First principles study of Mn-doping effect on the physical and chemical properties of mullite-family Al_2SiO_5

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1 Energy-volume relations

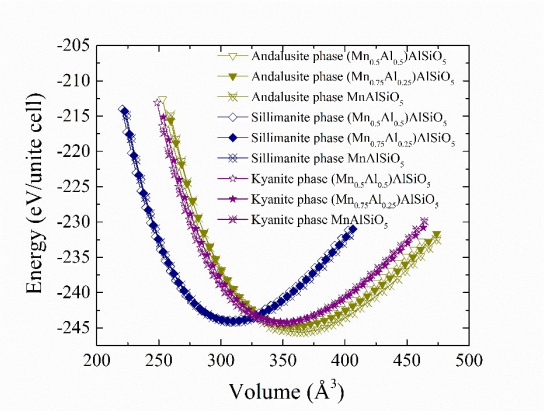


Fig. S1 The energy versus volume of andalusite, kyanite and sillimanite phase $(Mn_xAl_{1-x})AlSiO_5$ with x=0.5, 0.75 and 1.0.

2 The heat capacities of $(Mn_xAl_{1-x})AlSiO_5$

Because heat capacities (C_p) are important in applications, we calculated and discussed the C_p of $(Mn_xAl_{1-x})AlSiO_5$ (x=0, 0.25, 0.5, 0.75 and 1.0) in this paragraph. The calculated C_p is presented in Fig. S2. The C_p of $(Mn_xAl_{1-x})AlSiO_5$ with the same Mn content in different phases are similar. The C_p increases with increasing temperature, which is in line with other reports.[1,2] The calculated C_p is a reference for applications.

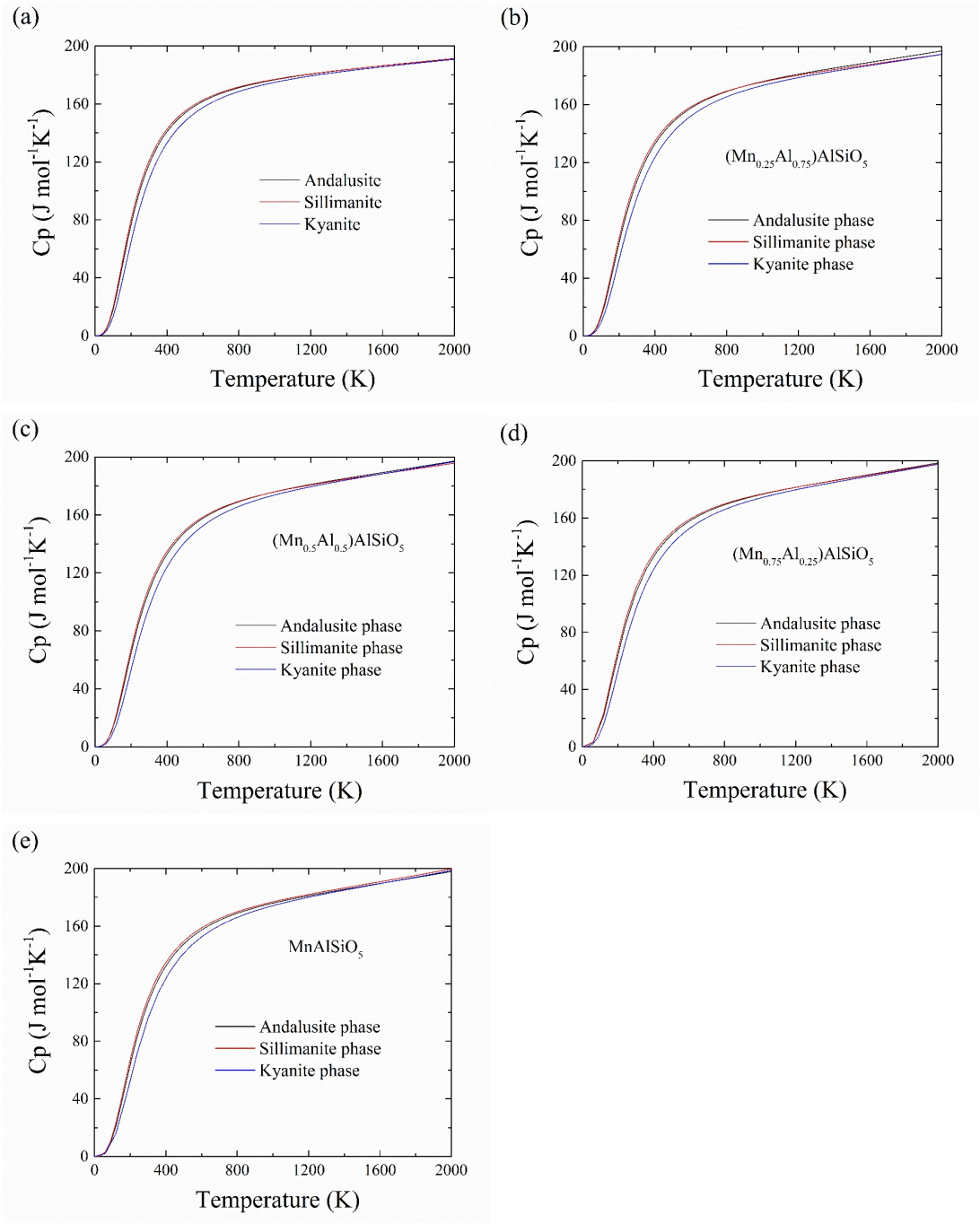
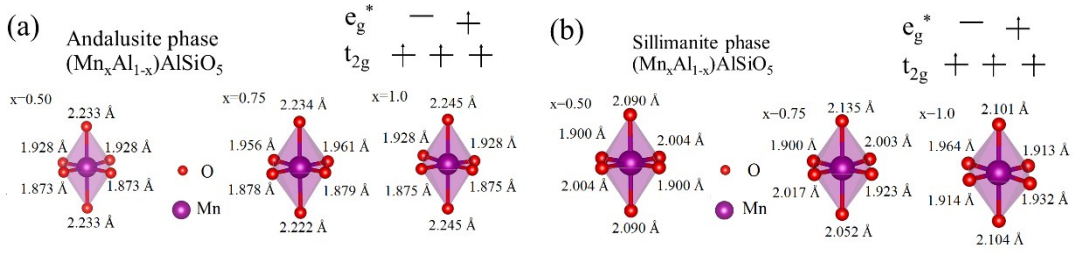


