Supporting Information

for

Destruction of Non-Centrosymmetry Through Chalcogenide Salt Inclusion

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Details of the structure refinement: The positions of the four Se, one Ge and one Sm, all belonging to the covalently connected network, were immediately located from the difference Fourier maps. There were three peaks with electron densities, 39.5, 23.13 and 9.94 e⁻/site, all belonging to the extra-framework atoms that remained to be assigned. An electron density of 39.5, which was also on a special position, was assigned as Se (Se5) while two other general positions were assigned as Na (23.13=Na1, 9.94=Na2). The refinement indicated substantial reduction in the R-value but with high thermal parameters (0.11) ($U [\text{\AA}^2]$) for Na2 and Se5. The site occupancies for both Se5 and Na2 were then freely refined to a value of 0.489 and 0.495 with esds 0.0078 and 0.01757 and also the thermal parameters came down to a reasonable value. So for the final refinement the occupancies of Se5 and Na2 were fixed to 0.25 (symmetry position of two fold axis) and 0.5, respectively, for the sake of charge neutrality. We also tried to refine the structure by putting Na (Na3) in Se5 site, while freely refining the site occupancies of all the Na-atoms. Although this model reduces the R-value and the thermal parameters to an acceptable value, there were other issues to rule out such an assignment. The refinement gave a site occupancy value of 0.75 for the newly assigned Na, which is unlikely because it is sitting in a two-fold rotation symmetry. More importantly there is a serious problem of balancing the charge, since only +1 charge was needed to balance the negatively charged framework, which was already provided by Na1 site, and the Na1 site did not have any vacancy. Another problem in the

later model is that Na3 has all Na-atoms at a distance of $2.7\text{\AA}$ in its trigonal prismatic environment, which was not acceptable.

Figure S1. The asymmetric unit of **I**, thermal ellipsoids are given at 40% probability.

Figure S2. The Raman spectrum of **I**.