Incommensurate structures and radiation damage in $K_2V_3O_8$ and $Rb_2V_3O_8$ mixed-valence vanadate fresnoites

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Structures and phase transitions of $K_2V_3O_8$ and $Rb_2V_3O_8$ mixed-valence vanadate fresnoites are studied with synchrotron single-crystal diffraction at low temperatures and ambient pressure. $K_2V_3O_8$ exhibits a phase transition to an incommensurately modulated structure at about 115 K. At 100 K, the satellite reflections can be indexed with two $q$ vectors $q_1 = (\alpha, \alpha, 0.5)$ and $q_2 = (-\alpha, \alpha, 0.5)$, where $\alpha \approx 0.3$. Although no mixed satellite reflection are observed, the modulated structure is better described in (3+2) than in (3+1) dimensional space, superspace groups $P4bm(aa1/2)(-aa1/20)g0$ and $Cmm2(0\beta1/2)00$, respectively. The geometries of the VO$_4$ and VO$_5$ building units are rigid and it is mainly slight rotations of these polyhedra and small variation of the intermediate K-O distances that are modulated (Fig. 1). The prolonged exposure to the high-brilliance synchrotron beam suppresses the incommensurate phase. The previously postulated phase transition to the incommensurate phase in $Rb_2V_3O_8$ at 270 K is not observed in our data. One of the reasons could be that the intense radiation also affects the modulation in this material.

Strategies to collect and analyze single-crystal diffraction data measured with very intense synchrotron radiation using modern low-noise pixel area detectors will be discussed.

Figure 1. K-O distances below 4.25 Å in the (3+2)-d structure of $K_2V_3O_8$ at 100 K as a function of the internal coordinate $t (u = 0.0)$ (top) and $u (t = 0.0)$ (bottom).