

# Reply to “Comment on “Effect of Chromium Substitution on Lattice Vibration of Spinel Lithium Manganate: A New Interpretation of Raman Spectrum of LiMn<sub>2</sub>O<sub>4</sub>”

Seong-Ju Hwang\* and Dae-Hoon Park

Division of Nano Sciences and Department of Chemistry,  
Ewha Womans University, Seoul 120-750, Korea

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We would like to thank Paolone, A. et al. for their valuable comment on our recent paper (*J. Phys. Chem. B* 2004, 108, 12713). We would like to clarify the following points raised in the comment.

**(1) Thermal decomposition of spinel compound by laser radiation.** As described in the original paper, we have examined carefully the sample surface before and after each Raman measurement in order to rule out the possibility of the sample degradation. During the experiments with a relatively weak laser power (<5 mW), we could not observe any change in the morphology of the sample surface, even though a thermal decomposition would cause a notable change in the sample surface. Actually, our Raman spectrum of LiMn<sub>2</sub>O<sub>4</sub> is in good agreement with many previously reported spectra by several different groups.<sup>1</sup> Especially, it is worthwhile to note that nearly the same spectral features as ours were reported from the micro-Raman measurement with a very weak laser (less than 1 mW, which is comparable to the laser power of 0.5 mW in the comment).<sup>1a</sup> More importantly, the Raman spectra in that study were collected by focusing the laser light on the LiMn<sub>2</sub>O<sub>4</sub> sample immersed in an aqueous electrolyte solution that can protect effectively the sample from thermal degradation by local heating. Furthermore, those authors made a clear statement that there was no spectral change even after the irradiation for 40 min. In this context, we are able to regard ref 1a as clear evidence that the previously reported Raman spectra of LiMn<sub>2</sub>O<sub>4</sub> including ours correspond to the true phonon spectra of the spinel lithium manganate.

According to the thermal analyses on the spinel lithium manganates,<sup>2</sup> the cubic spinel LiMn<sub>2</sub>O<sub>4</sub> experiences several phase transitions during the heat treatment, in which tetragonal spinel Li<sub>1-2x</sub>Mn<sub>2-x</sub>O<sub>4-y</sub> is formed in the temperature region of 780–915 °C, and this phase transforms to an orthorhombic LiMnO<sub>2</sub> at temperatures above 915 °C and consequently to Mn<sub>3</sub>O<sub>4</sub> beyond 1060 °C. While the orthorhombic LiMnO<sub>2</sub> shows an intense Raman peak at ~660 cm<sup>-1</sup> with shoulder peaks at low wavenumber side,<sup>1d</sup> an intense Raman peak at 666 cm<sup>-1</sup> is discernible for Mn<sub>3</sub>O<sub>4</sub> together with smaller features at 486, 384, 329, and 300 cm<sup>-1</sup>.<sup>3</sup> The spectrum of LiMn<sub>2</sub>O<sub>4</sub> in the original paper, which is similar to the spectrum recorded with 5 mW-powered laser in the comment, does not match with that of Mn<sub>3</sub>O<sub>4</sub> as well as with those of other possible thermal-decomposition products such as orthorhombic LiMnO<sub>2</sub> and tetragonal spinel Li<sub>1-2x</sub>Mn<sub>2-x</sub>O<sub>4-y</sub>. On the contrary, Paolone, A. et al. reported the other type of Raman spectra for the samples subjected to the extended exposure to laser light,<sup>3b</sup> which are very similar to the spectrum of Mn<sub>3</sub>O<sub>4</sub>. Also, we have observed

an intense peak around 660 cm<sup>-1</sup> commonly from the cubic spinel LiMn<sub>2</sub>O<sub>4</sub> and the tetragonal spinel Li<sub>2</sub>Mn<sub>2</sub>O<sub>4</sub>, in case the samples are damaged by an extended exposure for a high power laser irradiation. Such a peak would be an indicator for the thermal decomposition of LiMn<sub>2</sub>O<sub>4</sub> into Mn<sub>3</sub>O<sub>4</sub> or orthorhombic LiMnO<sub>2</sub>. However, we have never detected an intense peak at ~625 cm<sup>-1</sup> from the tetragonal spinel Li<sub>2</sub>Mn<sub>2</sub>O<sub>4</sub> sample, even though our X-ray diffraction (XRD) analysis reveals that a heat-treatment for this compound at above 1200 °C also gives rise to a phase transition into Mn<sub>3</sub>O<sub>4</sub>, like the cubic spinel LiMn<sub>2</sub>O<sub>4</sub>.<sup>2a</sup> This finding supports that the Raman spectra of LiMn<sub>2</sub>O<sub>4</sub> presented in our paper and the other reports<sup>1</sup> do not come from the product of thermal decomposition.

