RAMAN STUDY OF TYPE-I TIN CLATHRATES $Cs_8Sn_{44}\square_2$ AND $Rb_8Sn_{44}\square_2$

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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 $Cs_8Sn_{44}\square_2$ and $Rb_8Sn_{44}\square_2$ 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 (□) of Rb_8Sn_{44} [1] and Cs_8Sn_{44} [2] show partial ordering at room temperature. In the resulting Sn framework, each underoccupied position is arranged along a 4_1 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_8Sn_{44} [1] and at 90°C for Cs_8Sn_{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_8Sn_{44}, Rb_8Sn_{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.

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