Fig. S2 The heat capacity versus temperature of andalusite, sillimanite and kyanite phases $(Mn_xAl_{1-x})AlSiO_5$ with (a) x=0, (b)x=0.25, (c)x=0.50, (d) x=0.75 and (e) x=1.0.

3 Octahedra and density states splitting



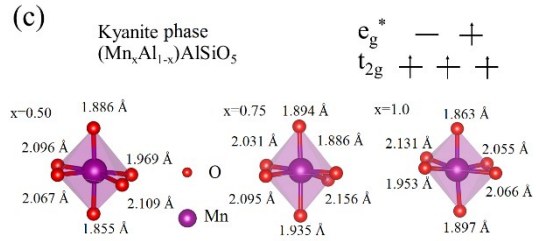


Fig. S3 The octahedra in (a) andalusite phase, (b) sillimanite phase and (c) kyanite phase $(Mn_xAl_{1-x})AlSiO_5$ with x=0.5, 0.75 and 1.0.

The octahedra of $(Mn_xAl_{1-x})AlSiO_5$ with x=0.5, 0.75 and 1.0 in andalusite, sillimanite and kyanite phases (Fig. S3 a, b and c).

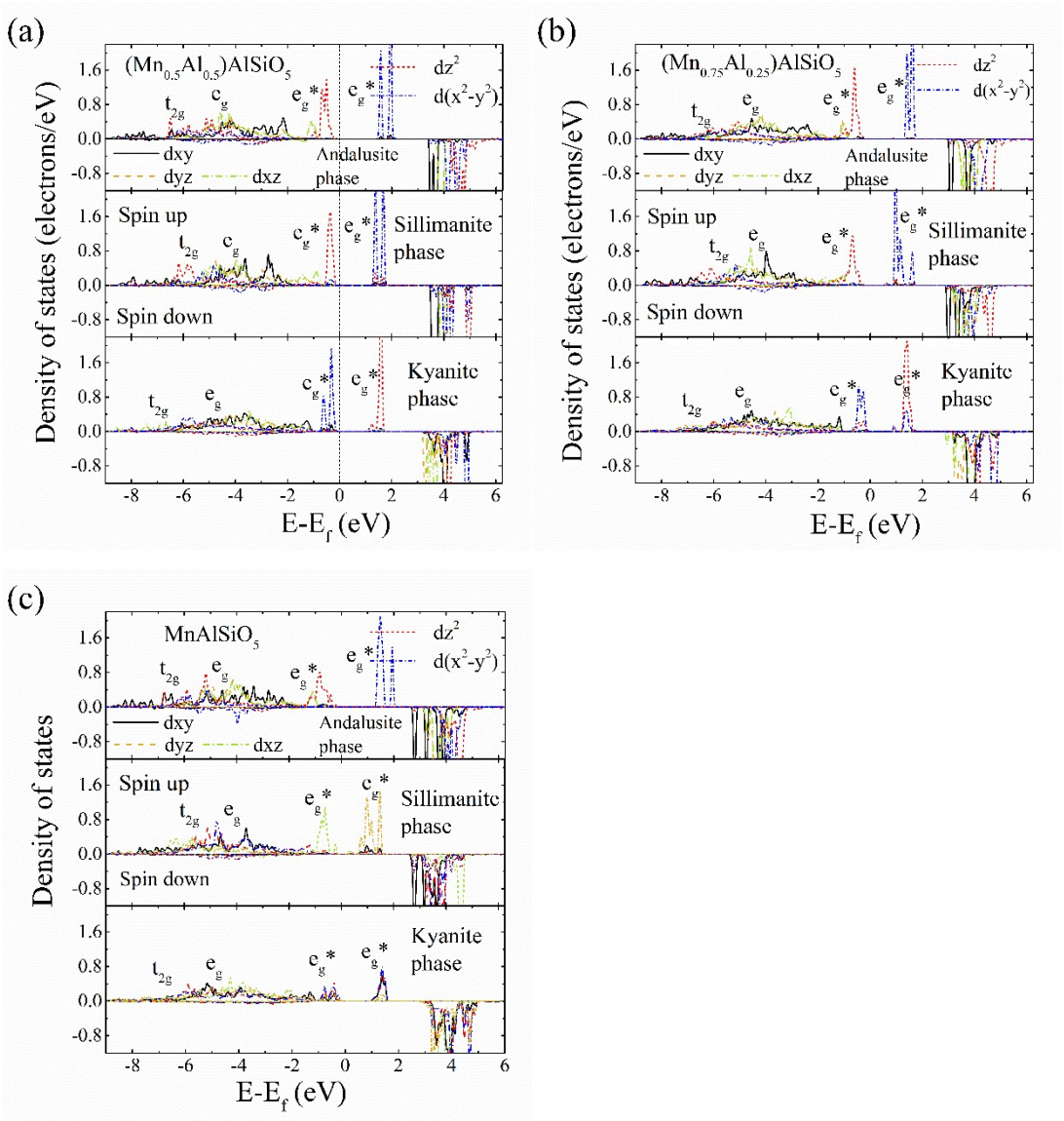


Fig. S4 The splitting partial density of states (PDOS) of Mn 3*d* orbital in andalusite, sillimanite and kyanite

phase $(Mn_xAl_{1-x})AlSiO_5$ with (a) x=0.5, (b) x=0.75 and (c) x=1.0.

The splitting partial density of states (PDOS) of Mn 3*d* orbital in andalusite, sillimanite and kyanite phase $(Mn_xAl_{1-x})AlSiO_5$ with x=0.5, 0.75 and 1.0 are shown in Fig. S4.

