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Photoinduced trapping of charge at sulfur vacancies and copper ions in photorefractive $Sn_2P_2S_6$ crystals

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ABSTRACT

Electron paramagnetic resonance (EPR) is used to monitor photoinduced changes in the charge states of sulfur vacancies and Cu ions in tin hypothiodiphosphate. A $Sn_2P_2S_6$ crystal containing Cu^+ ($3d^{10}$) ions at Sn^{2+} sites was grown by the chemical vapor transport method. Doubly ionized sulfur vacancies (V_S^{2+}) are also present in the as-grown crystal (where they serve as charge compensators for the Cu^+ ions). For temperatures below 70 K, exposure to 532 or 633 nm laser light produces stable Cu^{2+} ($3d^9$) ions, as electrons move from Cu^+ ions to sulfur vacancies. A *g* matrix and a $^{63,65}Cu$ hyperfine matrix are obtained from the angular dependence of the Cu^{2+} EPR spectrum. Paramagnetic singly ionized (V_S^+) and nonparamagnetic neutral (V_S^0) charge states of the sulfur vacancies, with one and two trapped electrons, respectively, are formed during the illumination. Above 70 K, the neutral vacancies (V_S^0) are thermally unstable and convert to V_S^+ vacancies by releasing an electron to the conduction band. These released electrons move back to Cu^{2+} ions and restore Cu^+ ions. Analysis of isothermal decay curves acquired by monitoring the intensity of the Cu^{2+} EPR spectrum between 74 and 82 K, after removing the light, gives an activation energy of 194 meV for the release of an electron from a V_S^0 vacancy. Warming above 120 K destroys the V_S^+ vacancies and the remaining Cu^{2+} ions. The photoinduced EPR spectrum from a small concentration of unintentionally present Ni^+ ions at Sn^{2+} sites is observed near 40 K in the $Sn_2P_2S_6$ crystal.

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