LOW-TEMPERATURE BEHAVIOUR OF $K_2Sc[Si_2O_6]F$: DETERMINATION OF THE LOCK-IN PHASE AND ITS RELATIONSHIPS WITH FRESNOITE- AND MELILITE-TYPE COMPOUNDS

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A new (3+2)-dimensional incommensurately modulated (IC) structure has been recently described for $K_2Sc[Si_2O_6]F$ in superspace group $P4_2/mnm(\alpha,\alpha,0)000s(-\alpha,\alpha,0)0000$ with a = 8.9878(1), c = 8.2694(2) Å, V = 668.01(2) Å^3, modulation wave vectors $\mathbf{q_1}$ = 0.2982(4)(**a***+**b***) and $\mathbf{q_2}$ = 0.2982(4)(-**a***+**b***) (HEJNY et al., 2016). In the structure, $[ScO_4F_2]$ octahedral chains and $[Si_4O_{12}]$ rings are interconnected to form a mixed octahedral-tetrahedral framework where large open voids are filled with K in variable coordination ranging. The structure of $K_2Sc[Si_2O_6]F$ is related to that of the melilite- and fresnoite-type compounds, $X_2Z[T_2O_7]$ and $X_2Z[T_2O_8]$, respectively (BINDI et al., 2006). Although melilite- and fresnoite-type compounds have a different structure with layers of $[Si_2O_7]$ dimers and layers of large X cations, they display remarkable similarities to $K_2Sc[Si_2O_6]F$, i.e. (1) tetragonal symmetry with two modulation wave vectors $\mathbf{q_1} = \alpha$(**a***+**b***) and $\mathbf{q_2} = \alpha$(-**a***+**b***) with α being an irrational value, (2) a modulation-dependant variability in the coordination of a large cation, (3) similar behaviour of corresponding inter-tetrahedral angles and (4) the observed high- and low-temperature behaviour. As concerns point (4), it is remarkable that all of the above mentioned structures transform to the so called normal structure N (a commensurate structure equivalent to the average structure of the modulated structure) with increasing temperatures. On temperature decrease, an increase of the modulation wave-vectors with a subsequent lock-in phase transition has been observed for Co- and Zn-åkermanite (SAZONOV et al., 2015). In order to search for an equivalent lock-in phase for $K_2ScSi_2O_6F$ the low-temperature behaviour has been studied by single-crystal X-ray diffraction. Up to 45 K the irrational component α of the modulation wave-vectors is quite constant varying from 0.2982(4) (RT), throughout 0.2955(8) (120 K), 0.297(1) (90 K), 0.298(1) (75 K), to 0.299(1) (45 K). At 25 K it approaches the commensurate value of 1/3 [i.e., 0.332(3)], thus indicating that the incommensurate-commensurate phase transition takes place between 45 K and 25 K. The commensurate lock-in phase of $K_2Sc[Si_2O_6]F$ has been solved and refined with a 3 × 3 × 1 supercell compared to the tetragonal incommensurately modulated structure stable at room temperature. This corresponds to a 3 × 1 × 3 supercell in the monoclinic, pseudo-orthorhombic setting of the low-temperature structure, space group $P2/m$, with lattice parameters a = 26.786(3), b = 8.245(2) c = 26.824(3) Å, α = 90.00(1)°.

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