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Energy Loss Near-Edge Fine Structure of Oxygen K of Spinel $Ni_xMn_{3-x}O_4$

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Energy loss near-edge structure (ELNES) of oxygen K-edge of 3d transition metal oxides is sensitive to the unoccupied density of states above the Fermi level, and can be used to study the unoccupied electronic levels which directly affect the physical and chemical properties of transition metal oxides. Extensive investigation of the ELNES of Mn oxides (MnO, Mn_2O_3, MnO_2) with octahedrally coordinated Mn has been reported [1]. In this work, we report a study of the ELNES of nickel manganite spinel, $Ni_xMn_{3-x}O_4$ (where x is determined by quantitative EDS), which is being studied as a next-generation thermal imaging material [2].

$Ni_xMn_{3-x}O_4$ has an inverse spinel structure with formula: $(Ni^{2+}_{x-\nu}Mn^{2+}_{1-x+\nu})[Ni^{2+}_{\nu}\ Mn^{2+}_{y}Mn^{3+}_{2-2(\nu+y)}\ Mn^{4+}_{\nu+y}][O_4]$, where ν denotes the degree of inversion; "( )" and "[ ]" denote tetrahedral and octahedral sites in spinel lattice, respectively. The local site occupancy, described by the values of x, y, ν which is critical for the conductivity of Ni-Mn spinels, has been determined in this work by using a fitting process [3] under the assumption of full site occupancy. The degree of inversion, given by ν, was taken from the literature [4] for different x. Three Mn oxides (MnO, Mn_2O_3, MnO_2) were taken as standards for the Mn L-edge of Mn^{2+}, Mn^{3+}, Mn^{4+} ELNES. Absolute energies were assigned by aligning the extraneous carbon K-edge to 284 eV for all samples. Fig. 1a shows the normalized ELNES of Mn L-edge of Mn^{2+}, Mn^{3+}, Mn^{4+} of the Mn oxides standards. The fitting process for the spinel samples linearly combines these reference spectra to obtain the best fit to the data. Fig. 1b shows an example for the result of the fitting process, indicating a good match between experimental and fitted spectra.

Fig. 2 shows ELNES of the oxygen K of spinel $Ni_xMn_{3-x}O_4$ with four different x values compared with that of MnO, NiO and MnO_2. Each spectrum can be divided into two parts: (1) The first peak (denoted as "**a**") and the second peak (denoted as "$\mathbf{3e_g\downarrow}$") correspond to transitions from O 1s to Mn 3d – O 2p hybridization levels; (2) The main peak, which is a sum of $\mathbf{3a_{1g}}$ (as a shoulder in ELNES of NiO and Ni-Mn spinel) and the peak $\mathbf{4t_{1u}}$, represents the transition from O 1s to Mn 4sp and Ni 4sp levels. The following features are noticeable for these ELNES: (i) For the pre-peaks 1 and 2, the Ni-Mn spinel and MnO_2 have similar split energy levels (ligand-field splitting defined as the energy separation between $\mathbf{2t_{2g}}$ and $\mathbf{3e_g}$ states, and exchange splitting defined as energy difference between spin-up and spin-down states) [1]. This pre-peak "**a**" includes the transition to both $\mathbf{2t_{2g}}$ spin-down $\mathbf{(2t_{2g}\downarrow)}$ and $\mathbf{3e_g}$ spin-up $\mathbf{(3e_g\uparrow)}$ states, which have indistinguishable energy. The second pre-peak $\mathbf{3e_g\downarrow}$ represents the transition to $\mathbf{3e_g}$ spin-down**.** (ii) Although both Mn^{4+} and Mn^{3+} have strong first pre-peaks in their O K ELNES, neither Mn^{4+} concentration nor Mn^{3+} concentration has direct influence on the intensity of the first pre-peak. Rather, it is the average Mn valence that has predominant influence on the unoccupied $\mathbf{2t_{2g}\downarrow}$ and $\mathbf{3e_g\uparrow}$ states (first pre-peak). The intensity of the first pre-peak decreases with decreased average Mn valence. (iii) For the main peak, the Ni^{2+} and

Mn^{2+}concentrations have predominant influence on the energy separation (ΔE) between $\mathbf{3e_g\downarrow}$ and $\mathbf{4t_{1u}}$. With increasing Ni^{2+} and decreased Mn^{2+}, ΔE increases. This work provides insight into how to probe the Mn 3d orbital occupancy of Ni-Mn spinel directly from the ELNES of oxygen K-edge.

