Synthesis and Structure of New Mixed Silver Cobalt(II)/(III) Diphosphate - $\text{Ag}_{3.68}\text{Co}_2(\text{P}_2\text{O}_7)_2$. Silver(I) Transport in the Crystal

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A new silver cobalt diphosphate, $\text{Ag}_{3.68}\text{Co}_2(\text{P}_2\text{O}_7)_2$, is synthesized by solid-state reaction route. Crystal structure and Ag^+ pathways simulation are studied by single-crystal X-ray diffraction and Bond Valence Site Energy (BVSE) model, respectively. The title material crystallizes in the triclinic system, space group P-1 with $a = 6.521(4)$ Å, $b = 9.623(6)$ Å, $c = 10.969(7)$ Å, $\alpha = 64.23(2)^\circ$, $\beta = 80.14(3)^\circ$ and $\gamma = 72.10(2)^\circ$. The structure presents $\text{Co}_4\text{P}_4\text{O}_{28}$ groups formed by two Co_2O_{11} units and two P_2O_7 groups. The junction between these groups is assured by two pyrophosphates to create a three-dimensional anionic framework showing interconnecting tunnels in a , b and c axis. The obtained structural model is supported by two validations tools: Charge Distribution (CHARDIT) analysis and Bond Valence Sum (BVS) calculation which validated the presence of Co^{2+} and Co^{3+} in the same sites. The Ag^+ cations balanced the negative charge with partial site occupations. The Ag^+ pathways simulation, using the Bond Valence Site Energy (BVSE) model, identified the mobile species and proposed migration pathways of the monovalent cations according vast tunnels in three dimensions. The material must be a 3D average ionic conductor, with theoretical activation energy about 1.7 eV. Correlation between structure and electrical properties has been discussed.

Keywords: diphosphate, structure, tunnels, pathways simulation, ionic conductor.

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