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Electrical Properties of Sintered Lithium Titanium Phosphate Ceramics ($Li_{1+X}M_XTi_{2-X}(PO_4)_3$, $M^{3+}=Al^{3+}$, Sc^{3+}, or Y^{3+})

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Activation energies of electrical conduction for bulk and grain boundary in $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ (M=Al, Sc, or Y) systems were determined. The activation energy for the bulk kept constant in spite of the M^{3+} substitution, while that for the grain boundary appreciably decreased. The total conductivity enhancement by the M^{3+} substitution was attributed to the decrease in the activation energy of the grain boundary component.

High ionic conductivities as well as excellent stability in the atmosphere have been requested for solid electrolytes of the all solid state types of batteries. In the electrolytes, lithium ionic conductors are superior in fabricating the batteries with a high energy density. Recently, NASICON-skeleton type solid electrolytes, i.e. $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ (M=Cr,1) Ga,2) Sc,3) or In4,5)) systems, have been reported to show excellent conductivities. Although $LiTi_2(PO_4)_3$ itself is poor (ca. 2×10^{-6} $S\cdot cm^{-1}$ at 298 K) in conductivity, the conductivity greatly increased (10^{-4} $S\cdot cm^{-1}$ at 298 K) by the partial displacement of Ti^{4+} with the M^{3+} ion. The reasons for the conductivity enhancement by the M^{3+} substitution have not been determined because of their close ionic radii. In our preceding papers,6,7) $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ (M=Al, Cr, Ga, Fe, Sc, In, Lu, Y, or La) systems were prepared. We attributed this conductivity enhancement to the increase in the sintered pellet density. Further, a dense $LiTi_2(PO_4)_3$ pellet also showed a high conductivity by binder utilization.8) However, electrical conductivities of a bulk and a grain boundary component have not been discussed in detail for these solid electrolytes.

In this study, we examine the electrical properties by a complex impedance method, and discuss the reason for the conductivity enhancement by the M^{3+} substitution.

The detail of the sample preparation is described in Ref. 7. A gold electrode was deposited by a vacuum evaporation. The electrical conductivity was measured by means of a complex impedance method (100 Hz - 1 MHz) with LCZ meters 4276A and 4277A from Hewlett Packard Co.

In our preceding paper,$^{7)}$ the influence of the M^{3+} replacement in $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ has been reported. The characteristic results are as follows. While a dense pellet of $LiTi_2(PO_4)_3$ (X=0) can not be obtained (porosity 34%), the porosity in $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ decreases (porosity <5%) with X value for all the systems examined. A single phase is obtained for the Al^{3+}- and the Sc^{3+}- substitution systems. The lattice constant decreases when Ti^{4+} site in $LiTi_2(PO_4)_3$ is partially substituted by Al^{3+} ion whose ionic radius is smaller than that of the Ti^{4+} ion. In the substituted systems with a larger Sc^{3+}, the lattice constant increases with the Sc^{3+} fraction. On the other hand, the replacement of the Ti^{4+} site with Y^{3+} is not successful because of its larger ionic radius. An attempt for the replacement with Y^{3+} results in the formation of a mixed phase of $LiTi_2(PO_4)_3$ and $Li_3Y_2(PO_4)_3$. The $Li_3Y_2(PO_4)_3$ phase is poor in conductivity with a high activation energy. We can classify these systems into three types of the M^{3+} substitution. As representatives of these three types, $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ (M^{3+}=Al^{3+}, Sc^{3+}, or Y^{3+}) systems were used in this study.

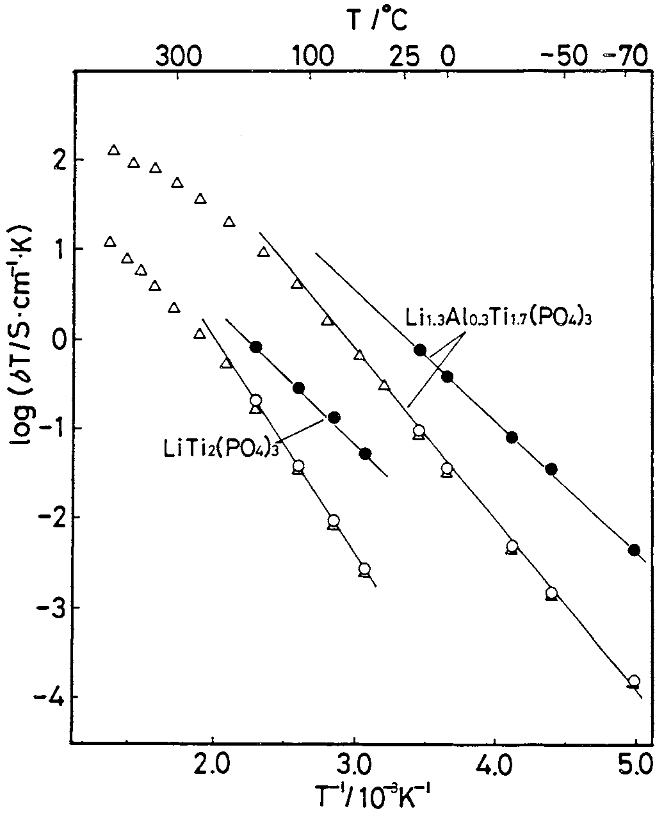

Fig. 1. The σT-$1/T$ relation of the bulk, the grain boundary and the total for the samples of $LiTi_2(PO_4)_3$ and $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$.

bulk (●)
grain boundary (○)
total (△)

In general, the resistances for the bulk and the grain boundary are determined by the complex impedance analysis for polycrystalline solid electrolytes.[9)] Two semicircles were observed for the examined samples by plotting a real and an imaginary part of the impedance from a high frequency to a low one. The σT-$1/T$ relations of the bulk, the grain boundary, and the total conductivities for the samples of $LiTi_2(PO_4)_3$ and $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ are shown in Fig. 1. The conductivities of the total are similar to that of the grain boundary. This indicates that the total conductivities are mainly controlled by the grain boundary component.

