JOURNAL OF SOLID STATE CHEMISTRY **71**, 164–171 (1987)

Lithium Ion Conduction in Substituted Li_5MO_4, M = Al, Fe

T. ESAKA* AND M. GREENBLATT†

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

Received June 19, 1986; in revised form November 24, 1986

The ionic conductivity of substituted Li_5AlO_4 and Li_5FeO_4 phases was measured by a complex impedance method. The high-temperature β phase was obtained in quenched Li_5AlO_4 but not in Li_5FeO_4. The Zn-substituted quenched samples form β-type phases in both systems and show much higher conductivities than those of pure Li_5MO_4. The best conductivities at 300°C are 1.5×10^{-3} and 7.0×10^{-3} $(\Omega\text{-cm})^{-1}$ for $Li_{5.9}Al_{0.1}Zn_{0.9}O_4$ and $Li_{5.5}Fe_{0.5}Zn_{0.5}O_4$, respectively. The results are discussed in relation to the structural properties.

Introduction

Li_5MO_4, M = Al, Ga, Fe, crystallizes in a low-temperature α and a high-temperature β polymorph; both phases are orthorhombic. The crystal structures are ordered variants of the antifluorite structure (Li_2O) (*1–7*), with one-quarter of the cation sites vacant. However, the space group symmetry of the α and β structures is different and in general the disorder of the cations and vacancies over the available tetrahedral sites is greater in the β phase. The β phase is metastable and a $\beta \rightarrow \alpha$ structural phase transition is observed when the β phase is cooled slowly from high temperature. The compounds can be conveniently represented by the formula $Li_5\square_2MO_4$, where $\square$ represents the vacancies. Thus these materials might be good Li ion conductors. Recently the ionic conductivity of α-type Li_5MO_4 phases have been measured (*8–12*). However, the intrinsic conductivities of the α phases reported are about four orders of magnitude lower than that of LISICON (*13*, *14*).

We have investigated the ionic conductivity of substituted Li_5GaO_4 phases and reported that the β phase has a significantly higher ionic conductivity than the α phase (*15*). The lithium conduction can be further improved by appropriate substitution of divalent cations for Ga^{3+} in the β phase (*15*).

Li_5AlO_4 is of interest as a solid electrolyte because of its stability in the presence of molten lithium and its high activation energy of conduction which is necessary for thermal battery application (*10*). In this study we have investigated the possibility of improving the ionic conductivity by stabilizing the β phase (with higher ionic conductivity) by Zn substitution. Our motivation to examine substituted Li_5FeO_4 phases was similar. Of the α-Li_5MO_4 phases, the Fe analog has the lowest activation energy

---

* Present address: Dept. of Environmental Chem. & Tech., Fac. of Eng., Tottori University, Tottori, Japan.

† Author to whom correspondence should be addressed.

0022-4596/87 $3.00

and the highest ionic conductivity (and largest unit cell volume) (*11*, *12*). Here we report results of ionic conductivity studies of substituted β-Li_5FeO_4 phases, which are substantially higher than that of the α phase. In addition, we show that unexpectedly the electronic contribution to the total conductivity is negligible and that Li_5FeO_4 appears to be thermodynamically stable against lithium metal.

Experimental

Reagent grade Li_2O, γ-Al_2O_3, Fe_2O_3, ZnO, MgO, ad GeO_2 were used as the starting materials. Li_2O was purified by sintering under vacuum at 750°C to decompose possible impurities of LiOH and/or Li_2CO_3. Stoichiometric compositions were mixed by grinding in an agate mortar in a He-filled dry box. The mixed powders were fired at 1000°C in air for 1 hr with excess Li_2O to minimize Li losses. The fired samples were ground, pressed into cylindrical pellets (6.5 mm diameter and 4–5 mm length) at 5 ton/cm^2, and heated again under the same conditions for 5 hr. The samples were then quenched from 1000°C to room temperature and used for the various measurements. The density of the sintered pellets varied between 85 and 87% of theoretical value. All phases obtained were examined by powder X-ray diffraction with Ni-filtered copper radiation and were found to be highly crystalline materials. ^{57}Fe Mössbauer measurements of some of the Li_5Fe O_4 phases were carried out as described previously (*16*).

