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Article

Intrinsic small polarons (Sn3+ ions) in photorefractive Sn2P2S6 crystals

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Abstract

Unique holelike small polarons are produced at divalent cation sites by optical excitation at low temperature in single crystals of Sn2P2S6, a monoclinic ferroelectric and photorefractive material. Electron paramagnetic resonance (EPR) is used to observe these self-trapped holes. During an illumination near 25 K with either 442 or 633 nm laser light, photoexcited holes become localized at Sn(2+) (5s(2)) ions and form paramagnetic Sn(3+) (5s(1)) ions. The Sn(3+) ions are thermally stable below 50 K. The principal values of the g matrix are 2.0031, 2.0176, and 2.0273 and the principal values of the (119)Sn hyperfine matrix are 12.828, 12.886, and 13.060 GHz. The large interaction with the (119)Sn (and (117)Sn) nucleus results in a highly asymmetric hyperfine pattern in the EPR spectrum. Weaker hyperfine interactions with two neighboring Sn ions are also observed.

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... An entire temporal range was measured in several attempts with different sampling times and different total times of measurement, to ensure a sufficient temporal resolution in every particular time interval. During the pulse duration ( $\approx 20$  ns) the sample transmission is gradually decreasing, pointing to photoexcitation of free carriers that might further form polarons [4]. These photoinduced entities decay within the time range from 0.1 ms to 1 ms or even longer. ...

... This allowed for identification of their physical origin and for estimating the activation energies from the Arrhenius plots. The comparison of the obtained data with the activation energies extracted from EPR measurements [3, 4] allowed for the conclusion that the initial light-induced absorption is caused by hole polarons (Sn<sup>2+</sup> with a trapped hole [4]), while it is the antimony dopant which is responsible, indirectly and directly, for beam fanning and the development of compensation gratings [5]. ...

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#### Time resolved nonlinear response of Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub>:Sb to nanosecond pulse excitation

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Jun 2017 · [J Phys Conf](#)

A. Shumelyuk · Yaroslav Skrypka · Serguey Odoulov · D. R. Evans

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... Either way, it is useful to compare the present result to a recent investigation of the stability of Sn<sup>3+</sup> sites in SPS, which have been identified as small polarons formed by holes. 28 Reference 28 observed that the electron paramagnetic resonance signal from Sn<sup>3+</sup> disappears near 47 K when raising the temperature of the sample after illumination. 28 They then used this temperature in the Randall and Wilkins approximation, 29 which derives an excitation energy  $E \approx 25k_B T_{max}$  from the temperature  $T_{max}$  where the peak in luminescence is observed while heating a sample. ...

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#### Optical determination of the charge carrier mobility in Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub>

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Oct 2016 · [APPL PHYS LETT](#)

Abhishesh Regmi · Ivan Biaggio · Alexander Grabar

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... The investigation of Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub>-type crystals is also important from the practical point of view because of the attractive photorefractive, acousto-optic and electrooptic properties which make them a prospective material for optical applications [15][16][17][18][19]. Moreover, a considerable piezoeffect has been found [20]. ...

**Dielectric, pyroelectric and ferroelectric properties of lead-doped Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> crystals**[Article](#)Feb 2019 · [PHASE TRANSIT](#)

● Ilona Zamaraitė · ● Sarunas Svirskas · ● Yulian Vysochanskii · A. Dziaugys

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... Also, EPR has shown that isolated Sn<sup>2+</sup> vacancies trap a hole during illumination at low temperatures [14]. Other defects in SPS identified by EPR include sulfur vacancies [15] and Sn<sup>3+</sup> holelike small polarons [16]. ...

**Dual role of Sb ions as electron traps and hole traps in photorefractive Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> crystals**[Article](#)

Dec 2016

B. E. Kananen · ● Eric Golden · S. A. Basun · ● Larry E. Halliburton

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... 30,31 The trapped-hole center is the intrinsic small polaron (Sn<sup>3p</sup> ions) at Sn<sup>2p</sup> sites. 32 In this paper, we focus on native defects in nominally undoped SPS crystals, and in particular, on Sn vacancies. The Sn vacancies are a shallow acceptor in SPS and thus provide an important trap for holes when gratings are written in photorefractive experiments. ...

**Sn vacancies in photorefractive Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> crystals: An electron paramagnetic resonance study of an optically active hole trap**[Article](#)Oct 2016 · [J APPL PHYS](#)

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... Unpaired electrons associated with either Ag<sup>0</sup> or Ag<sup>2+</sup> can be identified in the EPR spectra by the doublets resulting from the hyperfine interaction with the <sup>107</sup>Ag (nuclear spin I = 1/2, 51.8% abundant) and <sup>109</sup>Ag (I = 1/2, 48.2% abundant) nuclei. As documented in the literature, large nuclear hyperfine splitting is generally observed for atomic Ag [33,34] and small Ag<sup>n</sup>m<sup>+</sup> (m b n) clusters [35,36]. In addition, any EPR signals belonging to Sn<sup>3+</sup> ions can be identified by satellite lines arising from nuclear hyperfine coupling with the spin-1/2 nuclear isotopes <sup>117</sup>Sn and <sup>119</sup>Sn (natural abundances of 7.6% and 8.6%) which have been observed for Sn<sup>3+</sup> ions in inorganic matrices [37]. ...

**Electron Paramagnetic Resonance (EPR) studies on the photo-thermo ionization process of photo-thermo-refractive glasses**[Article](#)Nov 2016 · [J NON-CRYST SOLIDS](#)

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October 2012 · Physical review. B, Condensed matter

 A. T. Brant ·  Larry E. Halliburton · S. A. Basun · [...] · D. R. Evans

Single crystals of Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> are both ferroelectric and photorefractive. Antimony (Sb) ions are optically active in this material and play an important role in optimizing the photorefractive response. Electron paramagnetic resonance (EPR) is used to determine the site and charge states of the Sb ions in Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and to illustrate the photocharging behavior of these ions. In as-grown crystals, Sb<sup>3+</sup> ... [\[Show full abstract\]](#)

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November 1972 · The Journal of Chemical Physics

 N. S. Dalal · J. R. Dickinson · C. A. McDowell

Electron paramagnetic resonance (EPR) studies of defect centers produced by x or  $\Gamma$  irradiation of the hydrogen-bonded ferroelectrics KH<sub>2</sub>AsO<sub>4</sub>, KD<sub>2</sub>AsO<sub>4</sub>, RbH<sub>2</sub>AsO<sub>4</sub>, RbD<sub>2</sub>AsO<sub>4</sub>, and CsH<sub>2</sub>AsO<sub>4</sub> and of the antiferroelectrics NH<sub>4</sub>H<sub>2</sub>AsO<sub>4</sub> and ND<sub>4</sub>D<sub>2</sub>AsO<sub>4</sub>, are presented. The spectra, observed over 300–4.2°K, are characterized by a very large hyperfine interaction of the unpaired electron with the <sup>75</sup>As (I=3/2) ... [\[Show full abstract\]](#)

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