Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information

## Spectroscopic and Magnetic Investigations of Spin-frustrated Mn-doped $CoAl_2O_4$ Spinel

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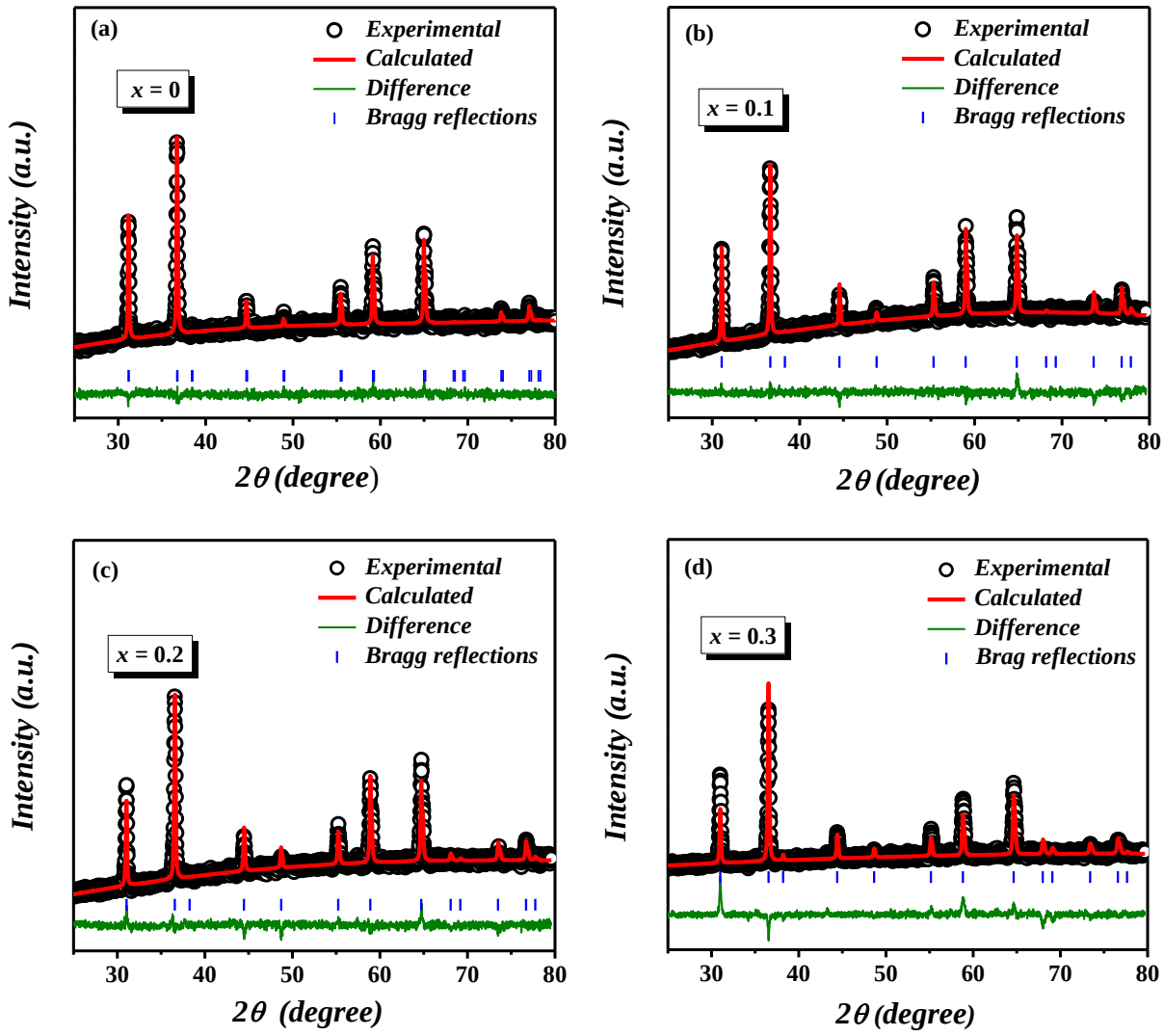


**Fig.S1** Room temperature Rietveld fitted x-ray diffraction patterns for $x$ = (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3 samples of $Co_{1-x}Mn_xAl_2O_4$. Structural parameters obtained from the Rietveld refinements are shown in Table S1 in the supplemental material.