**(2) Raman spectral variation caused by Cr substitution.** In their comment, Paolone, A. et al. tried to explain the spectral variation upon Cr substitution from an enhanced thermal stability of the cubic spinel phase and/or from a decrease of laser absorption through a change of band structure. To check out these possibilities, we have probed the variation of crystal structures of LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> caused by the heat-treatment. Although the replacement of Mn with Cr would improve the lattice stability of lithium manganates,<sup>4</sup> the heat-treatment at about 1230 °C was found to induce the phase transition commonly for both LiMn<sub>2</sub>O<sub>4</sub> and LiMn<sub>1.5</sub>Cr<sub>0.5</sub>O<sub>4</sub>. Also, we have measured the diffuse UV–visible spectra of LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub>, clarifying the negligible change of absorption spectra upon the Cr substitution. Therefore, the observed notable change in Raman spectra after the Cr substitution cannot be due to the enhancement of thermal stability and/or the change of band structure. In addition, they suggested that the depression of Mn<sub>3</sub>O<sub>4</sub> formation induced by the lowering of Mn/Cr ratio would be another reason for the enhancement of the 580 cm<sup>-1</sup> peak and the depression of the 625 cm<sup>-1</sup> peak upon the Cr substitution. However, we have found that, in the case of the tetragonal spinel, the Cr substitution does not result in any significant variation of Raman spectral features in 580–630 cm<sup>-1</sup> region.<sup>5</sup>

On the other hand, Paolone, A. et al. cast doubts on the observed frequency dependence of the 580 and 625 cm<sup>-1</sup> peaks upon Cr content. From the viewpoint of dissimilar atomic masses of Cr and Mn, they interpreted the negligible shift of 625 cm<sup>-1</sup> phonon line upon the Cr substitution as supporting evidence of their assignment. However, as they also mentioned, the vibration mode calculation of the cubic spinel LiMn<sub>2</sub>O<sub>4</sub> revealed that the Raman modes of this phase are related to the vibration of Li and O, not to those of Mn or Cr.<sup>1b</sup> It is therefore reasonable that the mass change of transition metal components has no direct influence on the frequencies of Raman peaks of this phase. Furthermore, the notable frequency difference between LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>2</sub>Mn<sub>2</sub>O<sub>4</sub> (605 cm<sup>-1</sup> vs 625 cm<sup>-1</sup>) cannot provide any further support on their assignments, because such a degree of peak shift also occurs between Li<sub>2</sub>Mn<sub>2</sub>O<sub>4</sub> and λ-MnO<sub>2</sub>.<sup>1</sup>

**(3) Reliability of extended X-ray absorption fine structure (EXAFS) analysis.** Paolone, A. et al. questioned our EXAFS fitting results showing the presence of local (or dynamic) Jahn–Teller (JT) distortion in LiMn<sub>2</sub>O<sub>4</sub> at room temperature. Even though there are conflicting reports on the EXAFS fitting analysis on this phase, surely we were able to obtain better fits for the room-temperature EXAFS data of LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> with two (Mn–O) bond distances model than with one (Mn–O) bond

\* Corresponding author. Tel: +82-2-3277-3420, Fax: +82-2-3277-3419, e-mail: hwangsj@ewha.ac.kr.

distance model, as reported previously.<sup>6</sup> More importantly, we detected a distinct enhancement of the FT peak corresponding to the (Mn–O) shell after the replacement of Mn with Cr, see Figure 3b of the original paper. Such an increase of the FT peak provides clear evidence on the reduction of structural disorder in (Mn–O) shell upon the Cr substitution, i.e., the decrease of JT distortion around Mn ions. This distinct variation of the FT spectra is much more straightforward than the minute variation of residual values from the quantitative EXAFS fitting analysis.

In conclusion, as Paolone, A. et al. pointed out, the influence of sample degradation is very important in performing micro-Raman study on the solid compounds. However, from all the above-described reasons, it is certain that the previously reported Raman spectra of  $\text{LiMn}_2\text{O}_4$ , including ours,<sup>1</sup> originate from the true vibration modes of the cubic spinel structure, not from those of the thermal decomposition product (i.e.,  $\text{Mn}_3\text{O}_4$  or orthorhombic  $\text{LiMnO}_2$ ). Instead, the thermal decomposition of the

spinel lithium manganates leads to the appearance of an intense peak at  $\sim 660\text{ cm}^{-1}$ , not in the region of  $600\text{--}625\text{ cm}^{-1}$ .

## References and Notes

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