Cation size variance effect on spin and orbital orders in $R\mathrm{VO}_3$

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Perovskite $R\mathrm{VO}_3$ (R : rare earth ions or Y) has orbital degrees of freedom between d_{yz} and d_{zx} orbitals in V^{3+} ions, and shows G-type orbital order (G-type OO) accompanied with C-type spin order (C-type SO) and C-type OO with G-type SO. The transition temperatures of each spin and orbital orders show the systematic dependence on the R-site ionic radius [1]. On the other hand, spin and orbital orders in $R\mathrm{VO}_3$ can be controlled by R-site cation size variance, expressed by $\langle r_i^2 \rangle - \langle r_i \rangle^2$ (r_i is the R-site ionic radius) [2].

We synthesized size variance introduced series of $R\mathrm{VO}_3$, where the average ionic radius of R-site was fixed. By measurements of the magnetization, synchrotron powder x-ray diffraction, resonant x-ray scattering, and neutron diffraction, we generated the global phase diagram of spin and orbital orders in $R\mathrm{VO}_3$. In the sample with any R-site ionic radius, the transition temperature of G-type OO and C-type SO are suppressed by increasing variance. On the other hand, the transition temperature of C-type OO/G-type SO (T_{SO2}) shows a different behaviour. In $\mathrm{Y}_{1-x}(\mathrm{La}_{0.195}\mathrm{Lu}_{0.805})_x\mathrm{VO}_3$ with the smaller R-site ionic radius, T_{SO2} is enhanced with increasing variance. In $\mathrm{Eu}_{1-x}(\mathrm{La}_{0.254}\mathrm{Y}_{0.746})_x\mathrm{VO}_3$ and $\mathrm{Sm}_{1-x}(\mathrm{La}_{0.322}\mathrm{Y}_{0.678})_x\mathrm{VO}_3$ with the middle R-site ionic radius, the pure material ($x = 0$) has no C-type OO/G-type SO. With increasing the size variance, the phase transition of C-type OO/G-type SO is emerged and the T_{SO2} is enhanced. In $\mathrm{Nd}_{1-x}(\mathrm{La}_{0.491}\mathrm{Y}_{0.509})_x\mathrm{VO}_3$ with the larger R-site ionic radius, however, the phase transition of C-type OO/G-type SO is not observed. These results indicate that the smaller R-site ionic radius and the larger R-site size variance stabilize the C-type OO/G-type SO state.

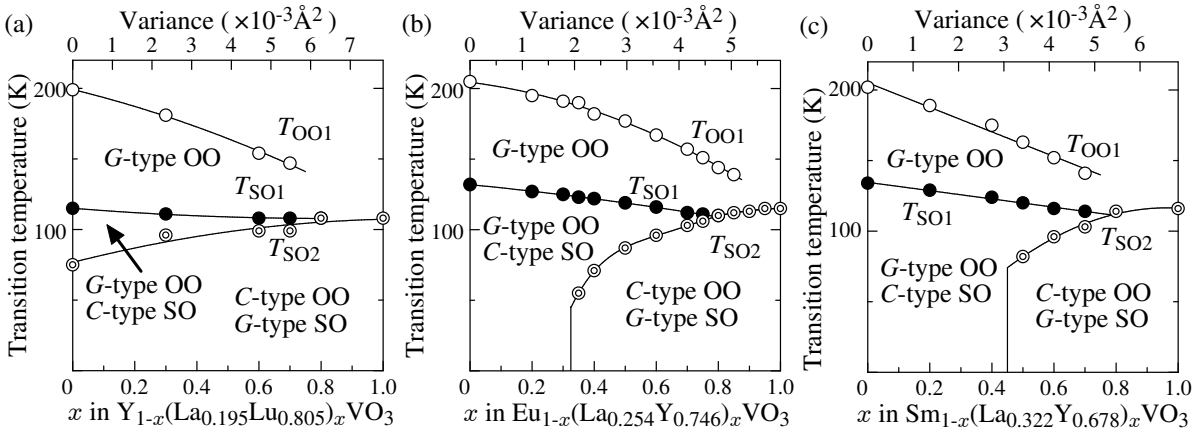

Figure 1: Spin and orbital phase diagram of the size variance introduced sample of (a) $\mathrm{Y}_{1-x}(\mathrm{La}_{0.195}\mathrm{Lu}_{0.805})_x\mathrm{VO}_3$, (b) $\mathrm{Eu}_{1-x}(\mathrm{La}_{0.254}\mathrm{Y}_{0.746})_x\mathrm{VO}_3$, and (c) $\mathrm{Sm}_{1-x}(\mathrm{La}_{0.322}\mathrm{Y}_{0.678})_x\mathrm{VO}_3$.

Reference

[1] S. Miyasaka *et al.*, Phys. Rev. B, **68**, 100406(R) (2003).
[2] J. -Q. Yan *et al.*, Phys. Rev. Lett, **99**, 197201 (2007).