**Table S1** Structural parameters obtained from Rietveld refinements of the room temperature x-ray diffraction pattern of $Co_{1-x}Mn_xAl_2O_4$ (Space group: $Fd\bar{3}m$) ($\alpha = \beta = \gamma = 90^o$ ). The errors are given in the parentheses.

**(a) $x$ = 0; $a$ = $b$ = $c$ = 8.1162(4) Å; $R_{wp}$ = 3.8; $R_p$ = 2.7; $\chi^2$ = 1.18; $\alpha$ = 0.0804(2)**

| Atom | *x* | *y* | *z* | Occupancy |
|---|---|---|---|---|
| Co (8a) | 1/8 | 1/8 | 1/8 | 0.9196(3) |
| Al (8a) | 1/8 | 1/8 | 1/8 | 0.0804(2) |
| Al (16d) | 1/2 | 1/2 | 1/2 | 0.9598(9) |
| Co (16d) | 1/2 | 1/2 | 1/2 | 0.0402(1) |
| O (32e) | 0.2620(1) | 0.2620(1) | 0.2620(1) | 1.000 |

**(b) $x$ = 0.1; $a$ = $b$= $c$ = 8.1272(3) Å; $R_{wp}$ = 2.71; $R_p$ = 2.09; $\chi^2$ = 1.15; $\alpha$ = 0.0780(4)**

| Atom | *x* | *y* | *z* | Occupancy |
|---|---|---|---|---|
| Co (8a) | 1/8 | 1/8 | 1/8 | 0.8318(7) |
| Al (8a) | 1/8 | 1/8 | 1/8 | 0.0780(4) |
| Mn (8a) | 1/8 | 1/8 | 1/8 | 0.0902(1) |
| Al (16d) | 1/2 | 1/2 | 1/2 | 0.9561(1) |
| Co (16d) | 1/2 | 1/2 | 1/2 | 0.0390(2) |
| Mn (16d) | 1/2 | 1/2 | 1/2 | 0.0049(7) |
| O (32e) | 0.2626(3) | 0.2626(3) | 0.2626(3) | 1.000 |

**(c) $x$ = 0.2; $a$ = $b$= $c$ = 8.1392(3) Å; $R_{wp}$ = 3.12; $R_p$= 2.30; $\chi^2$ = 1.27, $\alpha$ = 0.0762(2)**

| Atom | *x* | *y* | *z* | Occupancy |
|---|---|---|---|---|
| Co (8a) | 1/8 | 1/8 | 1/8 | 0.7434(5) |
| Al (8a) | 1/8 | 1/8 | 1/8 | 0.0762(2) |
| Mn (8a) | 1/8 | 1/8 | 1/8 | 0.1804(2) |
| Al (16d) | 1/2 | 1/2 | 1/2 | 0.9521(1) |
| Co (16d) | 1/2 | 1/2 | 1/2 | 0.0381(3) |
| Mn (16d) | 1/2 | 1/2 | 1/2 | 0.0098(9) |
| O(32e) | 0.2629(5) | 0.2629(5) | 0.2629(5) | 1.000 |

**(d) $x$ = 0.3 ; $a$ = $b$= $c$ = 8.1481(6) Å; $R_{wp}$ =4.30; $R_p$=2.91; $\chi^2$ = 1.60, $\alpha$ = 0.0742(3)**

| Atom | *x* | *y* | *z* | Occupancy |
|---|---|---|---|---|
| Co (8a) | 1/8 | 1/8 | 1/8 | 0.6758(6) |
| Al (8a) | 1/8 | 1/8 | 1/8 | 0.0742(3) |
| Mn(8a) | 1/8 | 1/8 | 1/8 | 0.2500(1) |
| Al(16d) | 1/2 | 1/2 | 1/2 | 0.9379(6) |
| Co(16d) | 1/2 | 1/2 | 1/2 | 0.0371(2) |
| Mn (16d) | 1/2 | 1/2 | 1/2 | 0.0250(2) |
| O(32e) | 0.2630(2) | 0.2630(2) | 0.2630(2) | 1.000 |