4 Helmholtz vibrational energy

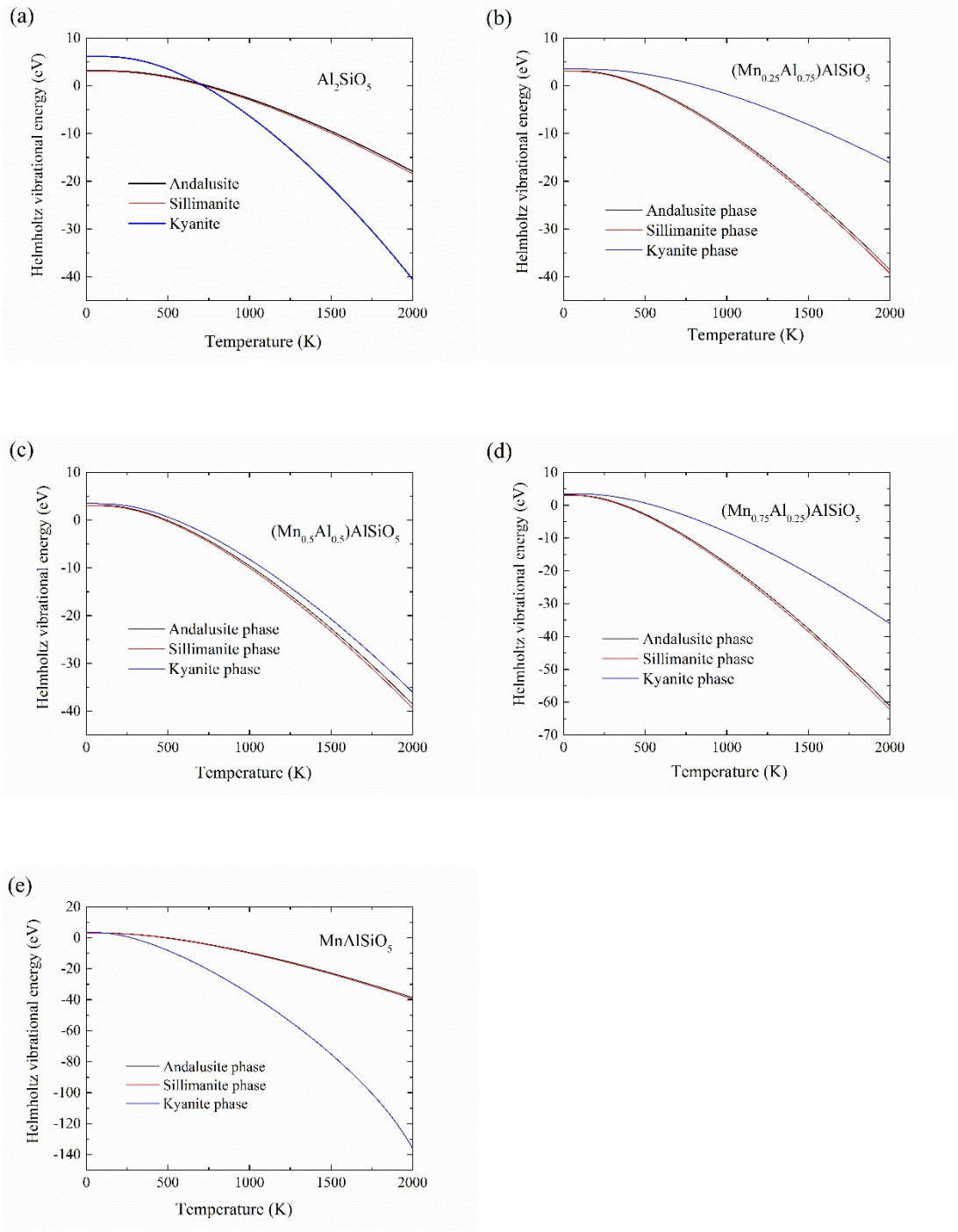


Fig. S5 The helmholtz vibrational energy versus temperature of andalusite, sillimanite and kyanite phases $(Mn_xAl_{1-x})AlSiO_5$ with (a) x=0, (b)x=0.25, (c)x=0.50, (d) x=0.75 and (e) x=1.0.

References

1. M. N. Rao, S. L. Chaplot, N. Choudhury, K. R. Rao, R. T. Azuah, W. T. Montfrooij and S. M. Bennington, *Phys. Rev. B*, 1999, **60**, 12061-12068.
2. M. N. Rao, P. Goel, N. Choudhury, S. L. Chaplot and S. Ghose, *Solid State Commun.*, 2002, **121**, 333-338.