Magnetic Properties of Diluted Jahn-Teller Active Cuprospinels

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Abstract

It is well known that 'Spinel oxides' with AB_2O_4 stoichiometry stabilizes in a cubic symmetry belonging to the space group *Fd*-3*m*, however, due to the presence of Jahn-Teller (JT) active ions like Cu^{2+} in $CuFe_2O_4$, a significant tetragonal distortion can be realized in which the crystal structure changes from cubic to tetragonal (*I*41/*amd*). In the current work, we report on the magnetic properties influenced by double dilution effect of Zn^{2+} and Ru^{3+} substituted at the JT active Cu^{2+} and Fe^{3+} sites, respectively resulting in the co-doped spinel $Cu_{1-x}Zn_xFe_{2-y}Ru_yO_4$. Such co-substitution was initiated to tune the tetragonality of $CuFe_2O_4$ and led to two distinct classes of stable crystal symmetries (*i*) Tetragonal: $CuFe_{1.95}Ru_{0.05}O_4$ and $Cu_{0.95}Zn_{0.05}Fe_{1.95}Ru_{0.05}O_4$, and (*ii*) Cubic: $Cu_{0.60}Zn_{0.40}Fe_{1.95}Ru_{0.05}O_4$. Interestingly, the JT distortion in the Cu-rich compounds got nullified upon increasing the Zn^{2+} concentration. Rietveld refinement of the x-ray diffraction (XRD) patterns obtained for all the three compositions revealed expansion of the unit cell volume accompanying the structural change from tetragonal to relaxed cubic symmetry. Analysis of the high temperature (300-900K) magnetization data (Fig. 1) reveals significant decrease in the ferrimagnetic Néel temperature (T_{FN}) with increase in Zn content (T_{FN} = 796 K for x = 0 and 508 K for x = 0.4 with y = 0.05). These results are discussed in consonance with the crystallographic data obtained form the X-ray diffraction (Fig. 1).

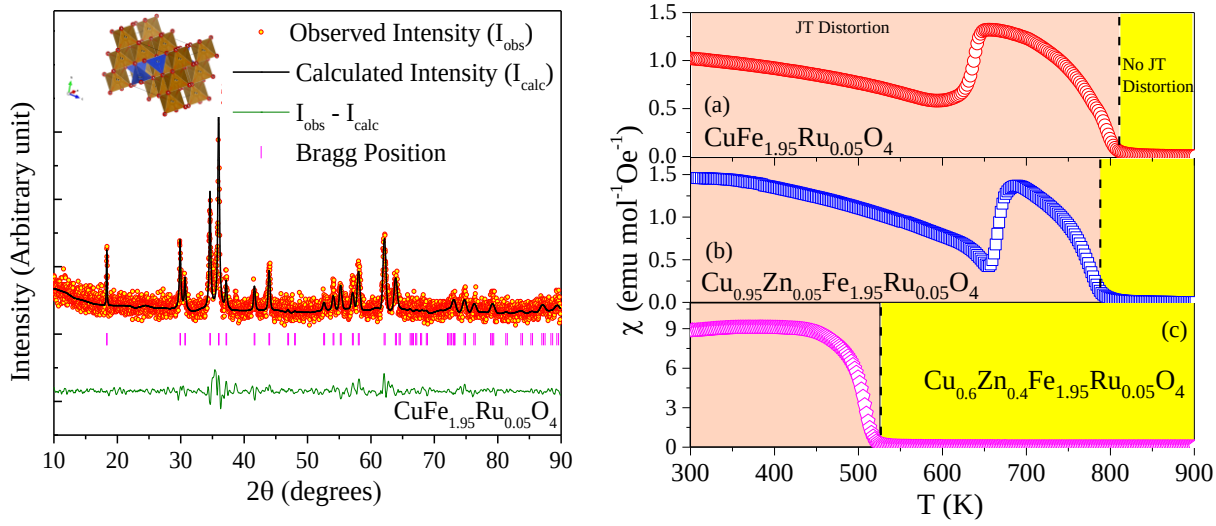

Figure 1: Left: Rietveld refinement of XRD pattern of $CuFe_{1.95}Ru_{0.05}O_4$ with its VESTA generated crystal structure in the inset. Right: Temperature dependence of dc-magnetic susceptibility χ for (a) $CuFe_{1.95}Ru_{0.05}O_4$, (b) $Cu_{0.95}Zn_{0.05}$ $Fe_{1.95}Ru_{0.05}O_4$, and (c) $Cu_{0.6}Zn_{0.4}Fe_{1.95}Ru_{0.05}O_4$.

References: [1] K.E. Sickafus, J.M. Wills, and N. W. Grimes, *Journal of the American Ceramic Society*, **82**(12), 3279 (1999)