

Electron paramagnetic resonance and photoluminescence studies of chromium in SrS

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(Received 5 November 1997; accepted for publication 14 January 1998)

Isotropic features with hyperfine structures in electron paramagnetic resonance spectra of SrS powder phosphors, which reflect the abundance of the natural Cr isotopes, are attributed to the isolated Cr impurity. The isotropy, which is typical for a 4A_2 ground state of a $3d^3$ ion in an octahedral crystal field, and the g value of 1.9795 verify that Cr is observed in its charged donor state Cr^{3+} . The observation of a broad photoluminescence band with a maximum at 900 nm, which can be attributed to an internal Cr^{3+} transition, supports the identification of the impurity as Cr^{3+} .

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SrS doped with rare earth ions is a widely used material for the active layer in thin film electroluminescent devices (TFELDs). For the blue component of a full color display, Ce^{3+} is used as the luminescent center. Its radiative efficiency depends on several technological and physical processes, since codopants or residual impurities play an important role. Their presence can, e.g., lead to the formation of killer centers, to charge compensation, or to a shift of the Fermi level. With electron paramagnetic resonance (EPR) studies, the nature of dopants such as Ce, Eu, and Mn in SrS was analyzed in the past.¹⁻⁶ Transition metal ions commonly substitute for cations, which implies the general possibility of amphoteric changes of their charge states, i.e., in addition to the lattice neutral charge state ($2+$), also donor-type ($2+/3+$) as well as acceptor-type ($2+/+$) states can be found. In this letter, EPR and photoluminescence (PL) studies of Cr impurities in SrS powders, which are intentionally doped with Ce and Pb or K are presented.

The cerium-doped SrS powders were prepared by high temperature processing as described in Ref. 7. In the present case, however, the powders have been additionally doped with Pb or K but never intentionally with Cr. The EPR spectra were measured in the X band at 9.5 GHz with a Bruker ESP 300E spectrometer, which was equipped with a He gas-flow cryostat. For the PL experiments, the samples were mounted in a cryostat with temperature control, in which the temperature was adjusted to 5 K. The optical excitation was carried out with a He-Cd laser operating at a wavelength of 325 nm. The PL signal was dispersed in a 1 m monochromator and detected with a cooled charge coupled device detector. The laser intensity was adjusted to 5 mW focused to a diameter of about 100 μm .

The powders show the well known EPR spectra of Ce^{3+} and Mn^{2+} , which are described in Refs. 1 and 2, respectively. Although only intentionally doped with Ce and Pb or K, all samples contain Mn, too. The EPR spectrum shown in Fig. 1 exhibits, in addition to the Mn^{2+} transitions, further lines, which will be discussed in this letter. These additional lines are not detected in all types of powder samples. The isotropic spectrum with a hyperfine structure, which consists of a central line and four smaller equally spaced satellite transitions, is attributed to the isolated Cr^{3+} center in SrS (cf. upper spectrum in Fig. 1).

The main argument for the identification as a Cr-related defect is given by the fact that the hyperfine structure reflects the natural abundance of isotopes. Cr is the only element which fulfills the observed splitting and intensity ratios. While the central line is due to the isotopes ^{50}Cr , ^{52}Cr , and ^{54}Cr without a nuclear spin, the four hyperfine satellites are a consequence of the isotope ^{53}Cr which has a nuclear spin of $3/2$ and a natural abundance of 9.55%.