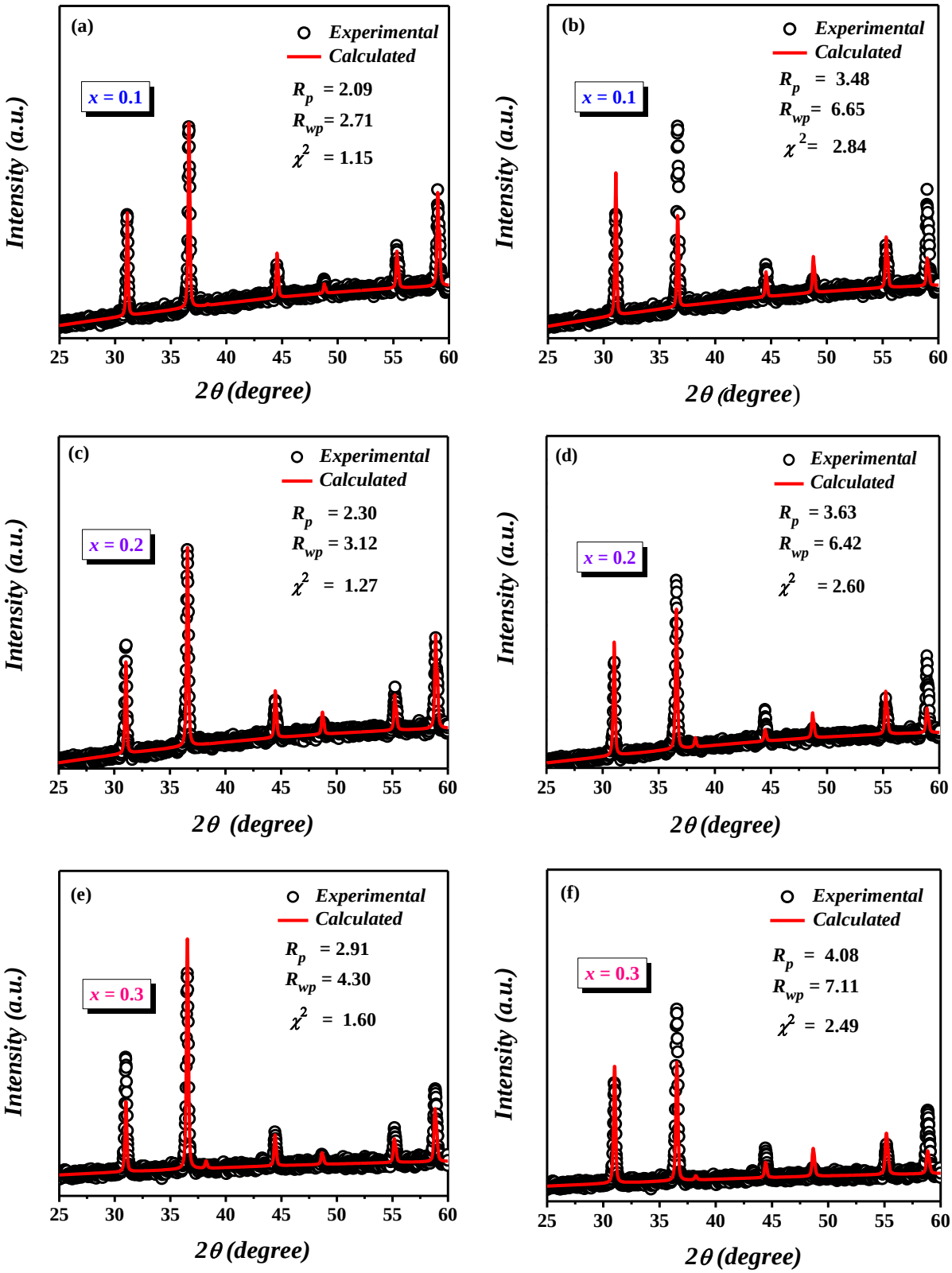


**Fig. S2** Room-temperature Rietveld fitted XRD patterns considering different distributions of the $Mn^{2+}$ and $Co^{2+}$ over the two types of sites for (a-b) $x$ = 0.1, (c-d) $x$ = 0.2, and (e-f) $x$ = 0.3.

