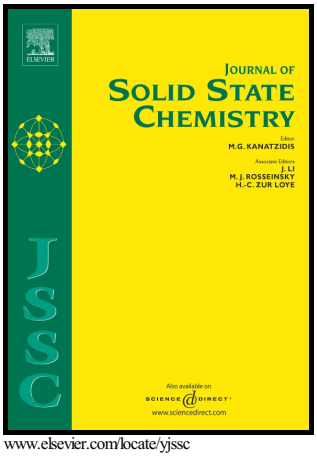

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Abstract

As results of a powder XRD study of sintered samples of the systems Na_2MoO_4–$MMoO_4$ (M = Co, Cd) quenched in air from 873 K, the literature data on the phase formation and homogeneity ranges of nonstoichiometric double molybdates in these systems were corrected. The compounds are monoclinic alluaudite-type $Na_{4-2x}Co_{1+x}(MoO_4)_3$ ($0.05 \le x \le 0.30$) and $Na_{4-2x}Cd_{1+x}(MoO_4)_3$ ($0.10 \le x \le 0.40$), orthorhombic lyonsite-type $Na_{2-2y}Co_{2+y}(MoO_4)_3$ ($0.05 \le y \le 0.25$), and triclinic $Na_{2-2z}Co_{2+z}(MoO_4)_3$ ($0.10 \le z \le 0.40$) of the $Na_2Mg_5(MoO_4)_6$ type. The temperature of the orthorhombic–to–triclinic phase transition was found to be 943 ± 10 K. Crystal structures of the alluaudite-type double molybdates (space group $C2/c$, Z = 4) with cobalt, manganese, and cadmium were determined. According to the atomic position occupations, the compositions for the crystals were found as $Na_{3.36}Co_{1.32}(MoO_4)_3$ (a = 12.6381(3), b = 13.4888(4), c = 7.1244(2) Å, β = 112.127(1)°, R = 0.0207), $Na_{3.13}Mn_{1.43}(MoO_4)_3$ (a = 12.7387(3), b = 13.6716(4), c = 7.1904(2) Å, β = 112.404(1)°, R = 0.0166), and $Na_{3.72}Cd_{1.14}(MoO_4)_3$ (a = 12.804(3), b = 13.913(3), c = 7.326(2) Å, β = 112.63(1)°, R = 0.0158). The crystal chemistry and compositions of the alluaudite-type molybdates and tungstates were considered and mainly one-dimensional character of the sodium-ion transport was shown for them. The measured values of the ionic conductivity of sintered samples of $Na_{3.6}M_{1.2}(MoO_4)_3$ (M = Mg, Ni, Zn, Cd) and $Na_{3.6}Mg_{1.2}(WO_4)_3$ exceeds 10^{-3} S cm^{-1} at 673 K.

Graphical abstract