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Sn vacancies in photorefractive $Sn_2P_2S_6$ crystals: An electron paramagnetic resonance study of an optically active hole trap

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E. M. Golden[1], S. A. Basun[2,3], D. R. Evans[3], A. A. Grabar[4], I. M. Stoika[4], N. C. Giles[1], *and* L. E. Halliburton[2,5, a)]

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ABSTRACT

Electron paramagnetic resonance (EPR) is used to identify the singly ionized charge state of the Sn vacancy (V_{Sn}^{-}) in single crystals of $Sn_2P_2S_6$ (often referred to as SPS). These vacancies, acting as a hole trap, are expected to be important participants in the photorefractive effect observed in undoped SPS crystals. In as-grown crystals, the Sn vacancies are doubly ionized (V_{Sn}^{2-}) with no unpaired spins. They are then converted to a stable EPR-active state when an electron is removed (i.e., a hole is trapped) during an illumination below 100 K with 633 nm laser light. The resulting EPR spectrum has *g*-matrix principal values of 2.0079, 2.0231, and 1.9717. There are resolved hyperfine interactions with two P neighbors and one Sn neighbor. The isotropic portions of these hyperfine matrices are 167 and 79 MHz for the two ^{31}P neighbors and 8504 MHz for the one Sn neighbor (this latter value is the average for ^{117}Sn and ^{119}Sn). These V_{Sn}^{-} vacancies are shallow acceptors with the hole occupying a diffuse wave function that overlaps the neighboring Sn^{2+} ion and $(P_2S_6)^{4-}$ anionic unit. Using a general-order kinetics approach, an analysis of isothermal decay curves of the V_{Sn}^{-} EPR spectrum in the 107–115 K region gives an activation energy of 283 meV.

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