

Li-Phosphate Minerals and Storage Batteries

Examples of the use of minerals in technological applications abound, and “materials mineralogy” has remained one of many exciting frontiers in the science. A frequent feature of *Elements* will be discussions and updates on recent mineralogical studies that focus on or are relevant to the materials applications of minerals.



Triphylite in a matrix of microcline, quartz, and muscovite, Chandlers Mills, New Hampshire. PHOTOGRAPH COURTESY OF SMITHSONIAN INSTITUTION (NMNH SPECIMEN #R9228), PHOTOGRAPHER KEN LARSEN.

The minerals of the lithiophilite (LiMnPO_4)–triphylite (LiFePO_4) series, for which there exists a complete solid solution in nature, provide our first example. Lithiophilite–triphylite occur in rather restricted environments—evolved granitic pegmatites enriched in both Li and P—and thus are relatively uncommon. These phases are isostructural with olivine and are therefore commonly referred to as having an olivine-type structure.

Recently, there has been considerable interest in the Li-phosphate olivine, triphylite, as a storage

cathode for rechargeable lithium batteries (Andersson et al. 2000; Chung et al. 2002; Huang et al. 2001; Padhi et al. 1997a, 1997b; Prosini et al. 2001; Yamada et al. 2001a, 2001b; Yang et al. 2002). Keys to the use of triphylite in batteries are its electrical and ion (Li) conductivities. Triphylite, as well as other phases with an olivine structure, is an electrical insulator, which is the main impediment to its use in batteries. Chung et al. (2002), however, have shown that controlled cation nonstoichiometry combined with doping can increase the electrical conductivity of triphylite by as much as 10^8 times, well above that of Li storage cathodes currently used in commercially available

batteries. They postulated that in a conventional cell design, triphylite may yield the highest power density yet developed in rechargeable Li batteries. Furthermore, they speculated that the same doping mechanism for increasing electrical conductivity in triphylite will apply to other olivine-structure phases, such as lithiophilite. Structural changes in triphylite due to solid solutions with iron may have significant effects on its solid electrolyte properties, including rates of Li diffusion and activation energies. Thus, knowledge of structural changes that result from solid solutions are important in the development and design of Li-phosphate storage cathodes. In a recent study by Losey et al. (2004), single-crystal X-ray diffraction experiments were performed on natural lithiophilite–triphylite samples with Fe/(Mn+Fe) ratios of 6, 27, 50, 79, and 89 (referred to as Trip06, etc.). The atomic arrangement of each sample was refined to elucidate the structural changes with composition in this series.

The octahedrally coordinated cations in the lithiophilite–triphylite series are completely ordered between the *M1* and *M2* sites. Only Li occupies the *M1* site, whereas the *M2* site is occupied by divalent Mn, Fe, and in some cases, Mg. The complete ordering of cations in these minerals is in contrast to the majority of olivine-structure phases, in which there is extensive disorder among the octahedrally coordinated cations. Although Mn and Fe occupy only the *M2* site in the lithiophilite–triphylite series, the solid solution between these two constituents affects both the *M2* and *M1* sites.

The substitution of Fe^{2+} ($r = 0.78$ Å; Shannon 1976) for Mn^{2+} ($r = 0.83$ Å) in the lithiophilite–triphylite series suggests, by Vegard’s law, that a concomitant shortening of the octahedron bond lengths should occur. Although the shortening of the bond lengths involving *M2* is expected, the bond-length variations in that polyhedron also induce variations in the *M1* polyhedron, occupied solely by Li. The *M1*-O1 and *M1*-O2 bond lengths decrease, whereas the *M1*-O3 bond length increases with increasing Fe-for-Mn substitution. This change occurs with no substitution of cations for Li in the *M1* site. These structural changes in the lithiophilite–triphylite solid solution may have an effect on the activation energy for Li diffusion, and thus the rate of diffusion. The activation energy of Li diffusion is directly related to the energy necessary to break all the *M1*-O bonds. Bond-valence considerations indicate that Li is more underbonded in lithiophilite and thus is less stable in the *M1* site in this end member. Consequently, breaking the six *M1*-O bonds will be energetically easier in lithiophilite, which in turn will lead to greater rates of Li diffusion, making lithiophilite a potentially better storage cathode.

Although members of the lithiophilite–triphylite series are rather rare minerals of restricted geological significance, the physical and chemical properties that make them amenable to applications in battery manufacturing, may someday turn out to be of great societal and economic importance.

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John Rakovan

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