The Valence States and Structure Symmetry of V and Cr in Spinel $LiTi_{2-x}M_xO_4$(M= V or Cr) Studied by X-ray Absorption Spectroscopy

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In spinel $LiTi_2O_4$ system, the crystal structure is made of LiO_4 tetrahedra and TiO_6 octahedra. With doping of impurities in Li or Ti sublattice, the extent of suppression or enhancement of the superconducting transition temperature depends on the magnetism of impurity and exchange coupling parameter between impurity and Cooper pairs. As reported in the literature, the nonmagnetic impurity substitution in tetrahedral T_d or octahedral O_h sites does not affect the superconductivity compared to the magnetic impurites. We have studied the physical properties of the dope-V or Cr $LiTi_2O_4$ system.

Since X-ray absorption probes dipole transition from core hole to unoccupied state of specific element according to incident photon energy, the chemical state and symmetry of the doped-V and Cr ions could be determined by L-edge absorption measurement.

Fig. 1 presents the V $L_{3,2}$-edge resulting from the dipole transition from 2p to 3d. The results show that the vanandium ion location in O_h octahedral site is consistent with the $Y_{1-x}Ca_xVO_3$ system [1]. The spectral profiles do not show any energy shift. The crystal splitting of white lines looks very much similar except for the concentration effect. The vanandium is found to be in trivalent state in the whole region from x=0 to x=0.4.

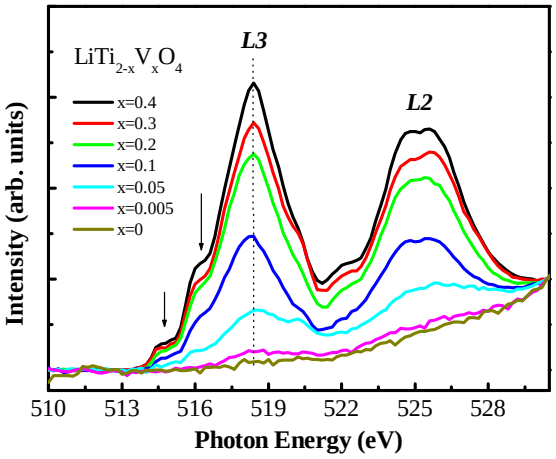

Figure 1. V *L*-edge spectra in $LiTi_{2-x}V_xO_4$ system. The absorption intensities were normalized at the background of x=0. The dashed line is meant to guide the eye.

From the Cr L-edge absorption spectra shown in Fig. 2, the Cr ion is observed to resided in the O_h octahedral site which is the same as the $FeCr_2O_4$ system [2]. As there is no energy shift and the same spectral shifts in $L_{3,2}$ absorption peak, we conclude that the Cr ion remains in trivalence state at the O_h symmetry without any higher oxidation state.

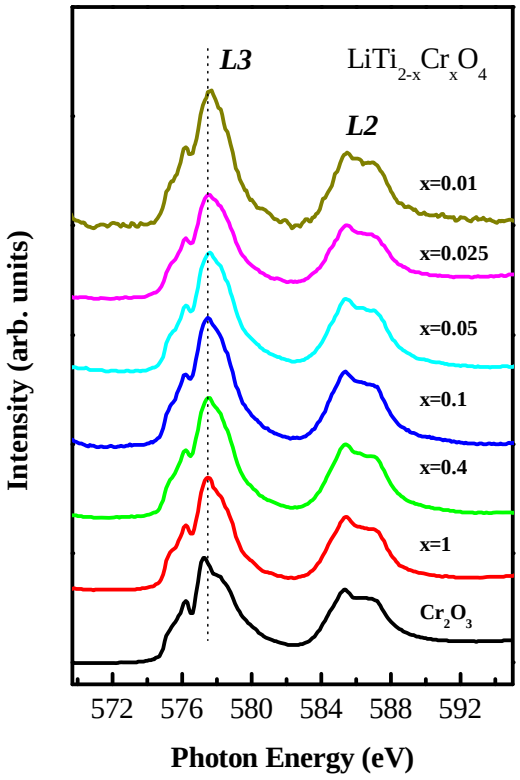

Figure 2. Cr L-edge spectra in $LiTi_{2-x}Cr_xO_4$ system. All spectra are normalized at the highiest peaks position. Pure commercial Cr_2O_3 powder was used as reference.

We conclude that V or Cr are doped in trivalent state only and occupy the octahedral sites, as with Ti. Due to charge compensation requirements, the Ti ion was found in mixed valenes states and the carrier density decreases with doping concentration.

References

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