Chalcogenide glasses exhibit unique optical properties such as infrared transparency, optical non-linearity, and photo-induced effects that have important consequences for a wide range of technological applications. However, to fully utilize these properties, it is necessary to better understand the atomic-scale structure and structure-property relationships in this important class of materials. Of particular interest in this regard are glasses in the stoichiometric system Na$_2$Se/BaSe–Ga$_2$Se$_3$–GeSe$_2$ as they are isoelectronic with the well-studied, oxide glasses of the type M$_2$O/M’O–Al$_2$O$_3$–SiO$_2$ (M = alkali, M’ = alkaline earth). This work investigates the structure of stoichiometric Na$_2$Se/BaSe–Ga$_2$Se$_3$–GeSe$_2$ and off-stoichiometric BaSe–Ga$_2$Se$_3$–GeSe$_2$±Se glasses using a combination of Fourier-transform Raman and solid state nuclear magnetic resonance (NMR) spectroscopies. The spectroscopic data is then compared to composition-dependent trends in physical properties such as density, optical band gap, glass transition temperature, and melt fragility to develop predictive structural models of the short- and intermediate-range order in the glass network. Ultimately, due to the ionic-covalent nature of atomic bonding within the network, it is found that Na/Ba–Ga–Ge selenide glasses are best described by structural models that contain characteristics from both the charge-compensated structural scenario of oxide glasses and the continuously-alloyed scenario of binary chalcogenide glasses. These models significantly improve our current understanding of the effects of modifier addition on the structure and properties of chalcogenide glasses, and thus enable a more efficient engineering of these highly functional materials for applications as solid electrolytes in batteries or as optical components in infrared photonics.