Controlling the superionic transition temperature through anion substitution in CuCrX_2 (X = S, Se, Te)

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The demand for sustainable energy storage has intensified interest in high-performance solid-state battery materials, particularly those exhibiting superionic conductivity at ambient temperatures. Superionic conductors, such as layered $A\mathrm{Cr}X_2$ (A= Ag, Cu; X= Se, S) chalcogenides, offer enhanced ionic mobility but typically require elevated temperatures to achieve high conductivity. In this work, we investigated the possibility and effects of alloying at the anion site in layered chalcogenide CuCrX_2. Here, we prepared a series of polycrystalline $\mathrm{CuCrSe_{2-x}Te_x}$ (x = 0, 0.1, 0.15, 0.175) and $\mathrm{CuCrSe_{2-y}S_y}$ (y = 0, 0.1, 0.25, 0.5, 0.75, 1.0, 2.0) compounds by solid state synthesis. X-ray diffraction analysis confirmed that the S-Se system exhibits complete solubility, whereas Te substitution at the anion site in $\mathrm{CuCrSe_2}$ is limited to x = 0.15. Variable-temperature X-ray diffraction and thermal diffusivity measurements were conducted to track the order-disorder/superionic transition temperature (T_c) of the compounds. The transition temperature was found to be highly composition-dependent, exhibiting a decreasing trend with the incorporation of larger anions; $\mathrm{CuCrSe_{1.85}Te_{0.15}}$ had the lowest T_c at 282 K, marking the first reported instance of $T_c < 300$ K for this crystal structure type. The elastic properties and speed of sound in the $\mathrm{CuCrSe_{2-x}Te_x}$ series were measured as a function of composition and temperature and the bonds were found to soften gradually as anion size increased. The temperature coefficient of the elastic constants exhibited only a small inflection at order-disorder phase transition, confirming that long-wavelength acoustic phonons remain largely unaffected by the transition. Thermoelectric (TE) characterizations were also performed, revealing that the TE figure of merit of the compounds remains nearly unchanged at high temperatures (493 K). These findings highlight anion engineering as a promising strategy for tuning solid-state ionic conductors, paving the way for more sustainable, efficient, and safer energy storage solutions.