Ion dynamics in perovskite-type lithium ion conductors

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Introduction

A number of lithium ion conductors derived from A-site deficient perovskites such as $La_{2/3}TiO_3$, $La_{1/3}TaO_3$ and $La_{1/3}NbO_3$ have been reported to exhibit high ion conductivity because they have many vacant A-sites available for migration of Li ions. On the contrary, A-site non-deficient perovskites such as $Li_{0.2}Na_{0.3}La_{0.5}TiO_3$, $Li_{0.5}La_{0.5}TiO_3$, and $(Sr_{1-x}Li_x)(M_{1-x}Ta_x)O_3$ (M: Ti, Zr, Sn) also show high ion conductivity. In the present study, we investigated ion dynamics in both types of lithium ion conductor by means of nuclear magnetic resonance (NMR) and impedance spectroscopy.

Experimental

Samples were synthesized by a solid-state sintering method. Commercial reagents of La_2O_3, Ta_2O_5, TiO_2, ZrO_2, SnO_2, $SrCO_3$ and Li_2CO_3 were used as starting materials. The electrical properties were measured with an LF impedance analyzer (HP4192A) in the frequency range from 5 Hz to 13 MHz. The applied voltage was 100 mV. For the measurement, Au paste was painted on either side of the disc and was fired at 550℃. Static ^{7}Li (I =3/2) NMR spectra were obtained with a ^{unity}INOVA 400 spectrometer (Varian) operating at ν_0 = 155.41 MHz which corresponds to an external magnetic field of B_0 = 9.38 T. Spectra were taken after irradiation of the sample with a $\pi/2$ pulse. Experiments were performed between -130 and 200℃. Spin-lattice relaxation times, T_1, was determined by using a classical inversion recovery sequence. ^{7}Li magic-angle-spinning (MAS) spectra were also recorded.

Results and Discussion

In the $(Sr_{1-x}Li_x)(M_{1-x}Ta_x)O_3$ solid solutions, the ionic conduction occurred at the composition with $x \geqq 0.35$, where the dc conductivity showed marked increase with increasing x; this result seems to support a percolation model in which lithium ions migrate via the

A-sites. Fig. 1 shows the static ^{7}Li NMR spectra of $(Sr_{1-x}Li_x)(Ti_{1-x}Ta_x)O_3$ with x = 0.4 measured at various temperatures. Each spectrum showed a single intense signal which arises from -1/2↔1/2 transition. The half width of the signals decreased with increasing temperature. No satellite transitions (±1/2↔±3/2) associated with a quadrupolar interaction of nuclei with electric field gradients at cation sites appeared in the spectra. Activation energy of the spin-lattice relaxation rate, T_1^{-1}, for $(Sr_{0.6}Li_{0.4})(Ti_{0.6}Ta_{0.4})O_3$ was 6 kJ mol^{-1}, which was comparable to those for the A-site deficient type of perovskites.

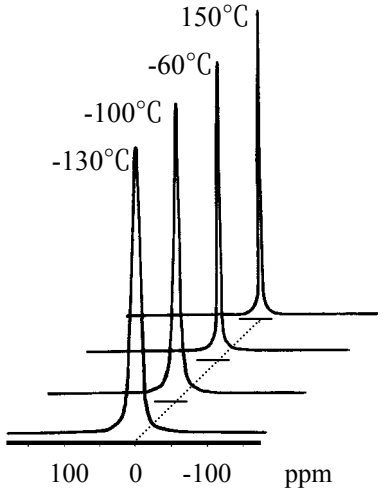

Fig.1 Static ^{7}Li NMR spectra obtained at various temperatures for $(Sr_{0.6}Li_{0.4})(Ti_{0.6}Ta_{0.4})O_3$.

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Research interests :

- Microstructural control of electroceramics through spinodal decomposition
- Ion dynamics in various solid electrolytes (lithium, oxygen, proton, etc.)