Conductivity measurements were made in air and dry helium gas by a two-probe complex impedance method using a Solartron 1250 frequency analyzer and Solartron 1186 electrochemical interface in the frequency range of 1 Hz to 65 kHz. The sample probe used for the conductivity measurements is shown in Fig. 1. Both faces of each sample pellet were coated with sputtered gold or evaporated gold, which served as the electrode. The conductivity measurements were carried out on at least two independent samples of the same composition, prepared and treated in the same way, to check reproducibility of the results. Typical complex impedance plots of semicircles were obtained at various temperatures. Data collection and analysis were carried out with a Hewlett–Packard computer.

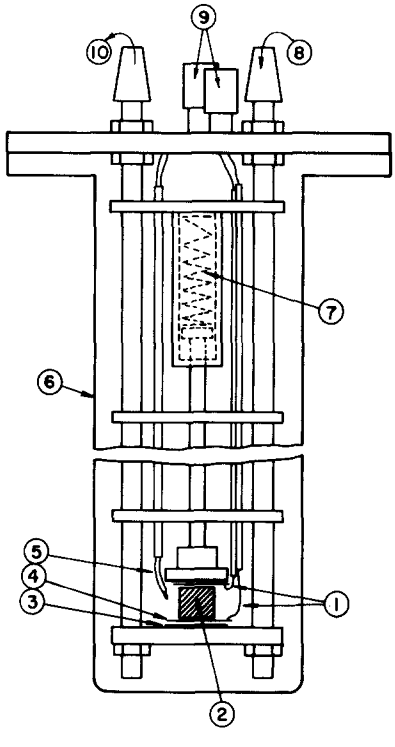

FIG. 1. Schematic diagram of the conductivity cell. (1) Pt leads; (2) sample disk; (3) alumina disk; (4) Pt plate; (5) thermocouple; (6) outer cover; (7) spring; (8) gas inlet; (9) terminal; (10) gas outlet.

Results and Discussion

Substituted Li_5AlO_4 Phases

In Li_5AlO_4 both the Li^+ and Al^{3+} ions occupy tetrahedral lattice sites in a cubic closed packed structure of oxygens in a

Li_2O-type lattice. Appropriate substitution by divalent cations can lead to either $Li_{5+x}\square_{2-x}Al_{1-x}M_x^{2+}O_4$ or $Li_{5-2x}M_x^{2+}\square_{2+x}AlO_4$ with concomitant changes in the Li content and vacancy concentration. Substitution by Zn and Mg was investigated. The composition of the starting materials was determined for replacement of Al^{3+} by Zn (or Mg) to yield $Li_{5+x}\square_{2-x}Al_{1-x}Zn_xO_4$. Similarly, the appropriate stoichiometry of starting materials was employed for the preparation of $Li_{5-2x}Zn_x^{2+}\square_{2+x}AlO_4$ (or Mg_x^{2+}). Solid solution single phases could only be formed with Zn substitution. The powder X-ray patterns of quenched samples of $Li_{5+x}Al_{1-x}Zn_xO_4$ (Fig. 3) and $Li_{5-2x}Zn_xAlO_4$ will be discussed subsequently. Efforts to substitute higher valent ions for the Al site to produce, for example, $Li_{5-x}Al_{1-x}Ge_xO_4$ phases were unsuccessful.

