4)_5$ and $AlNbO_4$.[6] Therefore, a strong and sharp Raman band at very high wave number region (about 940cm^{-1}) is assigned as the symmetric stretching of Ta-O_{apex} bond, reflecting the strength of Ta-O_{apex} bond. In addition, this band shifts to a higher wave number region as the size of lanthanide ion becomes smaller. The increasing trend of Ta-O_{apex} bond strength observed by Raman spectra is well consistent with the reverse trend of the Ta-O_{apex} bond distance from the Rietveld analysis.

As the large La ion is replaced by the smaller one (from La to Nd, Sm), the primitive unit cell volume is expected to be reduced with a decrease of ion conductivity. On the contrary, the ionic conductivity increases as shown in Fig. 3, accompanying an increase of activation energy. In order to understand such a trend, it is thought to be helpful to examine the local structure around tantalum ion for all three compounds. The short Ta-O_{apex} bond with highly covalent character would allow lower layer charge, resulting in a less interaction between the perovskite slabs responsible to ionic

conduction.

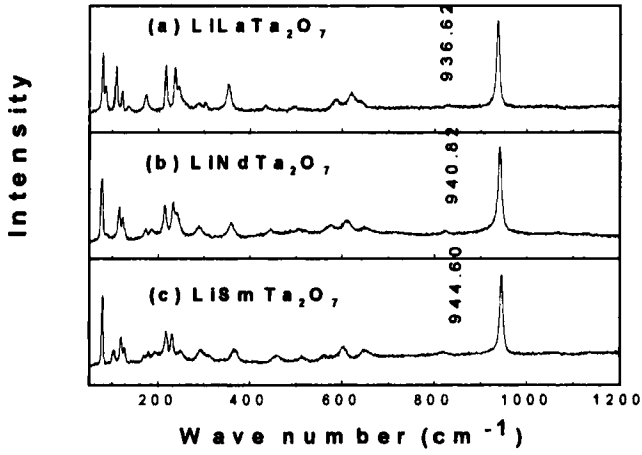

FIGURE 2 Raman spectra of (a) $LiLaTa_2O_7$ (b) $LiNdTa_2O_7$ and (c) $LiSmTa_2O_7$

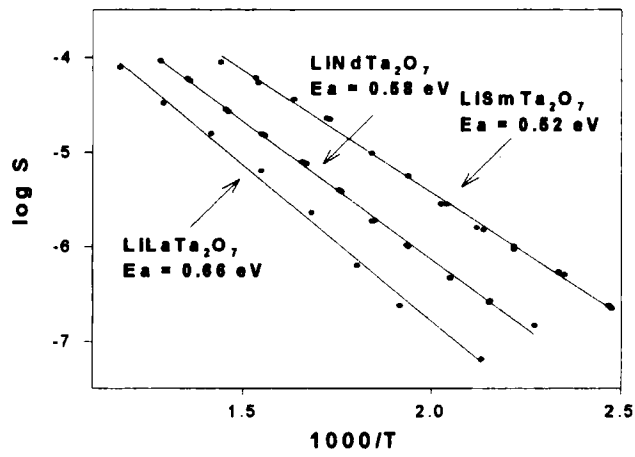

FIGURE 3 Temperature dependence of lithium ionic conductivities and

the activation energies of $LiLnTa_2O_7$ (Ln=La, Nd and Sm).

That is, the increased covalency of Ta-O_{apex} bond would give rise to a decrease of the covalency of Li-O_{apex} bond, which is consistent with previous discussion on the layered niobates and titanate.[4,7] Actually, we could find the distinguishable strengthening of Ta-O_{apex} bond by replacing Ln ion with smaller ones (from Ln =La to Nd,Sm), leading to an enhanced lithium ionic conduction. An interesting finding to be noted here is interlayer spacing between double perovskite slabs somewhat increases in spite of the lattice contraction. It is therefore, concluded that the sufficient interlayer spacing provides an effective pathway for lithium ionic conduction. It would be an important concept for a designing new ionic conductor with layered perovskite structure.

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References

[1.] M. Dion, M. Ganne and M. Tournoux, *Mat. Res. Bull.*, **16**, 1469 (1981).

[2.] J. Gopalakrishnan and Vasudeva Bhat, *Mat. Res. Bull.*, **22**, 413 (1987).

[3.] M. Sato, J. Abo, T. Jin and M. Ohta, *J. Alloys and Comp.*, **192**, 81 (1993).

[4.] J. Gopalakrishnan, S. Uma and V. Bhat, *Chem. Mater.*, **5**, 132 (1993)

[5.] F. Izumi, in The Rietveld Method, edited by R. A. Young (Oxford University

Press,Oxford,1993), Chap. 13.

[6.] J.-M. Jehng and I. E. Wachs, *Chem. Mater*, **3**, 100 (1991)

[7.] K. Park and S. H. Byeon, *Bull. Korean Chem. Soc.*, **17**, 168 (1996)