According to the usual behavior of transition metals in II-VI semiconductors,⁸ the possible charge states of Cr on cation sites in SrS are the lattice neutral Cr^{2+} ($3d^4$) as well as the two charged states Cr^+ ($3d^5$) and Cr^{3+} ($3d^3$). For Cr^{2+} however, it is very unlikely that its orbital-degenerated 5E ground state would lead to an isotropic EPR spectrum which indeed has been observed experimentally. Therefore, this charge state can be ruled out. Furthermore, the g value for the central line of the spectrum of a d^5 ion is expected to be close to the free electron value of 2.0023. We will show that the experimentally observed g value deviates significantly from that value and therefore, it is very unlikely that a Cr^+ center originates in the spectrum. The spectroscopical observations rather agree with the expectations for the charged donor state at which the Cr^{3+} ion is incorporated at

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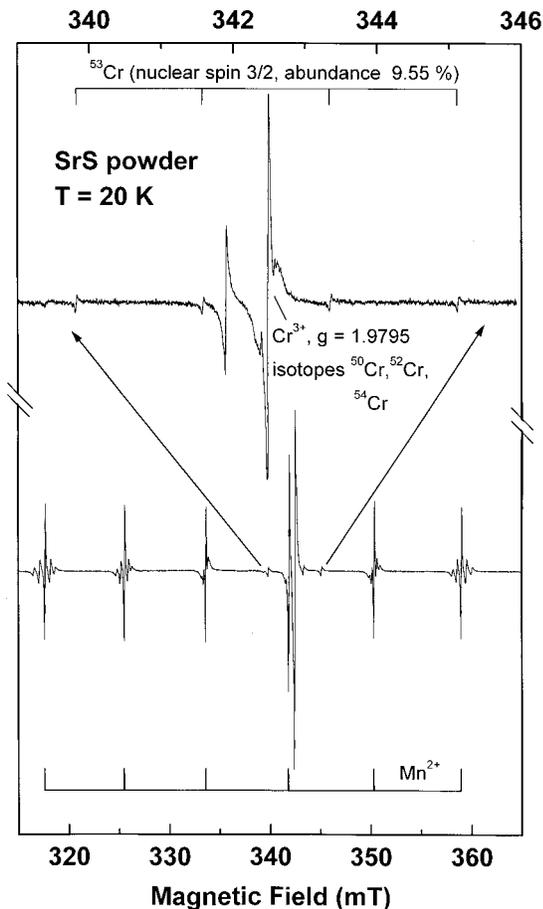


FIG. 1. EPR spectrum of an SrS powder at 20 K, which exhibits the Mn^{2+} related features (bottom), and a zoomed part of it containing the Cr^{3+} related part (top). The stick spectra shows the hyperfine structure due to the ^{55}Mn and ^{53}Cr nuclides. To improve the resolution for the Cr^{3+} spectrum the modulation amplitude and the microwave power were decreased. This results in a variation of the intensity ratio between the Mn^{2+} signals and the Cr ones because of different linewidths and saturation behaviors.

a substitutional cation site. In an octahedral crystal field, the 4F ground state of the free ion is split into two orbital triplets and one orbital singlet. Applying an appropriate spin Hamiltonian for an 4A_2 ground state⁹

$$\mathcal{H} = g\beta(\mathbf{B} \times \mathbf{S}) + A(^{53}\text{Cr})(\mathbf{S} \times \mathbf{I}), \quad (1)$$

where the first term represents the Zeeman interaction and the second term the electron–nuclear hyperfine interaction with the nuclear spin of the ^{53}Cr isotope, we obtain the parameters $g = 1.9795(2)$ and $A(^{53}\text{Cr}) = 16.4(1) \cdot 10^{-4} \text{ cm}^{-1}$. Such a g value was also found, e.g., for Cr^{3+} in MgO and has been accounted for as the consequence of spin-orbit coupling to the $^4T_2(F)$ excited triplet (cf., e.g., Ref. 9 and references therein). The symmetric line shapes and the narrow linewidths in the powder spectrum suggest an isotropic behavior, which is in fact expected for such a ground state in octahedral symmetry. Our results agree very well with the commonly accepted picture of the incorporation of transition metals into substitutional cation sites in II–VI materials.