Quenched samples of Li_5AlO_4 have the β-type orthorhombic crystal structure (high temperature form). Figure 2 shows the Arrhenius plots of conductivity measured in air for β-Li_5AlO_4 together with the data of α-Li_5AlO_4 (*11*). The conductivity is about one order of magnitude higher than that for α-Li_5AlO_4 on first heating: 2.8×10^{-4} $(\Omega\text{-cm})^{-1}$ at 300°C. An abrupt increase in the conductivity is observed at about 430°C and the conductivity becomes much higher at higher temperatures. For measurement in dry He gas, the same conductivity data were obtained in the lower temperature range, but the abrupt conductivity change at 430°C was not observed. These and previous results suggest that in a moist atmosphere the reaction

$$Li_5AlO_4 + 2H_2O \rightarrow 4LiOH + LiAlO_2$$

occurs and the melting of LiOH at ~430°C is responsible for the enhanced conductivity seen in air. The X-ray powder diffraction patterns of these samples in air or under dry conditions do not indicate the presence of LiOH, suggesting that its concentration is small ($<\sim5\%$) or that it is amorphous. Upon cooling, the conductivities become lower in the temperature range below 430°C and correspond approximately to the data of α-Li_5AlO_4 in (*11*). After the conductivity measurements, the sample was checked by powder X-ray diffraction, which confirmed that a phase transition $\beta \rightarrow \alpha$ had occurred.

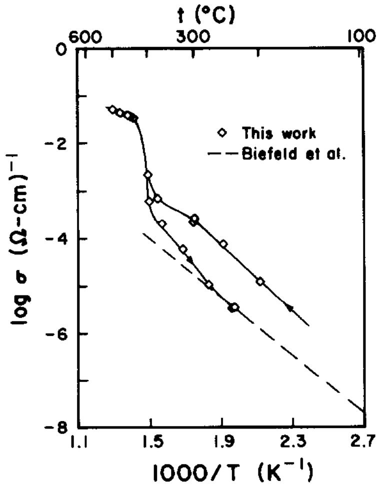

FIG. 2. Arrhenius plots of conductivity for Li_5AlO_4. The heating curve corresponds to the β phase and the cooling curve corresponds to the α phase.

In order to increase the concentration of vacancies in Li_5AlO_4, some lithium ions were replaced by Zn^{2+}. The results are almost the same as those of the system $Li_{5-2x}Zn_xGaO_4$ reported previously (*15*); the quenched samples for $x \leq 0.25$ show a β-type X-ray diffraction pattern, but for $x \geq 0.35$ several additional small peaks are observed, indicating a second phase. The shapes of the Arrhenius plots are similar to those of β-Li_5AlO_4 (Fig. 2); however, in $Li_{5-2x}Zn_xAlO_4$ zinc substitution did not improve the ionic conductivity.

Figure 3 shows the schematic powder X-ray diffraction data of the quenched samples of $Li_{5+x}Al_{1-x}Zn_xO_4$, in which the stoichiometry of the starting composition was designed so that some aluminum ions would be substituted by Zn^{2+}. The samples

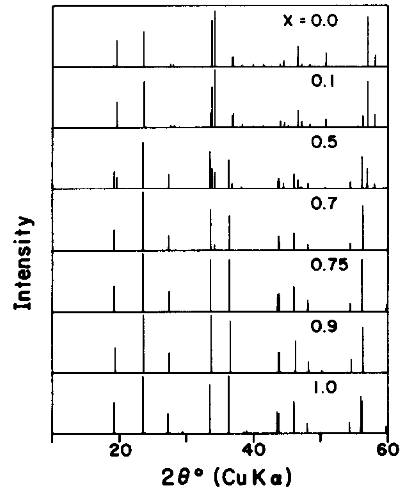

FIG. 3. X-ray diffraction data of $Li_{5+x}Al_{1-x}Zn_xO_4$ as a function of x.

where $0.10 \leq x \leq 0.70$ show the coexistence of β-Li_5AlO_4 orthorhombic phase and a second phase; the second phase corresponds to a tetragonal modification of β-Li_5AlO_4. For $0.75 \leq x \leq 1.0$ a single tetragonal phase is observed. In this system, we have not observed the smooth transition (orthorhombic to tetragonal) with increasing Zn content, which was seen in $Li_{5+x}Ga_{1-x}Zn_xO_4$ (*15*).