References

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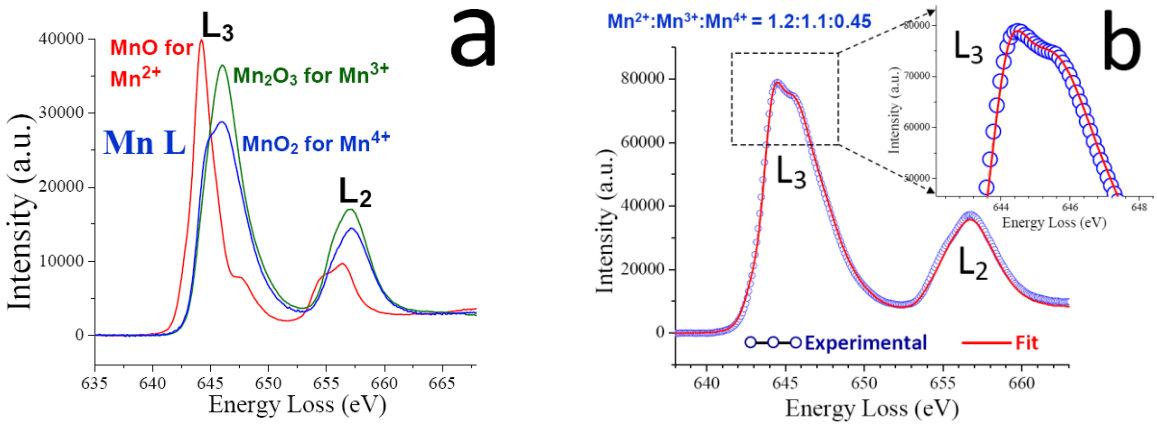

FIG. 1. (a) Normalized EELS of Mn L-edge of Mn^{2+}, Mn^{3+}, Mn^{4+} of the Mn oxides standards. (b) Result of "Fitting" showing a good agreement between experimental and fitting spectra (for simplicity, full site occupancy was assumed).

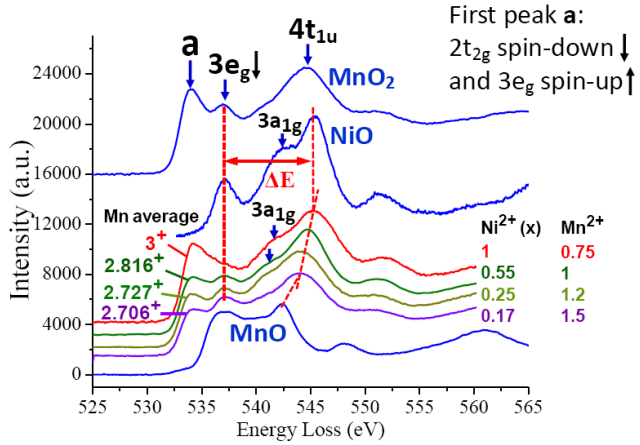

FIG. 2. ELNES of oxygen K of spinel $Ni_xMn_{3-x}O_4$ compared with that of MnO, NiO and MnO_2, revealing that Ni-Mn spinel has energy levels (above the Fermi level) similar to that of MnO_2. With increasing Ni^{2+} and decreased Mn^{2+}, ΔE increases; and with increasing Ni^{2+} (resulting in increased Mn oxidation state) the Mn 3d orbital occupancy decreases identified by increased intensity of the first pre-peak corresponding to unoccupied $\mathbf{2t_{2g}\downarrow}$ and $\mathbf{3e_g\uparrow}$ states.

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