Inclusion compounds composed mostly of Si, Ge or Sn atoms that encapsulate alkali- or earth alkali-metals are known as semiconductor clathrates, and Sn clathrates have received less attention than the others. The large framework cavities in the Sn clathrates favor the ‘rattling’ of the guest atoms. The compounds Cs$_8$Sn$_{44}$$\square_2$ and Rb$_8$Sn$_{44}$$\square_2$ are characterized as defect clathrates of type-I structure with two missing Sn atoms in the covalent Sn framework. Recently, it has been found that these vacancies (\(\square\)) of Rb$_8$Sn$_{44}$ [1] and Cs$_8$Sn$_{44}$ [2] show partial ordering at room temperature. In the resulting Sn framework, each underoccupied position is arranged along a 4$_4$ helical axis that runs through the center of the tetrakaidecahedra. These vacancy-containing compounds show a reversible order-disorder phase transition at 80°C for Rb$_8$Sn$_{44}$ [1] and at 90°C for Cs$_8$Sn$_{44}$ [2]. In the disordered phase above the transition temperature, the partially occupied 6c sites are distributed along a 4$_2$ axis.

The vibrational properties are important for material characterization and are also a key to understanding its thermal conductivity. Raman spectroscopy is useful to observe the guest rattler and the host framework vibrations of the clathrates [3, 4], and to find the vacancy-induced localized vibrational modes.

In this work, Raman vibrational studies of type-I clathrates Cs$_8$Sn$_{44}$, Rb$_8$Sn$_{44}$, and Rb$_{1.58}$Cs$_{6.42}$Sn$_{44}$ are reported, by considering the guest rattler and the host framework vibrations, and new Raman bands of vacancy-induced localized vibrational modes. We found the rattling vibrations of guests Cs and Rb atoms in a low frequency region 25-40 cm$^{-1}$. Higher-frequency Sn framework vibrations were observed above 44 cm$^{-1}$, and the vacancy-induced localized vibrations were found around 70 cm$^{-1}$ for the first time. We also present the temperature dependence of Raman spectra in order to investigate the high-temperature order-disorder phase transition associated with the vacancies.