The powder X-ray diffraction pattern of β-Li_5GaO_4 is significantly different from that of the β-Li_5AlO_4, reflecting the differences in unit cell parameters and space group in these two compounds (a = 6.424 Å, b = 6.305 Å, c = 4.623 Å, and *Pmmn* for β-Li_5AlO_4; a = 9.288 Å, b = 8.983 Å, c = 4.632 Å, and *C*222 for β-Li_5GaO_4) (*1, 3, 4*). Apparently the Li^+ and M^{3+} ions order completely differently in these two compounds. However, in the zinc-substituted phases the tetragonal structures that form are identical for both, indicating that the disorder of the tetrahedral cations are similar.

Representative Arrhenius plots of conductivity measured in air are shown in Fig. 4. The zinc-substituted samples show conductivity behavior analogous to β-Li_5AlO_4 when heated in ambient atmosphere: an abrupt conductivity change at about 430°C and deviation between conductivity on heating and cooling. The difference in conductivity on thermal cycling was smaller with increasing x and nearly disappeared for $x \geq 0.90$, probably because the β phase is stabilized with increasing Zn content. In order to avoid confusion, the conductivity data on cooling are omitted from this figure except for $x = 0.1$. Figure 4 shows that with increasing zinc content the conductivity increases gradually. The best conductivity at lower temperatures observed in $Li_{5.9}Al_{0.1}Zn_{0.9}O_4$ is 1.5×10^{-3} $(\Omega\text{-cm})^{-1}$ at 300°C. This sample also has the lowest activation energy (E_a) of conduction, 0.51 eV. These conductivity data were identical within experimental error to those measured in dry He gas, which indicates that the presence of small concentrations of LiOH has a negligible effect on the ionic conductivity of both the α and β phases. For samples having higher zinc content (lithium content) $x > 0.9$, the conductivity decreased, proba-

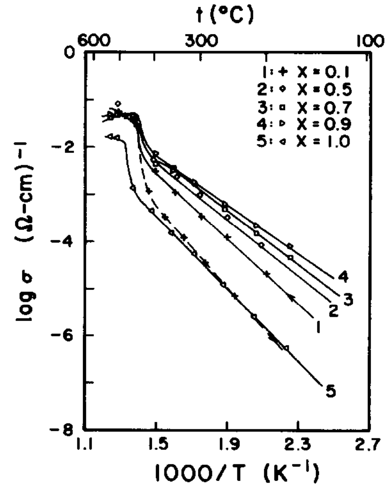

FIG. 4. Arrhenius plots of conductivity for $Li_{5+x}Al_{1-x}Zn_xO_4$. The dashed line is the cooling curve; solid lines are data for heating.

bly because a greater part of the vacancies are occupied and unavailable for diffusion.

Biefeld *et al.* have reported an electronic contribution (3–20%) to the conductivity in α-Li_5AlO_4 at $t \leq 360°C$ (*9, 10*). In β-$Li_{5+x}Al_{1-x}Zn_xO_4$ an obvious frequency dispersion observed in the low-frequency region of the complex impedance plots strongly suggests that ionic conduction is predominant. Thus, a 1–3% electronic contribution may be attributed to the total conductivity. We have measured the dc vs ac resistances of a sample which is often used to check the contribution of electronic conductivity in predominantly ionically conducting samples. The ratios of ac to dc resistances, obtained from voltage-current relations below 500 mV, are 0.01–0.03, much higher than what we have observed in other lithium conductors. This may be ascribed to the high reactivity of Li_5AlO_4 with moisture and possibly with oxygen and the formation of surface defects and/or impurities. However, if a passivating film formed to block electronic conductivity, one would expect a much higher DC resistivity than observed. Moreover, the most likely passivating surface films, LiOH or Li_2O, have very low ionic conductivities under the conditions of our experiments. Therefore, formation of such films on the surface of the title compound is contrary to the high ionic conductivities observed.