**Table S2** The values of $\chi^2$ of Mn-doped $CoAl_2O_4$ samples for different distributions of $Mn^{2+}$ and $Co^{2+}$ over the two types of sites.

| | $\chi^2$ | Atom | Co (8a) | Al (8a) | Mn (8a) | Al (16d) | Co(16d) | Mn (16d) |
|---|---|---|---|---|---|---|---|---|
| ***x* = 0.1** | **(a)** 1.15 | **Ocuupancy** | 0.8318(7) | 0.0780(4) | 0.0902(1) | 0.9561(1) | 0.0390(2) | 0.0049(7) |
| | **(b)** 2.84 | | 0.8538(7) | 0.0760(2) | 0.0702(4) | 0.9471(2) | 0.0380(1) | 0.0149(8) |
| ***x* = 0.2** | **(c)** 1.27 | **Ocuupancy** | 0.7434(5) | 0.0762(2) | 0.1804(2) | 0.9521(1) | 0.0381(3) | 0.0098(9) |
| | **(d)** 2.60 | | 0.7776(8) | 0.0720(3) | 0.1504(2) | 0.9392(3) | 0.0360(2) | 0.0248(9) |
| ***x* = 0.3** | **(e)** 1.60 | **Ocuupancy** | 0.6758(6) | 0.0742(3) | 0.2500(1) | 0.9379(6) | 0.0371(2) | 0.0250(2) |
| | **(f)** 2.49 | | 0.6594(5) | 0.0704(3) | 0.2702(4) | 0.950(1) | 0.0352(1) | 0.0148(9) |

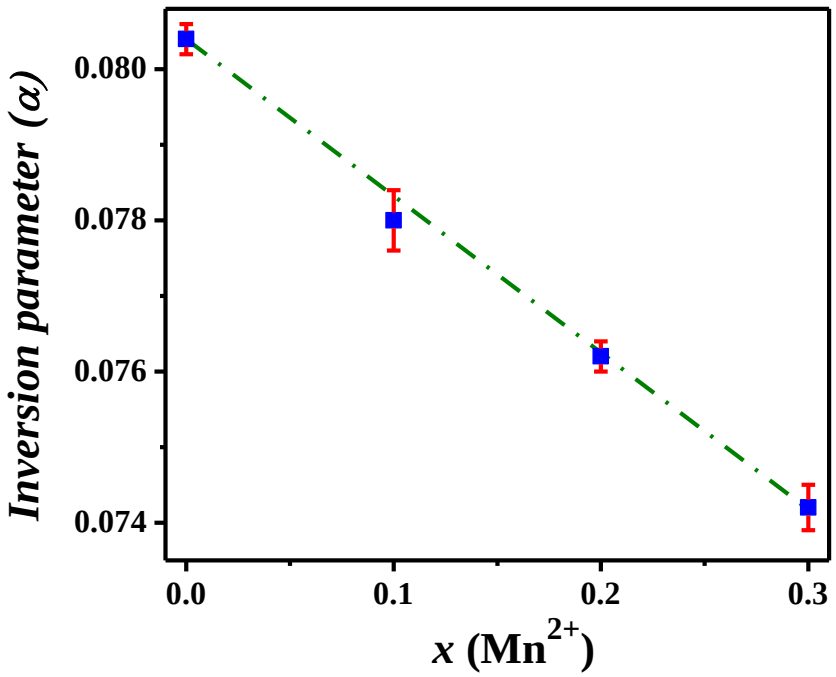


**Fig. S3** Variation of *Inversion parameter (α)* with the compositions, as obtained from the Rietveld analysis of the best-fitted XRD patterns.