The conductivities of the bulk and the grain boundary at 298 K vs. X value for the $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ (M=Al, Sc, and Y) systems are presented in Fig. 2. An analogue for the activation energies is also shown in Fig. 3. Although the activation energy of the bulk did not change with the increase in X value for all the systems examined, the bulk conductivity was considerably enhanced with the M^{3+} substitution. The change in a skeleton size

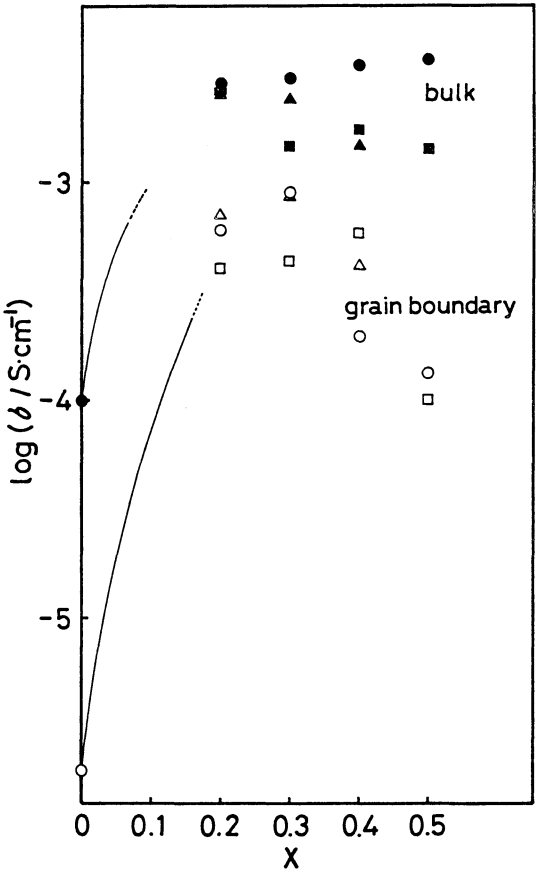

Fig. 2. The conductivities of the bulk and the grain boundary at 298 K in the $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ system.

M=Al: bulk(●), grain boundary(○)
M=Sc: bulk(▲), grain boundary(△)
M=Y : bulk(■), grain boundary(□)

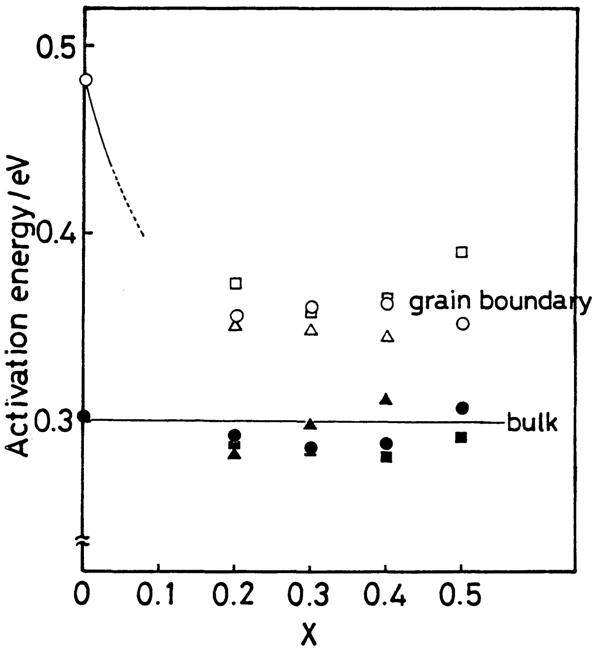

Fig. 3. The activation energies of the bulk and the grain boundary in the $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ system.

M=Al: bulk(●), grain boundary(○)
M=Sc: bulk(▲), grain boundary(△)
M=Y : bulk(■), grain boundary(□)

by the M^{3+} substitution for the $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ system hardly influence the Li^+ mobility since the conductivities and activation energies of the bulk with the smaller Al^{3+} substituted system were similar to those of larger Sc^{3+} substituted one. Furthermore, the mixed phase ($LiTi_2(PO_4)_3$ and $Li_3Y_2(PO_4)_3$) system also showed a high bulk conductivity. The conductive bulk phase in this system is only $LiTi_2(PO_4)_3$. The second phase, $Li_3Y_2(PO_4)_3$, acts as a binder for the dense pellet. Consequently, the reason for the bulk conductivity enhancement could not be directly attributed to the bulk structure. The activation energy of the grain boundary component decreased by the M^{3+} addition. The sinterability also increased with the M^{3+} addition. For $LiTi_2(PO_4)_3$ (X=0) sample, the activation energy of the grain boundary showed high value with poor sinterability. The decrease in the activation energy at the grain boundary seems to be correlated with the difference in sinterability. For $LiTi_2(PO_4)_3$, a thin barrier, which is formed at the grain boundary, shows a high activation energy for the Li^+ ion conduction. This barrier phase would be disappeared by the increase in the sinterability. As a result, the conductivity of the grain boundary is enhanced by two order of magnitude for all the systems with the M^{3+} substitution.

The increase in the total conductivity by the trivalent cation substitution for the sintered $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ system is attributed to the decrease in the activation energy of the grain boundary.

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