Substituted Li_5FeO_4 Phases

As mentioned earlier and reported previously (*15*), we have not observed improved conductivity in Li_5MO_4-based systems (M = Al, Ga) when the stoichiometry of starting composition was designed so that the concentration of vacancies would increase with increasing substitution by aliovalent cations (i.e., $Li_{5-2x}M_x^{2+}M^{3+}O_4$). Therefore, in this system, we have investigated the conductivity with increasing concentration of lithium ions in $Li_{5+x}Fe_{1-x}M_x^{2+}O_4$ (M = Zn, Mg).

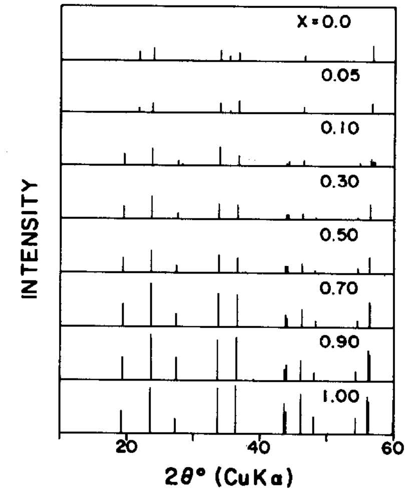

FIG. 5. X-ray diffraction data of $Li_{5+x}Fe_{1-x}Zn_xO_4$ as a function of x.

Figure 5 shows the schematic powder X-ray diffraction patterns of quenched samples of $Li_{5+x}Fe_{1-x}Zn_xO_4$. For pure Li_5FeO_4 and for $x = 0.05$ only the α, low-temperature phase formed. However, for $x \geq 0.10$, the β phase was obtained in quenched samples. The X-ray patterns of the β phases are analogous to those of the tetragonal modification of β-Li_5GaO_4 (*15*). Demoisson *et al.* have already reported the orthorhombic lattice parameters of pure β-Li_5FeO_4 (*6*), a = 6.479 Å, b = 6.472 Å, c = 4.634 Å, which suggests that the crystal lattice is pseudotetragonal. With increasing Zn content in the compositional range $0.1 \leq x \leq 1.0$, the diffraction peaks shift to lower angles, indicating an increase of lattice parameters with increasing Zn substitution. As the ionic radius of Zn^{2+} (0.60 Å) is considerably larger than that of Fe^{3+} (0.49 Å) (*17*), this result is not unexpected and confirms that the Zn^{2+} is substituting for Fe^{3+} as intended (i.e., the effective ionic radius of Li^+ in a tetrahedral site is 0.59 Å; hence, if Zn^{2+} would replace Li^+, no increase in cell volume would be expected; furthermore, additional phases would be seen in the X-ray pattern since the

