Optical properties of lithium titanium oxide nanocrystals

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Lithium titanium oxide ($Li_4Ti_5O_{12}$) is a wide band gap material (E_g = 3.6 eV), so pure, undoped crystals have very high electronic resistivity, of the order of 10^{12} Ωcm. However, the strongly bound titanium oxide structure lefts place for diffusion of lithium ions. Due to high mobility of Li ions, it is used as ionic conductor in lithium-ion batteries. In order to obtain good electric conductivity, is grown in form of nanocrystals and mixed with good conductors, for example carbon nanotubes. Such mixture has electrical conduction about of 10^{-3} $\Omega^{-1}cm^{-1}$, high enough for Li battery applications. Here we present time-resolved photoluminescence (PL) and Raman spectroscopy of pure $Li_4Ti_5O_{12}$ and doped with Ag. The doping leads probably to $Li_{1-x}Ag_xTi_5O_{12}$ alloy.

The three-step solid state synthesis including ball milling process with alcohol medium was used to obtain the lithium titanium-oxide powder of spinel structure. The LTO powders grains were modified with Ag nanoparticles. The scheme of preparation we presented in our earliest work[1]. $Li_4Ti_5O_{12}$ powder has a uniform, nearly cubic structural morphology with a narrow size distribution about 500 nm.

The Raman spectra were recorded at room temperature using Renishaw inVia 1000 micro-Raman system. A Nd:YAG laser was used with the excitation wavelength of 532 nm and a reduced laser power up to 2 mW. Raman spectra features of $Li_4Ti_5O_{12}$ powder are in good agreement with five predicted phonon modes of the cubic spinel structure (A_{1g} + E_g + $3F_{2g}$) indicating the formation of pure $Li_4Ti_5O_{12}$ phase. Relatively narrow lines demonstrate the formation of well-crystalline $Li_4Ti_5O_{12}$ material.

It is known that Ag particles can induce surface enhanced Raman scattering effect.
PL dynamics was studied from 4 to 300 K with use of a streak camera. The PL spectra consisted (see Fig.) of weak band-to-band emission at about 3.6 eV and strong deep defect band at about 2.5 eV. The defects were most probably related to diffusion of lithium. The energy of this band increased with temperature was probably due to activation of Li transport. The PL lifetime of this band at 4 K was of the order of few ns, similarly like for deep defects in wide band-gap semiconductors.

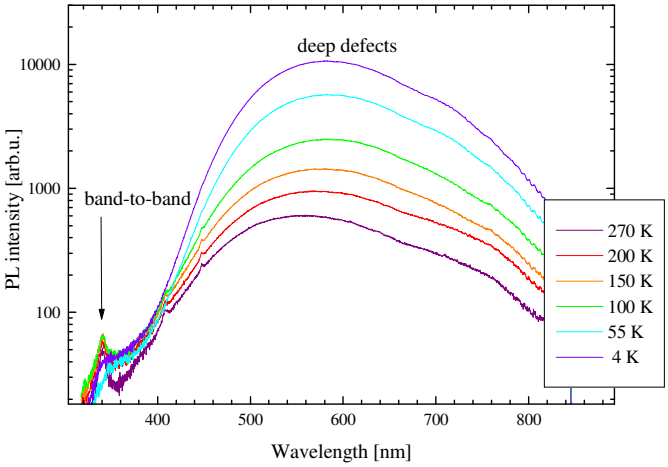

Fig. PL spectra of $Li_4Ti_5O_{12}$ for different temperatures.

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