Lithium Insertion into Phases with NZP Structure

U. V. Varadaraju,[a] K. Antony Thomas,[a] Bommasamudram Sivasankar,[b] and G. V. Subba Rao[a]

[a] *Materials Science Research Centre, Indian Institute of Technology, Madras 600 036, India*
[b] *Department of Chemical Engineering, A. C. College of Technology, Anna University, Madras 600 025, India*

Insertion of Li into the vacant sites (channels) of certain NZP phases ($ATi_2P_3O_{12}$, A = Li, Na, and $NbTiP_3O_{12}$) using Bu^nLi at room temperature has been established; the preparation and preliminary structural and i.r. data of the phases are described.

Nasicon ($Na_3Zr_2Si_2PO_{12}$), the Na superionic conductor, belongs to the class of NZP ($NaZr_2P_3O_{12}$) phases possessing hexagonal symmetry with a 3D-framework with interconnected channels for the Na^+ ions.[1—3] Chemical substitution is possible in NZP; thus, $LiTi_2P_3O_{12}$ and $\square\ NbTiP_3O_{12}$ ($\square$ = vacancy) are isostructural phases.[2,4] We have been able, for the first time, to insert Li into certain of the NZP phases using Bu^nLi. Lithium insertion is possible *only* when the lattice has chemically reducible species (*e.g.*, Ti or Nb). Preparation and preliminary structural and i.r. data are now described.

The parent compounds, AM_2X (A = Li or Na; M = Ti or Zr; X = P_3O_{12}) and NbTiX, were prepared in powder form by high temperature solid state reaction and characterized by *X*-ray diffraction (x.r.d.) (Philips; Cu-K_α radiation). The hexagonal lattice parameters agreed with the literature.[3,5] Lithiation was carried out using Bu^nLi (Merck, 1.6 M, or prepared from Bu^nBr and Li in n-hexane) at 25 °C in an Ar-filled glove bag. Chemical analysis was performed in the usual manner.[6] The compounds were recovered by filtration, washed with hexane, and dried. I.r. spectra were recorded in the range 4 000 to 200 cm^{-1} (KBr disc; Perkin-Elmer 983). The pure white compounds $LiTi_2X$ and NbTiX turn blue or blue–black on contact with Bu^nLi in hexane. The intensity of the colour increases with time and the reaction is complete in 12—20 h (1 g sample; 50 ml solution). The compounds are stable to air and moisture but long-term exposure (1—2 weeks) produces slight delithiation. Delithiation can be accelerated by dilute acid treatment or oxidation by I_2 in acetonitrile (room or elevated temperatures).

Singly and doubly lithiated phases could be prepared from $LiTi_2X$ and NbTiX while $LiZr_2X$ and $NaZr_2X$ could not be lithiated. Hence, for lithiation, chemically reducible species (Ti^{4+} or Nb^{5+}) must be present in the host lattice, and the colouration is thus due to reduction of M^{n+} species. Analysis of the x.r.d. patterns of Li_xNbTiX (x = 0,1,2) indicated that the hexagonal structure of the parent NbTiX phase (x = 0) is retained but there is a slight decrease in the a-axis and consistent increase in the c-axis. (The least-squares-fitted lattice parameters are: x = 0: a = 8.55, c = 21.99 Å; x = 1: a = 8.50, c = 22.39 Å; x = 2: a = 8.53, c = 22.43 Å). However, distinct changes in the x.r.d. patterns, characteristic of a monoclinic distortion, are evident in singly and doubly lithiated $LiTi_2X$ phases. The distortion was found to be small and the x.r.d. pattern could be indexed on the basis of a hexagonal unit cell. The lattice parameters are: $LiTi_2X$: a = 8.53, c = 20.88 Å; Li_2Ti_2X: a = 8.52, c = 20.87 Å; Li_3Ti_2X: a = 8.63, c = 20.68 Å. Thus, significant changes occur only on going from Li_2Ti_2X to Li_3Ti_2X.

The i.r. spectra of most of the NZP analogues have been well-studied.[7] Present i.r. studies do not indicate significant changes in the spectra of NbTiX and Li_xNbTiX whereas distinct changes are noted in Li_xTi_2X (x = 1,2,3) phases. These are evident in the regions 1 050—900 (ν_{sym} and ν_{asym}; PO_4 tetrahedra), 650—550, 400 (δ_{sym} and δ_{asym}; PO_4 tetrahedra), and 370—350 cm^{-1} (ν_{A-O} and ν_{M-O}; AO_6 and MO_6 octahedra). The observed changes in lattice parameters and i.r. spectra can be rationalized since the added Li occupies vacant lattice sites in the NZP structure (so-called type I and/or type II sites). Preliminary studies show that Li insertion is also possible with $NaTi_2X$, $Ca_{0.5}Ti_2X$, and other A_xTi_2X (A

= metal) and NbZrX phases, all of which contain reducible species in the crystal lattice.

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