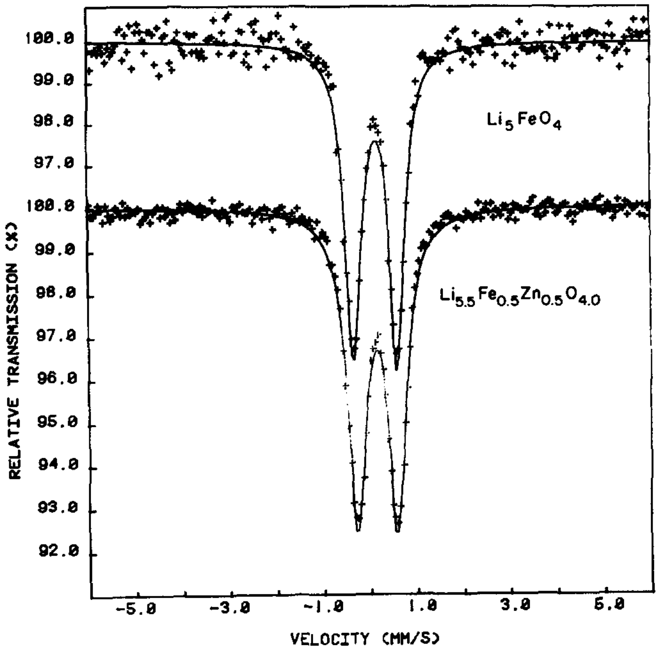

FIG. 6. ^{57}Fe Mössbauer spectra at 298 K of Li_5FeO_4 and $Li_{5.5}Fe_{0.5}Zn_{0.5}O_4$.

stoichiometry of the starting materials was designated to form $Li_{5+x}Fe_{1-x}Zn_xO_4$ phases).

Ramdani and Brice reported that β-Li_5FeO_4 is formed by sintering of the α-phase in an oxygen atmosphere above 800°C and that the presence of Fe^{4+} stabilizes the formation of the β phase (*12*). However, ^{57}Fe Mössbauer measurements of our β-Li_5FeO_4 and $Li_{5.5}Fe_{0.5}Zn_{0.5}O_4$ samples show the presence of Fe only in the +3 oxidation state (Fig. 6). Moreover, we do not find the high electronic contribution to the conductivity in any of our samples, as was previously reported (*12*).

Figure 7 shows typical Arrhenius plots of conductivity on first heating. The results are almost identical to those of $Li_{5+x}Al_{1-x}Zn_xO_4$: there is an anomalous increase in the conductivity at about 430°C and a difference in the conductivity between the heating and cooling cycles similar to that shown in Fig. 2. In this figure, the data on cooling are omitted to avoid confusion. α-Li_5FeO_4 has poor conductivity; with increasing zinc content the conductivity is

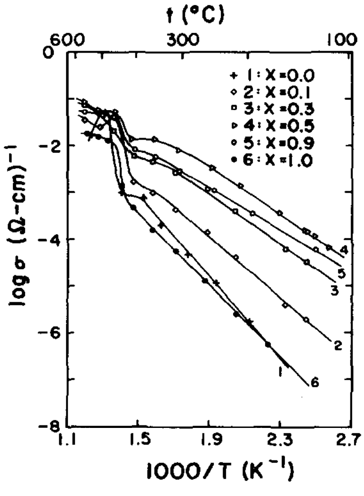

FIG. 7. Arrhenius plots of conductivity for $Li_{5+x}Fe_{1-x}Zn_xO_4$.

improved and $Li_{5.5}Fe_{0.5}Zn_{0.5}O_4$ shows the best conductivity ($\sigma = 7.0 \times 10^{-3}$ $(\Omega\text{-cm})^{-1}$ at 300°C). In the composition range $0.5 \leq x \leq 0.8$, the conductivity is nearly equal and high. However, at $x \geq 0.9$ the conductivity decreases and the sample $x = 1.0$ has the lowest conductivity of all the β-$Li_{5+x}Fe_{1-x}Zn_xO_4$ phases.

We also measured the conductivity of representative samples in a dry helium atmosphere. Pure Li_5FeO_4 shows a small atmosphere dependence. It is not certain whether this is due to the partial electronic conduction mentioned in (*12*) or the effect of moisture (*11*). Considering the results of the Mössbauer measurements, electronic conductivity due to mixed-valent iron in Li_5FeO_4 is not expected (Fig. 6). In contrast, the conductivities of Zn-substituted samples are almost independent of atmosphere except for the high-temperature range which suggests that Zn-containing samples are more stable against reaction with moisture.

Similar behavior is found in Mg-substituted phases of β-$Li_{5+x}Fe_{1-x}Mg_xO_4$ in which single phases form for $0.10 \leq x \leq 0.40$. However, the conductivity in this series of compounds is significantly lower than in the Zn-substituted samples.