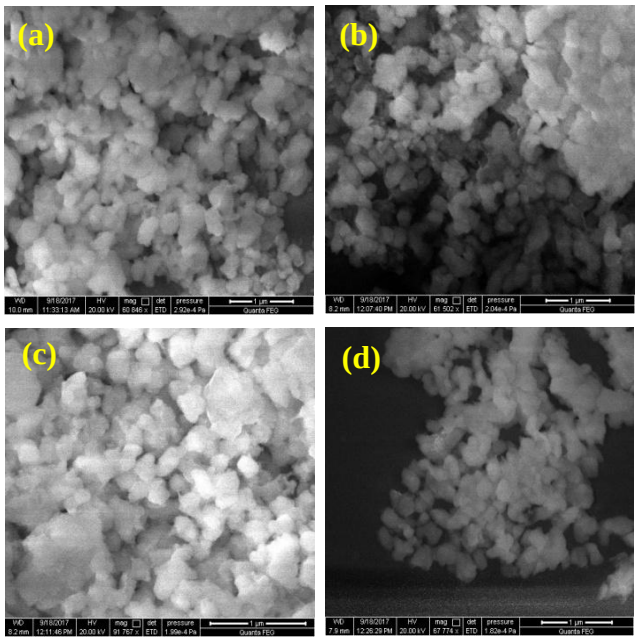


**Fig. S4** SEM micrographs of $Co_{1-x}Mn_xAl_2O_4$ (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$.

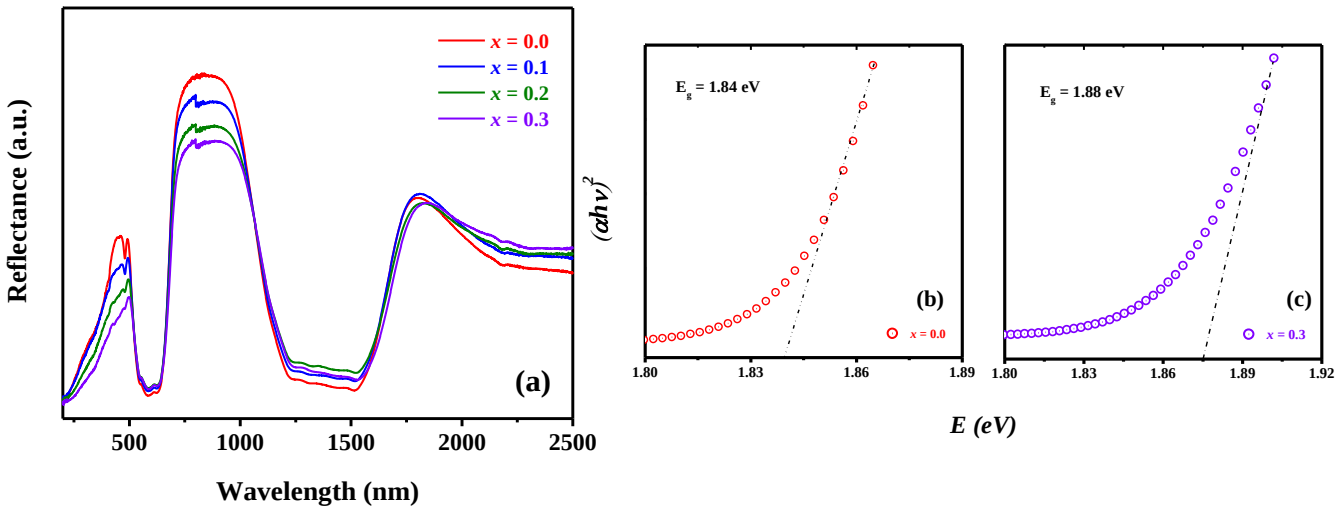


**Fig. S5** (a) Room temperature Reflectance spectra for $Co_{1-x}Mn_xAl_2O_4$. Tauc plots $[(\alpha h\nu)^2$ *vs.* photon energy ($E$)] for (b) $x = 0$ and (c) $x = 0.3$.

