Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

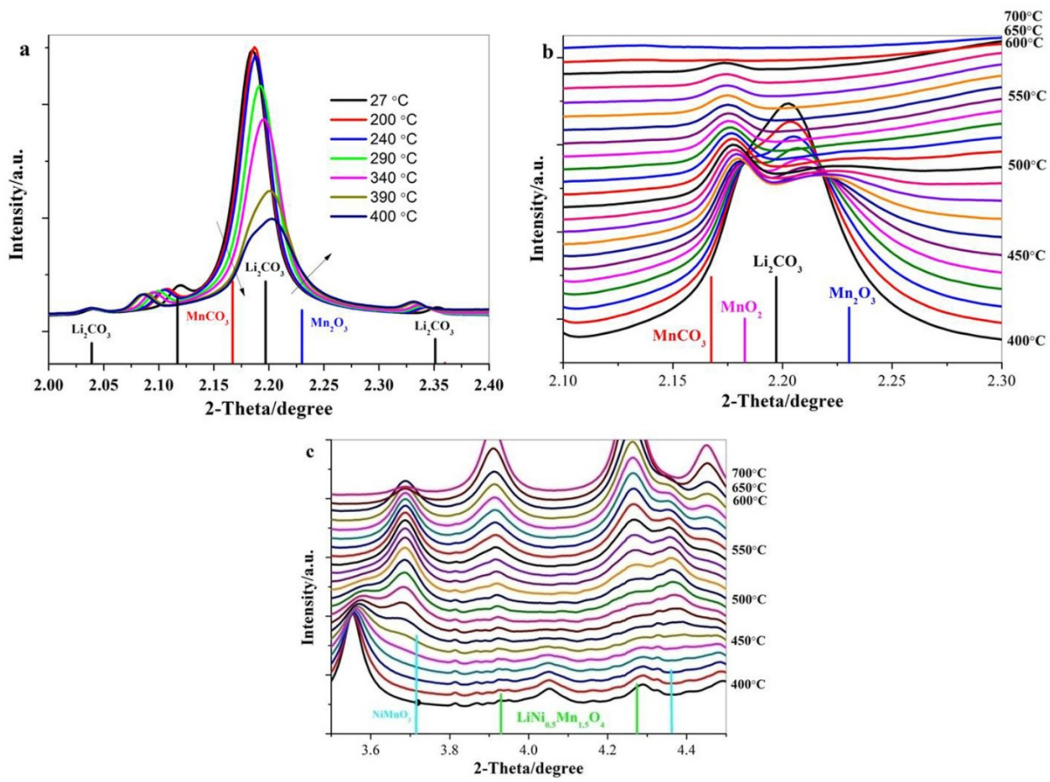

Figure S1 (a) HEXRD patterns collected at various temperature with a 2θ region of 2.00-2.40°, (b) HEXRD patterns collected from 400 °C to 700 °C within a 2θ region of (b) 2.10-2.30° and (c) 3.5-4.5°.

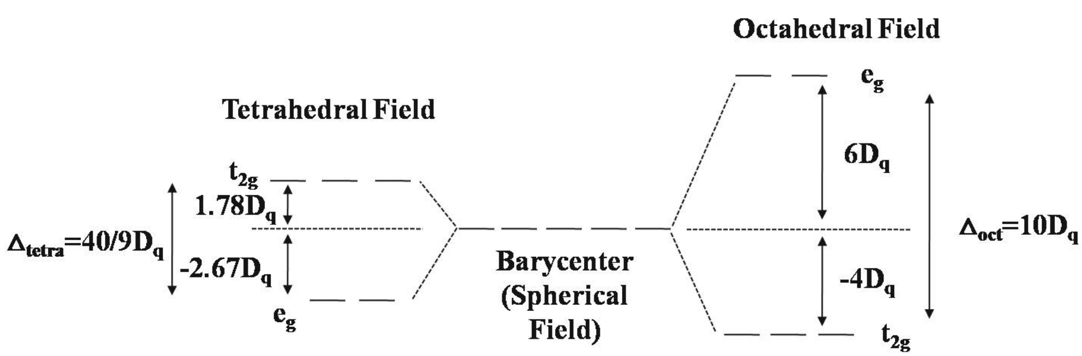

Figure S2 Crystal field stabilization energy for octahedral and tetrahedral field.

Table S1 Configuration and Stabilization energy for transition metal ions in crystal fields

		Octahedral		Tetrahedral	
Cation	Number of d electrons	Configuration	Stabilization energy	Configuration	stabilization energy
Ni^{2+}	8	$(t_{2g})^6(e_g)^2$	$-12D_q$	$(e_g)^4(t_{2g})^4$	$-3.56D_q$
Ni^{3+}	7	$(t_{2g})^5(e_g)^2$	$-8D_q$	$(e_g)^4(t_{2g})^3$	$-5.34D_q$
Ni^{4+}	6	$(t_{2g})^4(e_g)^2$	$-4D_q$	$(e_g)^3(t_{2g})^3$	$-2.67D_q$
Mn^{4+}	3	$(t_{2g})^3(e_g)^0$	$-12D_q$	$(e_g)^2(t_{2g})^1$	$-3.56D_q$
Mn^{2+}	5	$(t_{2g})^3(e_g)^2$	0	$(e_g)^2(t_{2g})^3$	0
Co^{4+}	5	$(t_{2g})^3(e_g)^2$	0	$(e_g)^2(t_{2g})^3$	0

In octahedral field, the energy gap ($\triangle$oct) is referred to as $10D_q$, the crystal field splitting energy. And the crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. In an octahedral case, the t_{2g} set becomes lower in energy than the orbitals in the barycenter. As a result of this, if there are any electrons occupying these orbitals, the metal ion is more stable in the ligand field relative to the barycenter by an amount known as the CFSE. Conversely, the e_g orbitals (in the octahedral case) are higher in energy than in the barycenter, so putting electrons in these reduces the amount of CFSE. Therefore, the total

CFSE of transition metal ions equal to the sum of the *d* electron number in the t_{2g} orbital and e_g orbital multiply by their energy. The case of tetrahedral filed is similar to the octahedral fields except the impact of e_g and t_{2g} on CFSE is reverse and the splitting energy of tetrahedral fields is only 4/9 of the octahedral fields.

For example, Ni^{2+}, $CFSE_{oct}=2\times (6Dq) + 6\times (-4Dq) = -12D_q$

$CFSE_{tetra}=4\times 1.78Dq + 4\times (-2.67Dq) = -3.56D_q$