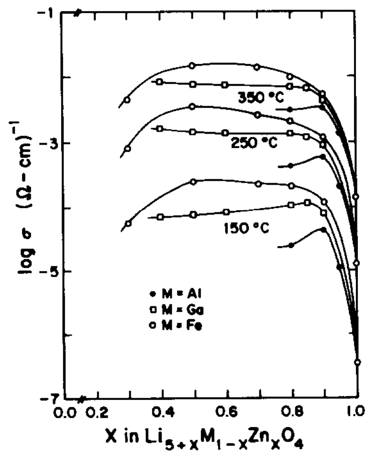

FIG. 8. Conductivity isotherms for the tetragonal phases of $Li_{5+x}M_{1-x}Zn_xO_4$ (M = Al, Ge, Fe).

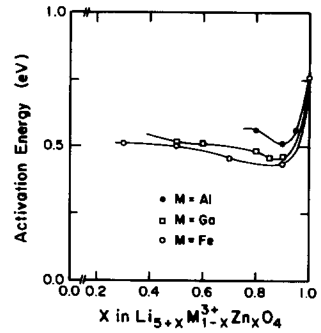

FIG. 9. Activation energies for the tetragonal phases of $Li_{5+x}M_{1-x}Zn_xO_4$ (M = Al, Ge, Fe).

In order to check the electronic contribution to the conduction in the best conducting sample ($Li_{5.5}Fe_{0.5}Zn_{0.5}O_4$), we used two methods: the ac and dc resistance of a sample were compared and a lithium cell using a sample as an electrolyte was investigated. The dc resistance was always two or more orders of magnitude larger than the ac resistance. The cell $Li|Li_{5.5}Fe_{0.5}Zn_{0.5}O_4|PbO_2$ from room temperature up to 300°C indicated stable EMFs which correspond approximately to $-(\Delta G_f(2Li_2O) - \Delta G_f(PbO_2))/4\mathcal{F}$. These results suggest that the electronic conduction in $Li_{5.5}Fe_{0.5}Zn_{0.5}O_4$ is very low. It could be argued that the low electronic conduction may be due to the formation of ionically conducting surface layers which block any electronic current in dc experiments. Furthermore, the apparent stability of the sample against lithium metal may also be attributed to the formation of a protecting layer, which acts as an electrolyte and generates the expected thermodynamic EMF. However, there is no evidence for the formation of extensive surface layers in these phases as we discussed before, based on the ac/dc measurements and the relatively high ionic conductivities observed.

In Figs. 8 and 9, conductivity isotherms and activation energies (E_a) of conduction, respectively, for tetragonal $Li_{5+x}M_{1-x}Zn_xO_4$ (M = Al, Ga, Fe) phases show that for a given value of x, the conductivity of tetragonal $Li_{5+x}Fe_{1-x}Zn_xO_4$ phases is significantly higher and the E_a is lower than corresponding tetragonal $Li_{5+x}M_{1-x}Zn_xO_6$ (M = Al, Ga) compounds. This may be attributed to the larger effective ionic radius of Fe^{3+} (0.49 Å) compared to those of Al^{3+} (0.39 Å) and Ga^{3+} (0.47 Å), providing a larger effective diffusion path for lithium ions.

Conclusion

Quenched samples of Li_5AlO_4 with β-type high temperature structure show higher ionic conductivity than the α analog. However, the β phase is metastable and transforms to the α phase upon heating to 500°C.

β-Li_5AlO_4 phases are also formed in the quenched samples of $Li_{5-x}Zn_xAlO_4$ (x = 0.0–0.25). However, the conductivity is not improved.

In $Li_{5+x}Al_{1-x}Zn_xO_4$ ($0.10 \le x \le 0.70$), the conductivity increases with increasing zinc content irrespective of the formation of a mixed β-Li_5AlO_4 orthorhombic phase and its tetragonal modification. For $0.75 \le x \le 0.90$, where a single tetragonal phase is observed, the conductivity becomes much higher. $Li_{5.9}Al_{0.1}Zn_{0.9}O_4$ has the maximum conductivity of 1.5×10^{-3} $(\Omega\text{-cm})^{-1}$ at 300°C.