A more detailed analysis of the central line shows that a broader signal is superimposed by a narrow one. We interpret the narrow line ($\Delta B_{\text{pp}} = 0.03 \text{ mT}$) as the $1/2$ to $-1/2$ electron spin transition within the $S = 3/2$ spin manifold. The broader signal ($\Delta B_{\text{pp}} = 0.22 \text{ mT}$) originates from the two re-

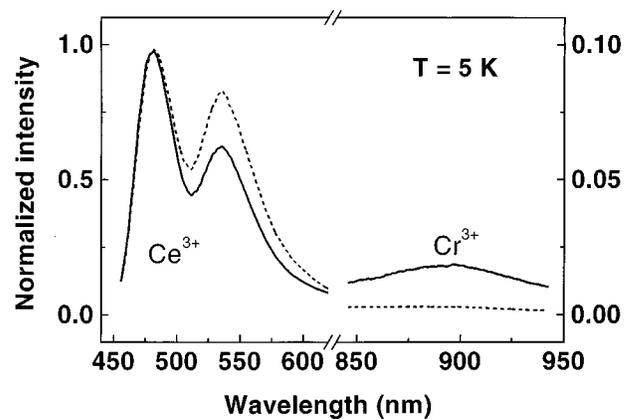


FIG. 2. The PL spectrum (solid line) of an SrS powder in which the Cr^{3+} impurity was verified by EPR in comparison to the PL spectrum (dashed line) in which no Cr was observed by EPR.

maintaining allowed transitions $3/2$ to $1/2$ and $-1/2$ to $-3/2$. It is well known that random strain leads to a line broadening for the $\pm 3/2$ to $\pm 1/2$ transitions, while the $1/2$ to $-1/2$ transitions are hardly influenced by it.

In order to confirm the results of the EPR analysis, the SrS powders were also investigated by PL spectroscopy. While the PL spectra of all samples are dominated by the well known Ce^{3+} emission¹⁰ between 460 and 580 nm, a broad additional emission at 900 nm was observed only in those powders for which the EPR analysis verified the Cr^{3+} impurity (see Fig. 2). Since this new emission is only observed for SrS powders which contain Cr, we ascribe it tentatively to the internal $^4T_2(F) - ^4A_2(F)$ transition of Cr^{3+} . In low crystal fields the 4T_2 state of the d^3 configuration is expected to be the lowest excited state leading to a broad band emission in the infrared range.¹¹

The origin of the Cr^{3+} impurity in some of the SrS powders has satisfactorily not been demonstrated yet. One possibility seems to be an accidental contamination of the starting materials with Cr of those powders for which Cr^{3+} was verified. However, a residual Cr contamination of all powders of the present set of samples cannot completely be ruled out since the Fermi level in the powders can vary depending on the specific preparation procedure of each sample. As mentioned above, the EPR of Cr in SrS powders is not very sensitive for the neutral Cr^{2+} charge state. Therefore, in samples where Cr occurs only in this state, no EPR signal of Cr can be detected. The oxidation state of Cr can be influenced by the nature and excess of alkali dopants which are intentionally added in order to provide a charge compensation for the Ce^{3+} ions. In this case, only in powders in which the excess of, e.g., alkali acceptors changes the lattice-neutral Cr^{2+} state into the charged donor Cr^{3+} state is an EPR observation possible.

In conclusion, EPR studies on SrS powders have substantiated the occurrence of the isolated Cr^{3+} impurity by the Cr hyperfine finger print and the g factor of 1.9795. Because of the isotropic behavior of the spectra, the Cr^{3+} is suggested to be substitutionally incorporated at an undisturbed cation site. A broad Cr^{3+} related PL band was detected at a wavelength of 900 nm.

The authors are greatly indebted to W. Ulrici for valuable discussions. This work has been supported by the Euro-AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

pean Commission through the Brite Euram Contract No. BRE2.CT 93.0452 and by the German Ministry of Education, Science and Research (BMBF) under Contract No. 01 BK 520/3.

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