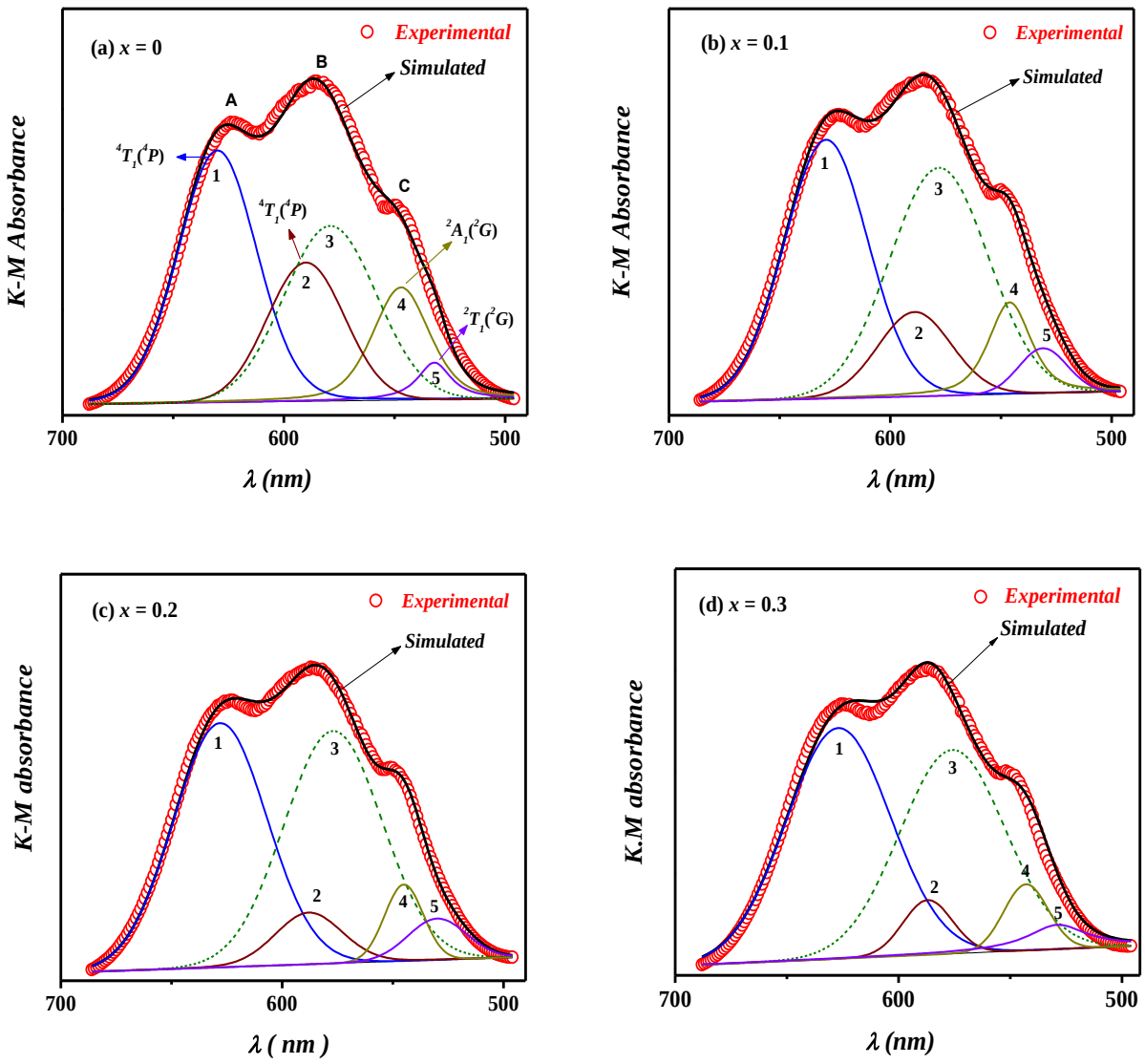


**Fig. S6** De-convoluted UV spectrum of $Co_{1-x}Mn_xAl_2O_4$ where (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$.

**Table S3** De-convoluted peak position obtained from room temperature UV spectrum of $Co_{1-x}Mn_xAl_2O_4$.

| Sample | Peak Position (nm) | Intensity (%) | Peak Position (nm) | Intensity (%) | Peak Position (nm) | Intensity (%) | Peak Position (nm) | Intensity (%) | Peak Position (nm) | Intensity (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | 4 | | 5 | |
| ***x* = 0** | 630 | 36 | 590 | 18 | 579 | 28 | 547 | 13 | 532 | 3.12 |
| | | | | | | | | | | |
| ***x* = 0.1** | 629 | 38 | 589 | 11 | 578 | 38 | 546 | 8 | 531 | 3.66 |
| | | | | | | | | | | |
| ***x* = 0.2** | 628 | 42 | 588 | 6 | 577 | 42 | 543 | 5.31 | 530 | 4.25 |
| | | | | | | | | | | |
| ***x* = 0.3** | 627 | 45 | 586 | 5 | 576 | 40 | 543 | 5.46 | 528 | 4.09 |