For pure Li_5FeO_4, the high temperature β phases cannot be obtained at room temperature by quenching. However, in the Zn-substituted samples, $Li_{5+x}Fe_{1-x}Zn_xO_4$ ($x \ge 0.10$), the β phase forms upon quenching. The behavior of conductivity in this phase is very similar to that of β-$Li_{5+x}Al_{1-x}Zn_xO_4$. $Li_{5.5}Fe_{0.5}Zn_{0.5}O_4$ shows the best conductivity of 7.0×10^{-3} $(\Omega\text{-cm})^{-1}$ at 300°C. The samples of $Li_{5+x}Fe_{1-x}Zn_xO_4$ with tetragonal symmetry show relatively higher conductivities and lower activation energies than those of $Li_{5+x}Ga_{1-x}Zn_xO_4$ or $Li_{5+x}Al_{1-x}Zn_xO_4$ with analogous structure and the same x. These results indicate that the larger size of Fe is more effective than Ga and Al in forming a conduction path for lithium ions in Li_5MO_4 compounds. Li_5FeO_4 and the Zn-substituted phases appear to be primarily Li^+ ion conductors: the electronic contribution to the conductivity, which might be due to mixed-valent Fe^{3+}/Fe^{2+}, is negligible. Furthermore these compounds appear to be stable against Li metal.

Acknowledgments

We thank E. Wang and Professor R. H. Herber for the Mössbauer measurements. This work was supported by the Office of Naval Research and the National Science Foundation—Materials Research Instrumentation Grant DMR-8408266.

References

1. R. Hoppe and H. Konig, *Z. Anorg. Allg. Chem.* **430,** 211 (1977).
2. F. Stewner and R. Hoppe, *Z. Anorg. Allg. Chem.* **380,** 241 (1971).
3. F. Stewner and R. Hoppe, *Z. Anorg. Allg. Chem.* **381,** 149 (1971).
4. F. Stewner and R. Hoppe, *Z. Anorg. Allg. Chem.* **381,** 140 (1971).
5. F. Stewner and R. Hoppe, *Acta Crystallogr. B* **27,** 616 (1971).
6. G. Demoisson, F. Jeannot, C. Gleitzer, and J. Aubry, *C.R. Acad. Sci. Paris C* **272,** 458 (1971).
7. R. Luge and R. Hoppe, *Z. Anorg. Allg. Chem.* **513,** 141 (1974).
8. I. D. Raistrick, C. Ho, and R. A. Huggins, *Mater. Res. Bull.* **11,** 953 (1976).
9. R. T. Johnson, Jr., R. M. Biefeld, and J. D. Keck, *Mater. Res. Bull.* **12,** 577 (1977).
10. R. M. Biefeld and R. T. Johnson, Jr., *J. Solid State Chem.* **29,** 393 (1979).
11. R. M. Biefeld and R. T. Johnson, Jr., *J. Electrochem. Soc.* **126,** 1 (1979).
12. A. Ramdani and J. F. Brice, *Ann. Chim. Fr.* **6,** 569 (1981).
13. U. V. Alpen, M. F. Bell, and W. Wichelhaus, *Electrochim. Acta* **23,** 1395 (1978).
14. H. Y-P. Hong, *Mater. Res Bull.* **13,** 117 (1978).
15. T. Esaka and M. Greenblatt, *Solid State Ionics* **21,** 255 (1986).
16. M. Greenblatt, E. Wang, H. Eckert, N. Kimura, R. H. Herber, and J. V. Waszczak, *Inorg. Chem.* **24,** 1661 (1985).
17. R. D. Shannon, *Acta Crystallogr. A* **32,** 751 (1976).